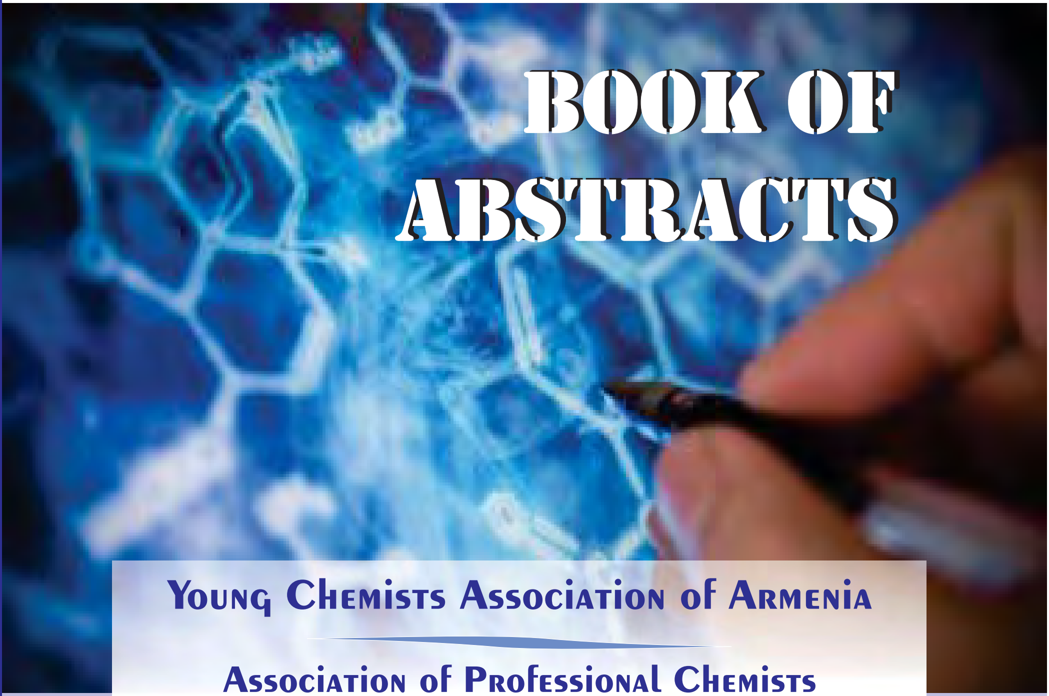
CHEMISTRY TODAY-2014

4-th International Conference of Young Scientists
August 18-22, 2014
Yerevan, Armenia

> *"The meeting of two personalities is like the contact*
> *of two chemical substances:*
> *if there is any reaction, both are transformed"*
>
> *Carl Jung*



BOOK OF ABSTRACTS

Young Chemists Association of Armenia

Association of Professional Chemists
of Georgia

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4th International Conference of Young Scientists

“Chemistry Today – 2014”

BOOK OF ABSTRACTS

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INVITED LECTURES

I-1. SULFLOWER AND OTHER CHEMICAL FLOWERS

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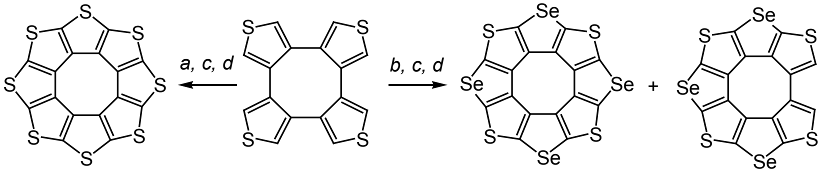
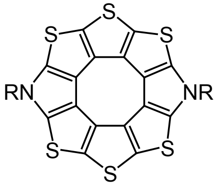
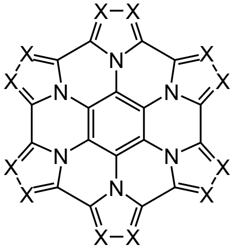
Recently we have described synthesis of the first fully heterocyclic circulene Sulflower **1**, which is a new type of heterocyclic molecules. The properties of Sulflowe were comprehensively studied, including fabrication of field-effect transistors. Reaction of initial tetrathiophene **2** with selenium under standard and variously modified conditions leads to formation of target sulfur-selenium circulene **3** and "dehydrohelicene" **4**. The synthesis of others heterocyclic circulenes is now in progress.



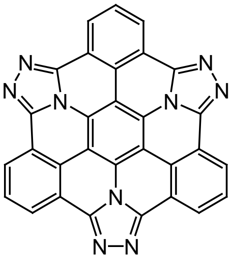
1 **2** **3** **4**

a) 16 eq. LDA + 16 eq. sulfur, Et_2O
b) 16 eq. LDA + 16 eq. selenium, Et_2O
c) HCl
d) vacuum sublimation





X= CH, N



I-2. PROBING THE STRUCTURE AND DIMENSIONS OF UNFOLDED PROTEINS WITH SINGLE-MOLECULE FRET SPECTROSCOPY

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Recent Förster resonance energy transfer (FRET) experiments show that heat-unfolded states of proteins become more compact with increasing temperature [1]. At the same time, some NMR and SAXS results indicate that cold-denatured proteins are more expanded than heat-denatured proteins [2,3]. To clarify the connection between these observations, we investigated the unfolded state of yeast frataxin, with single-molecule FRET. Frataxin is one of the very few available systems whose cold denaturation occurs at temperatures above 273 K [4,5], allowing to probe the properties of the unfolded state both under conditions of complete heat- and almost complete cold denaturation (and in between) without extrapolation from high denaturant concentrations or extremes of pH. Meanwhile, single-molecule FRET allows the unfolded state dimensions to be probed not only in the cold- and heat-denatured range, but also in between, i.e., in the presence of folded protein, and can thus be used to link the two regimes. The results show a continuous compaction of unfolded frataxin from 274 K to 320 K, with a slight re-expansion at higher temperature. Cold- and heat-denatured states are thus essentially two sides of the same coin and reflect the overall temperature dependence of the unfolded state dimensions. The pronounced difference in the temperature of highest conformational stability of the folded state (~290 K) and the temperature where the unfolded state is most compact (~320 K) illustrates that the entropic and energetic contributions underlying protein folding and unfolded state collapse differ, even though both processes are expected to be closely linked to hydrophobic hydration phenomena.

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I-3. MACROCYCLIC AZOMETHINES FOR OPTICAL IMAGING

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Optical imaging with dyes permits visualization of biological activities [1-4]. Dyes that are sensitive to physicochemical environments (such as pressure, cell membrane potential, ion concentration, acidity, partial pressure of oxygen and etc.), are subject to changes in absorption or emission of light. The resulting changes act as optical probes to transform biological activities into optical signals that can be converted into optical images.

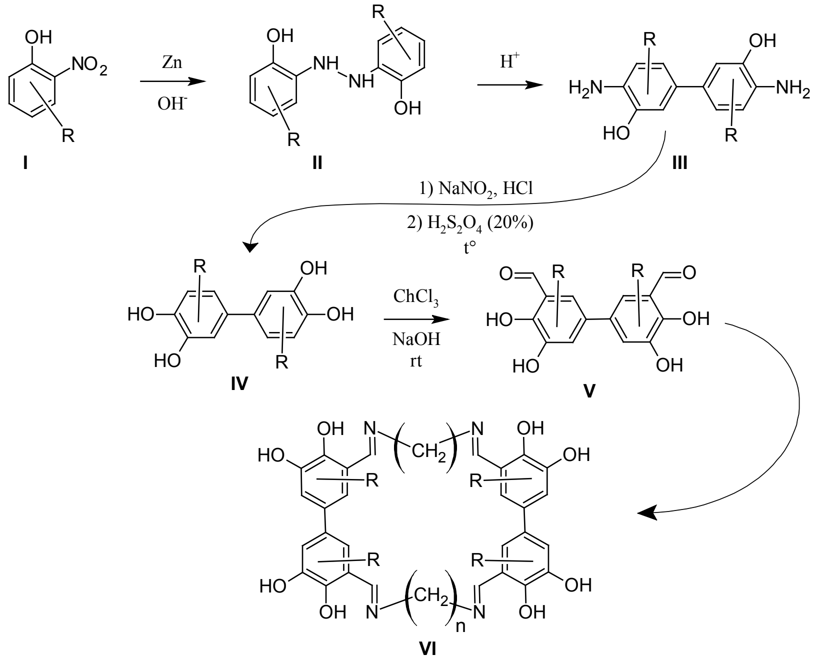
Among the compounds with fluorescent properties, azomethines are one of the important dyes [5].

Nowadays azomethines are used as substrates to prepare a large number of industrial and biologically active compounds via ring closure, cycloaddition and replacement. Moreover azomethines are also known to have antimicrobial, antifungal, antitumor biological activities [6],and are used as herbicides. They are also applied in industry as dyes and pigments with luminescent properties. Azomethines are used as ligands for complexation of metal ions giving the complex compounds of rich physical, chemical and biological properties [7,8]. For that reason a huge number of mono- and bisazomethines are described in the literature. Moreover, while abundant information on the reactivity and physical-chemical properties of 5-member cyclic azomethines (oxazoles) exists, macrocyclic azomethines have not been the subject of any investigations. In addition, macrocyclic compounds like crown ethers and cryptand have received great attention in the last few years both in chemistry and in biology.

Based on all these observations we have undertook the synthesis of macrocyclic azomethines, bearing properties of both azomethines and macrocyclic compounds highly interesting and beneficial for the field development. We have reported the method of synthesis of 20-membered cyclic polyazomethine compounds [9]. Some chemical and physical properties of these macrocycles have been also investigated [10]. They are excellent azo partners and have ability to give tetrakis azo dayes via one-pot azo coupling reaction.

The synthesis of desired macrocyclic azomethines having hole diameter in the range of 1-10 nm have been synthesized according to the scheme shown below. Various nitrophenols **I** have been selected as starting materials, which reduction by zinc in the alkali media with following benzidine rearrangement result corresponding benzidine derivatives **III**. The last ones were diazotized by sodium nitrite and hydrochloric acid at 0-5 °C and obtained diazonium salts were undergone decomposition/hydrolysis by the treatment of hot diluted (20%, 95 °C) sulphuric acid without isolation of diazonium salts.

Synthesized tetrahidroxy biphenyls **IV** were reacted with chloroform in the presence of sodium hydroxide and corresponding biscarbonyl derivatives **V** were isolated as a pale yellow crystals. The last step – condensation reaction between **V** andvariousalkane diamines in the isopropanol gave desired macrocycles.



where: R=H, Br, SO_3H; n=0,2,4,6

Scheme. Synthetic pathway for the synthesis of macrocyclic azomethine.

On the base of performed investigation, we are able to declare that offered compounds are characterizing with interesting properties, namely:

- Easy and inexpensive preparation method
- Flexible technology, giving opportunity of further purposeful modification of the properties with easy transformations (to carry out electrophilic substitution reactions, to form stable complex compounds, etc)
- Good/excellent physical, chemical and technical properties (fastness against physical, chemical and biological treatment)
- Special optical properties of biomarkers (absorption - in the near-UV region, emission – in the visible region; blue-violet luminescence in the solid state, low excitation energy, etc).

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I-4. DONOR-ACCEPTOR CYCLOPROPANES IN SYNTHESIS OF CARBO- AND HETEROCYCLES

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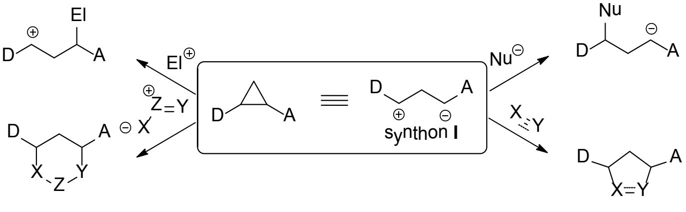
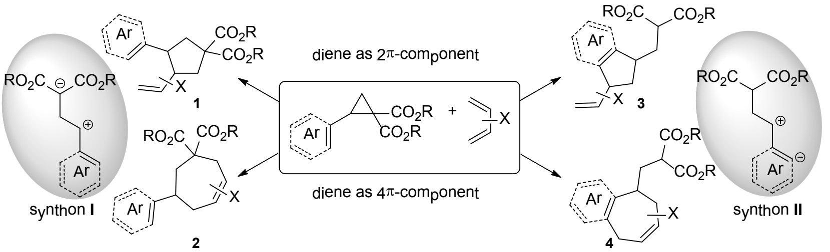
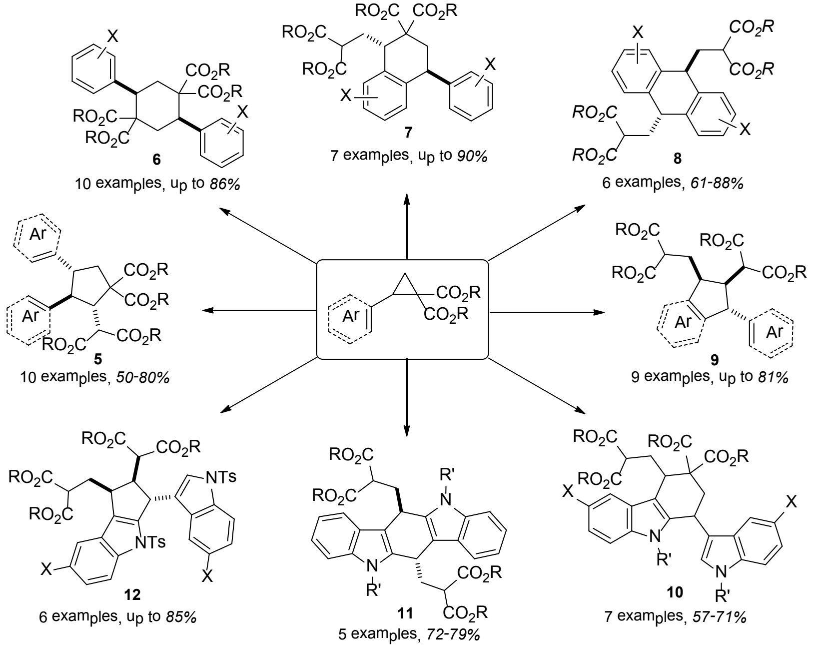
Cyclopropanes bearing donor and acceptor substituents in vicinal positions are referred to as donor-acceptor cyclopropanes [1]. These substituents polarize significantly C–C bond providing increase of both cyclopropane reactivity and reaction selectivity. As a result, donor-acceptor cyclopropanes react efficiently with nucleophiles by homo-Michael addition via activated C–C bond breaking. Equally, these cyclopropanes demonstrate nucleophilic behaviour in reaction with various electrophilic agents. Donor-acceptor cyclopropanes able to form cyclic products when react with compounds containing both nucleophilic and electrophilic centers. Moreover, introduced nucleophilic and electrophilic moieties can be used for further cyclizations, annulations and cycloadditions producing carbo- or heterocycles.
Donor-acceptor cyclopropanes enter also into Lewis acid-triggered [3+2]-cycloadditions with compounds bearing reactive double or triple bonds. Reacting with 1,3-dipoles, donor-acceptor cyclopropanes form products of [3+3]-cycloadditions serving as dipolarophiles. In all these processes, donor-acceptor cyclopropanes behave as equivalents of 1,3-dipoles (synthon **I**).



Recently we showed that reaction of 2-(hetero)arylcyclopropane-1,1-diesters (which are the most studied donor-acceptor cyclopropanes) with 1,3-dienes can proceed by four different ways as: a) 1,3-dienes can react as 2π- or 4π-components and b) cyclopropanes can react as synthetic equivalents of two different 1,3-dipoles (synthons **I** and **II**, respectively) [2].



Donor-acceptor cyclopropanes undergo also Lewis acid-induced cyclodiimerization affording a broad range of dimeric products depending on the substituents in (hetero)aryl donor group, the Lewis acid applied, solvent, reaction temperature, *etc.* We optimized reaction conditions for selective formation of diarylcyclopentanes **5**, *cis*-diarylcyclohexanes **6**, 4-aryltetralins **7**, 9,10-dihydroanthracenes **8**, 1-arylindanes **9** as well as the related tetrahydrocarbazoles **10**, dihydroindolo[3,2-*b*]carbazoles **11**,cyclopenta[*b*]indoles **12** and some other cyclodimers [3]. In some case, products of "cross-dimerization" were also synthesized.



Tetralins **7**, indans **9** and all indole-derived dimers are close analogues of bioactive natural compounds; some of them were found to demonstrate significant cytotoxicity against cancer cells being non-toxic towards “normal” fibroblasts.

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I-5. SYNTHESIS AND FUNCTIONALIZATION OF POLYMERIC MATERIALS AND POLYMER BRUSHES EXHIBITING VERSATILE SUPRAMOLECULAR INTERACTION STRUCTURED VIA MICROCONTACT CHEMISTRY

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Structuring of metal, glass and semiconductor substrates with polymers or with colloids such as nanoparticles or vesicles is a key challenge for surface based material science. Such substrates have the potential to find widespread application in optical and electronic devices, microarrays and materials for information storage. I will present site specific immobilization of nitroxide mediated polymerization initiators via microcontact chemistry employing thiol-ene click chemistry on glass supported alkene-terminated self-assembled monolayers. The polymer initiator covered substrates are used for preparation of poly(styrene) and poly(acrylate) brushes with defined and tunable brush thicknesses. Brush thickness dependent site specific protein adsorption of streptavidin and concanavalin A on structured polystyrene brushes is reported. Poly(styrene) brushes with a thickness of 40 nm or larger showed protein repellence whereas brushes below 15 nm thickness reveal protein adhesive properties.

I will also describe the synthesis of bifunctional block copolymers bearing orthogonally reactive backbone substituents such as 1,1,1,3,3,3-hexafluoroisopropoxycarbonyl groups as active esters and $\alpha-$hydroxyalkylphenylketones (2-hydroxy-2-methyl-1-phenylpropan-1-one) as additional photoactive moieties via reversible addition fragmentation chain transfer (RAFT) polymerization. As monomers 1,1,1,3,3,3-hexafluoroisopropyl acrylate (HFIPA) and 2-hydroxy-2-methyl-1-(4-vinyl)phenylpropan-1-one (HAK) are used. The incorporated HFIPA and HAK moieties are used for sequential chemoselective postmodification. The photoactive block can be functionalized through a nitroxide photoclick trapping reaction in the presence of functionalized nitroxides and the active ester moieties of the p(HFIPA)-block are readily thermally amidated using various amines. The chemically modified polymers feature a narrow molecular weight distribution. The process is successfully applied to the synthesis of a small polymer library and also to the preparation of homo and block polynitroxides using 4-amino-TEMPO as amine component in the transamidation reaction. The polynitroxides obtained are characterized by cyclic voltammetry (CV), FTIR, and UV-Vis. [1-4]

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KEYNOTE PRESENTATIONS

K-1. SYNTHESIS SOME OF BIOACTIVE ADAMANTANE FRAGMENT CONTAINING NEW DIPEPTIDES VIA UGI REACTION

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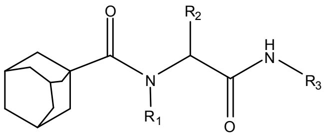
Adamantyl-containing compounds are utilized for a number of applications in medicinal chemistry(Amantadine, Rimantadine, Paramantine,Protexin,Bromantane, Kemantaneand many others areused widelyin medicine).The adamantane derivatives are characterised by antiviral,antimicrobial,anticancerogenic, anticataleptic, immunotropic, neuro-psychotropic and other activities [1].

The adamantyl group is present in seven compounds incurrent clinical use for the treatment of neurodegenerativedisorders, viral infections and type 2 diabetes, andin many more substances that are in development aspotential therapeutics. In many cases the adamantlygroup has been found to improve pharmacological properties of a parent compound, without increasing its toxicity [2].

On the other hand, dipeptides are characterized by a wide range of biological activities and are widely used in the drug industry [3]. It is know a lot of synthetic methods to obtain Peptides, but developments in isocyanides based multicomponent reactions is more interesting [4-6]. In that way the adamantane containing peptides which are obtained via Ugi-reaction is less studied. Therefore, new developments for the synthesis of adamantane containing new peptides and study of its properties are of a great interest.

The aim of the research is to synthesis of adamantan containing new dipeptides by using 1-aminoadamantane, adamantan-2-one and adamantan-1-carboxylic acid, in which 1-3 structure was obtained**.**



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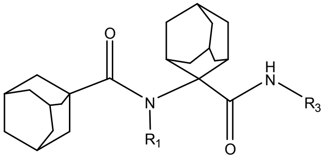

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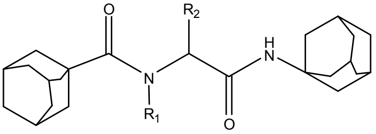

3

R_1=C_6H_4-O-CH_3; C_6H_{11}; C_6H_5; C_4H_9.
R_2=i-C_3H_7; C_6H_4-O-CH_3; $C_{10}H_{14}$; C_2H_5; m-Cl-C_6H_4.
R_3=CH_2-$COOC_2H_5$; Ad.

The structure of the obtained products was established by NMR spectral date.

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K-2. ANTHRAQUINONE AS A PRIVILEGED STRUCTURE IN DRUG DISCOVERY TARGETING NUCLEOTIDE BINDING PROTEINS

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The P2 purinergic receptors are a major class of receptors in the human body activated by nucleotides, such as ATP, ADP, UTP or UDP. They are subdivided into G protein-coupled or metabotropic P2 receptors (GPCRs), designated P2Y, and ligand-gated ion channels or ionotropic receptors, termed P2X (LGICs). Both families, GPCRs as well as LGICs constitute important drug targets.

In recent years, it was estimated that as many as 50% of available drugs act directly via stimulating or blocking GPCRs. Nucleotides acting at P2 receptors are readily hydrolyzed by ectonucleotidases yielding the corresponding nucleosides, for instance adenosine, which itself can activate the P1 family of purinergic receptors (adenosine receptors).

The anthraquinone dye Reactive Blue 2 (RB-2) has been reported to act as a non-selective antagonist of nucleotide receptors (P2X1, P2X2, P2X4, $P2Y_1$, $P2Y_2$, $P2Y_4$, $P2Y_6$, $P2Y_{11}$, and $P2Y_{12}$ receptors) and also as a non-selective inhibitor of ectonucleotidases. RB-2 was used as a lead structure for developing ligands with enhanced potency and selectivity for a particular nucleotide-binding protein target.

Novel synthetic protocols have been developed for accessing this very important new class of compounds (see Figure below). Circa 200 anthraquinone derivatives have been synthesized[1-5], many of which are new compounds previously inaccessible by standard methods.

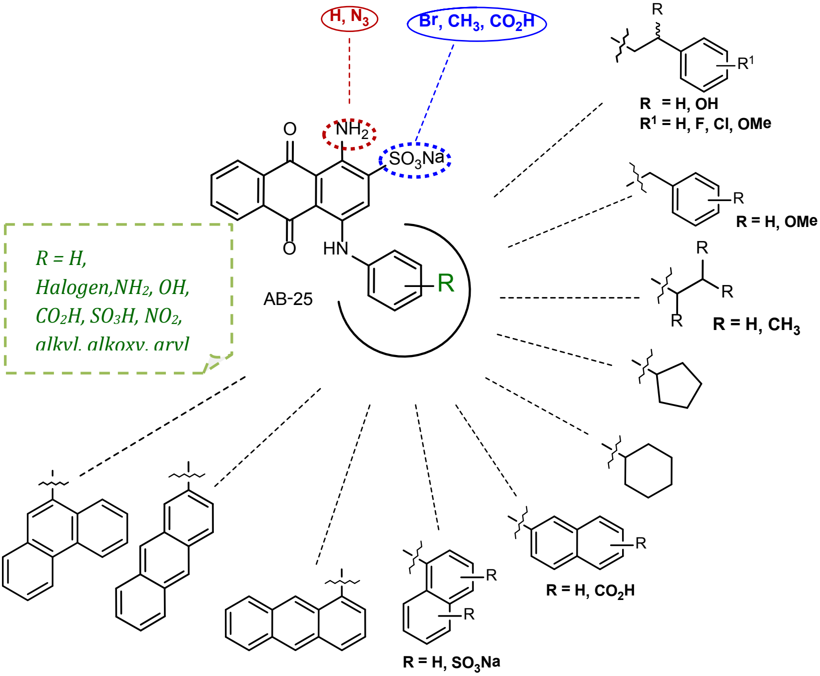
These methods were used for developing novel pharmacological tools and potential drugs, e.g.;

(i) platelet aggregation inhibitors which are competitive antagonists at the $P2Y_{12}$ receptor, an ADP-receptor predominantly expressed on blood platelets. $P2Y_{12}$ is a very important target for antithrombotic drugs, and

(ii) to develop ecto-5’-nucleotidase inhibitors (ecto-5’-NT). ecto-5’-NT has recently been identified as a potential target for novel anti-cancer drugs.

So far, very few ecto-5'-nucleotidase inhibitors have been described in the literature;

(iii) to discover the first potent and selective P2X2 channel blockers. The new compounds will allow subsequent testing in animal models.



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K-3. ON THE POSSIBILITY OF VISUALIZATION OF AMINO ACIDS INNER ELECTRIC FIELDS BY NMR SPECTROSCOPY

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Electrostatic interactions play the main role in biochemical processes where amino acid residues of biomolecules are involved. The electric field pattern of biomolecule, especially of its active center is principal for understanding mechanisms of proteins functionality.

Unfortunately today there is no conventional method for direct determination of electrostatic fields inside of a globule. The existing ones require the modification of protein by including sensitive groups or atoms and allow only rough estimation of field value only at one point, where EF sensitive group or atom is attached.

We underwent the investigation of the potential of one-bond spin-spin coupling constant (SSCC) for visualization of electric fields of molecules. We have shown sufficient contribution of electrostatic interactions into the changes of SSCCs in media with different electrostatic properties. [1]

We have shown that the ionic state of amino acids can be easily determined by measuring SSCCs as well as an ionic equilibrium in solution can be studied.

According to our approach the deviation of SSCC from value corresponding to isolated molecule is proportional to the value of EF acting along the bond, and, in its turn, is the superposition of fields, generated by the surrounding charges and reaction field of the media. This approach allows construction of the pattern of electric fields of molecule by transforming of each measured deviated value of SSCC from its isolated value into the acting electric field value along the bond.

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K-4. NOVEL REARRANGEMENT OF 5-VINYL 1,2,3-THIADIAZOLES TO THIENOPYRIDAZINES

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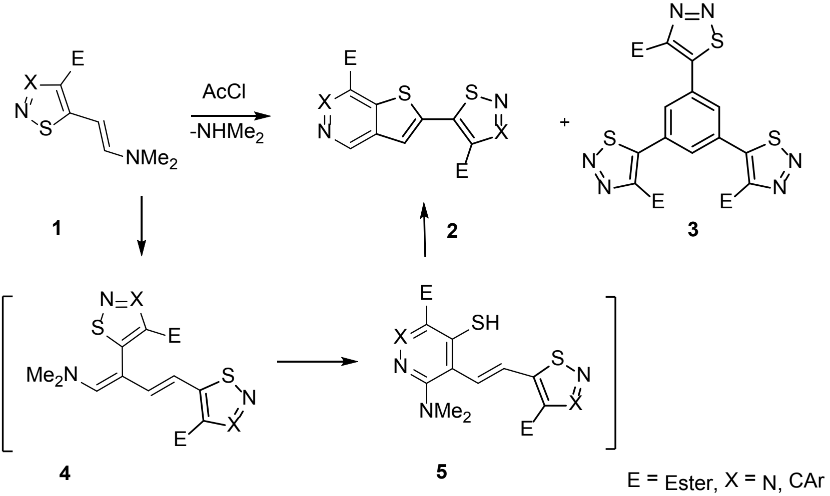
We have found that 3-(1,2,3-thiadiazol-5-yl and isothiazol-5-yl) enamines undergo the novel self-condensation initiated by acetyl chloride leading to 1,3-disubstituted dieneamines of type **4** [1, 2]. The increase of temperature is shown to change direction of the reaction in favor of novel thieno-azines **2** and 1,3,5-trisubstituted benzenes **3**. The formation of compounds **2** represents the unique transformation of sulfur containing ring involving novel rearrangement of 5-vilyl azole ring to 4-mercaptoazine circle. The structures of prepared compounds were confirmed by NMR-, mass-spectra and by X-ray analysis of single crystals. The mechanism, scope and limitations of the reaction will be reported.



E = Ester, X = N, CAr

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ORAL PRESENTATIONS

O-1. SYNTHESIS OF PIPERAZINE SUBSTITUTED PYRANO[4,3-*d*]THINEO [2,3-*b*]PYRIDINES

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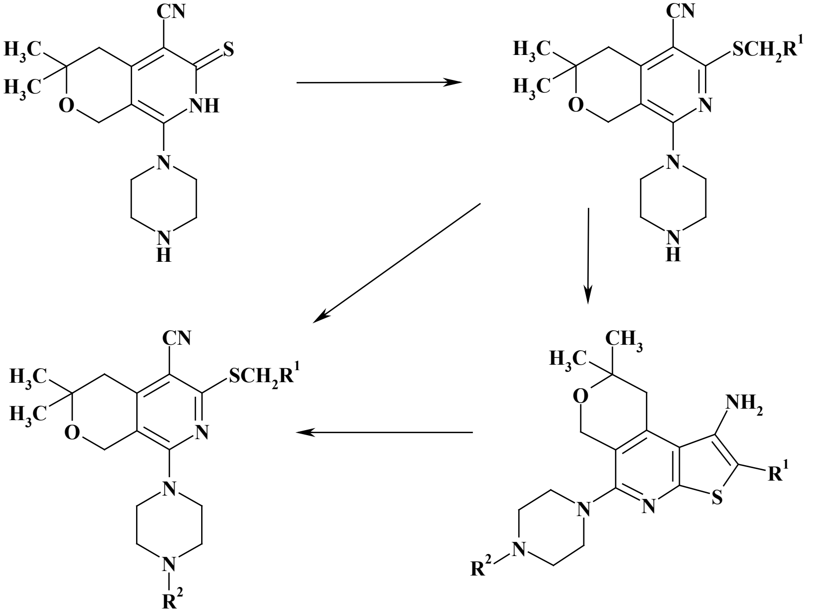
Functionally substituted piperazines possess diverse biological activities [1,2] and have wide applications in medecine [3]. The derivatives of pyrano[3,4-c]pyridines synthesized by us are widely used in organic synthesis for the construction of new heterocyclic systems, in particular pyrano[4,3-*d*]thieno[2,3-*b*]pyridines [4-6].

In the present study, we have developed a method for obtaining derivatives of thioalkyle piperazine substituted pyrano[3,4-*c*]pyridines, which are then cyclized to the corresponding thieno[2,3-*b*]pyridines according to the following scheme:



R^1=H, COOMe, COOEt, $CONH_2$, CN, $CONHCH_2C_6H_5$:
R^2=CH_2COOMe, COOEt, CH_2COONH_2, $CH_2CONHC_6H_5$, $CH_2C_6H_5$, $CH_2COC_6H_5$

As a starting compound for the synthesis was used 3,3-dimethyl-8-piperazin-1-yl-6-thioxo-3,4,6,7-tetrahydro-1*H*-pyrano[3,4-*c*]pyridine-5-carbonitrile [2], which has three reactive sites. The elektrophilic substitution is possible both in the piperazine ring-, and in the thiol group, as well as in the endocyclic nitrogen atom. We have developed special conditions allowing to carry out regioselective substitution of the thiol group of pyridine ring, followed by the further a substitution in the piperazine ring. At the last step, the substituted pyrano[3,4-*c*]pyridine is then cyclized resulting in the formation of thieno[2,3-*b*]pyridines as a final product.

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O-2. EVALUATION OF SOIL ROOT GROWTH *Ziziphora tenuior* BY XRF TECHNIQUES

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Abstract

In order to survive, the plant species are dependent on the environment, and are continuously affected by their environment as they also made impact on it. In this research, the habitat of *Ziziphora tenuior* specie, in south of Kerman province, was studied by means of XRF technique. The amounts of 7 elements were determined by XRF technique, among which the results of sodium was more noteworthy than the others. It can be said that this specie shows a significant effect on the soil sodium absorption.

Keywords: *Ziziphora tenuior*, XRF techniques, Soil root growth,SAR

Introduction

Each plant species is a part of its environment and also dependent on it, and its existence out of the environment is not imaginable.[1] Therefore, the plant species, in order to survive, are dependent on the environment, and are continuously affected by their environment as they also made impact on it.[2] On the other hand, the change and variation of desert regions throughout the time under the influence of different factors, have led to creation of different landforms.Plant coverage is one of these factors, so the existing natural factors in desert regions along with affecting on each other, can also be harmonized, one of these case studies is the investigation of plant coverage relation with physical and chemical properties of soil.[3] Plant can cause the reduction of some elements in the soil of their habitat by absorbing them. This factor results in richness or weakness of the landforms relative to different elements. *Ziziphoratenuior* is from *Labiatae* family and belongs to subfamily of *Ziziphora.[4]*This is a multi- year plant and its bushes are thick and have a height of 20 to 50 cm. its flowers are violet. In many hot and dry zones of Iran, this plant has been used as an antibacterial, anti-influenza and intestine disinfector medication.[5] In the past some studies were conducted on the mutual impacts of the plant and the soil on each other.[6,7] but about this special specie, there has not been any previous study.

Materials and Methods

The soil samples were collected from 3 -5 cm distance of the root with the approximate depth of 10 cm. The control soil sample was collected from 2 m distance of the root. For being applied in XRF spectrometer, the samples were prepared in the form of a glass tablet for analysis of the main elements. The preparation of the soil samples were first made by passing through an IR sieve which results in the uniform particles, then by mixing the sample powder with meth borate or tetra borate, they were made in the form of the transparent tablets.[8] The applied XRF spectrophotometer was made by Philips (model pw4025) in which a Si-PIN and a thin Beryllium window were used. The device made its analysis with the help of MiniPal software.

Results and Discussion

The soil samples were evaluated by XRF technique for 7 different oxides which are effective in plants growth and determination of the type of the soil. For each oxide, a value for the control soil and one for root soil sample were obtained. The results obtained from XRF analysis are presented in table 1. These values showed significant variations for calcium oxide and sodium oxide, but for the 5 other studied oxides no significant change was observed. In contrast with calcium, sodium has many positive and negative effects on the growth of the plant whose intensity is dependent on the level of this element in the soil of the plant's habitat.

Table1.

No.	Metal oxide	Control soil	Soil root growth
1	**Na_2O**	1.94	1.16
2	**K_2O**	2.65	2.57
3	**MgO**	2.81	2.53
4	**CaO**	2.85	3.52
5	**MnO**	0.23	0.24
6	**Al_2O_3**	11.32	10.27
7	**Fe_2O_3**	6.87	6.68

Conclusions

It can be expressed that this specie shows a notable and significant difference in absorption of soil sodium in comparison with the other elements, in a way that the absorption of sodium in presence of this specie showed a 60% increase. These results are due to the ability of some plants in surface absorption of the cations by the root.[9] On the other hand, the amount of calcium oxide increased in the root soil which could be an indicator of existence of calcium carbonate or calcium sulfide in the root soil. If there was calcium carbonate in the soil, it had no significant effect on the growth of plant but if the amount of calcium sulfide got high in the soil, it could have negative effects on plant's growth.[10] However the plant was not able to make a considerable impact on the amount of potassium, manganese, iron, aluminum and magnesium. Generally, it can be said that each plant species has a determined relation with some specific properties of the soil.

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O-3. PHOTOINDUCED SYMMETRY−BREAKING INTRAMOLECULAR CHARGE TRANSFER IN A QUADRUPOLAR PYRIDINIUM DERIVATIVE

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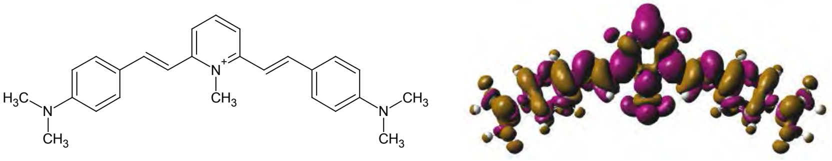
During the last years chemists are paying increasing attention to organic compounds bearing electron donor (D) and acceptor (A) groups linked by π−conjugated bridges owing to their non−linear optical (NLO) properties for application in imaging, photodynamic therapy, sensing, memory storage, micro− and nano−fabrication. Dipolar (D−π−A) molecules have been extensively investigated,[1] whereas the more complex photobehaviour of quadrupolar systems (D−π−A−π−D or A−π−D−π−A) still needs to be deeply understood. The study of two−photon absorption materials represents one of the hottest topics in today’s research[2] due to a great deal of applications.[18-31] The highly symmetric quadrupolar systems have surprisingly shown, in some cases, spectral and photophysical properties significantly affected by the surrounding medium.[2,3] Therefore, for these chromophores the studies carried out up to date suggest the presence of polar electronic states.

We report here a joint experimental and theoretical study of a quadrupolar pyridinium derivative of potential interest as NLO material (see Scheme 1, left). The spectral and photophysical behaviour of this symmetric system result greatly affected by the polarity of the medium (see Figure 1). A very efficient photoinduced intramolecular charge transfer, surprisingly more efficient than in the dipolar asymmetric analogue, is found to occur by femtosecond resolved transient absorption spectroscopy. TD−DFT calculations are in excellent agreement with these experimental findings and predict large charge displacements in the molecular orbitals describing the ground, and the lowest excited singlet state (see Scheme 1, right). The theoretical study revealed also that in highly polar media the symmetry of the excited state is broken (Figure 2) giving a possible explanation to the fluorescence and transient absorption spectra. The present study may give an important insight into the excited state deactivation mechanism of cationic (D–π–A–π–D)$^+$ quadrupolar compounds characterised by negative solvatochromism, which are expected to show significant TPA. Moreover, the water solubility of the investigated quadrupolar system may represent an added value in view of the most promising applications of TPA materials in biology and medicine.



Scheme 1. Quadrupolar pyridinium derivative molecular structure (left) and difference in S_0 and S_1 electron densities (right).

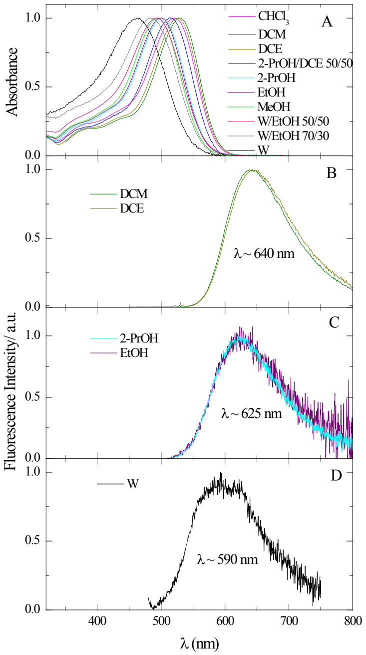


Figure 1. Normalised absorption (A) and emission (B, C, D) spectra in solvents of different polarity (left), and how the solutions in CHCl$_3$ and in water look like (top).

Figure 2. Comparison between the S_0 (left) and S_1 (right) optimised geometries in MeCN.

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O-4. THE MATHEMATICAL DESCRIPTION FOR THE WORK OF THE POLY(P-AMMINOACETANILIDE) BASED ELECTROCHEMICAL NITRITE SENSOR

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The electrodes, based on conducting polymers have already gained their use in electroanalysis, because of the clear response, selectivity, homogeneity in electrochemical deposition, good adhesion to the electrode surface and metallic conductivity [1]. Electropolymerization is one of the most used method for the synthesis of conducting polymers [2 –4].

At the other hand, nitrite ions (NO_2^-) are nocive for the human health and ambient [5 – 6]. So, the confection of credible analytical techniques (spectrophotometrical, photochemical, chromatographical and electroanalytical), capable to detect nitrite has gained attention for the last 10 years.

New electrochemical nitrite sensor, based on poly(p-amminoacetanilide) has been developed [7] and it is based on the reactions:

$$H^+ + NO_2^- \rightarrow HNO_2$$

$$2HNO_2 + CP\,(red) \rightarrow 2NO + 2H_2O + PC\,(Ox) \qquad \text{(chemical stage)}$$

$$PC(Ox) + 2e^- + 2H^+ \rightarrow PC(Red) \text{ (electrochemical stage)}$$

In this work, the sensor is described mathematically. The conclusions of the modelling are in accord with the experimental facts.

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O-5. ANALYSIS OF THE SOIL ROOT GROWTH OF *THYMUSVULGRIS*BY FLAME ATOMIC ABSORPTION

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Abstract

As the soil affects the plants species, the plant species can also have effects on the soil. The difference of leaf litter, root activities, reabsorption of nutrition elements and the growth and absorption of the existing cations in the soil are among the major factors of the plant species effectiveness on the soil characteristics. In this research, the habitats of *Thymus vulgris* specie, in south of Kerman province, was studied by means of Flame atomic absorption technique. The levels of seven elements were determined among which the amount of nickel was more noteworthy in comparison to the other elements. From the obtained results it can be concluded that if the amount of nickel in the plant is in the allowed range, then it can be applied as an herbal plant; however, this plant can be used as a bioremediation plant.

Keywords: *Thymus vulgris*, Flame atomic absorption, Soil root growth

Introduction

As the soil affects the plants species, the plant species can also have effects on the soil.[1] The difference of leaf litter, root activities, reabsorption of nutrition elements and the growth and absorption of the existing cations in the soil are among the major factors of the plant species effectiveness on the soil characteristics. Moreover, determination of the ability of the plants to change the characteristics of the soil is an important factor in species immigration and soil reclamation.[2] Soil- plant mutual reaction and morphological and physiologic condition of the plants determines which one is dominant: plant or soil. Generally, it can be said that each plant species is created via the development of a series of physiognomy (appearance) and physiological properties which have enhanced its life chance in a determined environment. Although a combination of the environmental factors in a place controls the growing plants in that region, but the plants' properties, themselves could be important; these properties are associated to the physiology and physiognomy of the plant.[3] Therefore the study of plant species in association with the physical and chemical properties of soil can relatively reveal the physiological and physiognomic properties of the species and their impacts on their habitat.

Thymus vulgaris is a multi-year plant which belongs to Lamiaceae family. The origin of this plant is reported to be Mediterranean regions. Its height ranges from 20 to 50 cm. It has small, reciprocal and to some extent Lanceolateleaves which are covered with gray fluff. The flowers are small, white and purple or pink which collectively appear on the above parts of the stems coming off from the leaves sides in the cycles. The fruit of this plant is a dark brownish achene with the length of one ml.[4] Different physical and chemical methods have been developed for elimination of heavy metals from the environment, the application of some of these methods are not economically reasonable, and on the other hand, some of them have some negative ecological effects on physical, chemical and biological properties of the soil.[5] In recent years, application of living organism such as microorganism has attracted much interest due to being environmental friendly and cost- effective, these methods are called bioremediation.[6] If the plants are used, this method will be called phytoremediation.[7] If a plant is able to exchange these elements, it can be employed as a bioremediation plant. There was no research conducted on the mentioned specie to be used for comparison with the present results, and this is the first report on this plant species.

Materials and Methods

The soil samples were collected from 3 -5 centimeters distance of the root with the approximate depth of 10 cm. The control soil sample was collected from 2 m distance of the root. In order to prepare the metal cation containing solutions, first the existing organic substances in soil must be removed and then the solution would be prepared. For this purpose, 5 grams of soil was hydrated by several drops of distilled water, and then 15 ml of nitric acid was added to that, then the mixture was heated slowly. This action was repeated up to complete burning of the organic substances of the plant. After 45 minutes of heating and completeness of nitric acid reactions, 10 mL of nitric acid and 10 mL of concentrated per chloric acid were added to the residual mixture, the resulting mixture was then heated slowly till the moist minerals were obtained. The residual minerals were then solved in 4 ml of concentrated nitric acid, and the volume of the solution was reached to 5ml by addition of 1% per chloric acid. The obtained solutions were then evaluated by flame atomic absorption device made by Varian spectra (model A220).

Results and Discussion

The soil samples for 7 different elements capable of having impact on the growth of plant for determination of soil type were evaluated by means of flame atomic absorption device. For each element, the result for the control soil and the one for soil of the desired plant's root were obtained. The results of flame atomic absorption analysis are presented in table 1. These results show the significant variations for the case of nickel and zinc, while no significant results were observed for the other 5 studied elements. Considerable and significant reduction in the amount of nickel in soil of plants habitat can be a sign of this element absorption by Thymus vulgaris.

Table1. Amounts ofmetal elementsin soilnear therootsand control samples

No.	Metal ion	Control soil	Soil root growth
1	**Ag**	1.46	1.88
2	**Cr**	2.32	2.91
3	**Cu**	6.09	6.67
4	**Ni**	8.28	7.34
5	**Co**	4.76	5.06
6	**Zn**	52.71	28.32
7	**Ba**	11.08	10.62

Conclusions

Notable reduction of nickel (more than 50%) in the root surrounding soil in comparison to the control soil could be an evidence of this element absorption by Thymus vulgaris, in this content this plant has showed high capability of nickel absorption. Since the daily consumption limit of nickel for an average person is 1.2 mg, if the amount of nickel accumulation in the plant is in the allowed range, its use as a herbal plant is safe. But if it is out of allowed range, the consumption of this plant by the native people must be prohibited. In this case, Thymus vulgaris can be employed as a plant with high capacity of bioremediation for cleaning up the environment from high levels of Nickel.

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O-6. AN EFFICIENT APPROACH FOR THE SYNTHESIS OF BIS(THIAZOLES)

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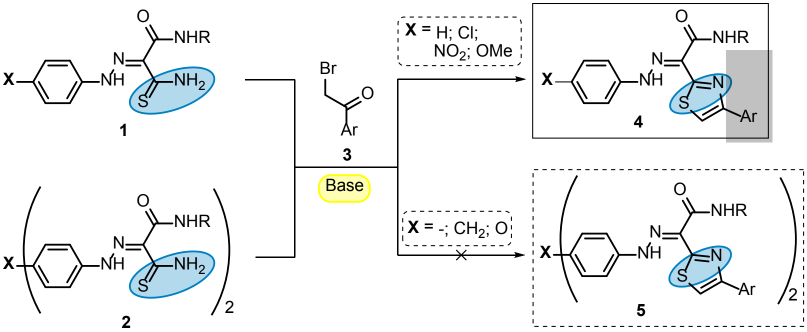
Thiazole fragment is a part of different natural and synthetic bioactive compounds that applied in pharmaceutics, clinical chemistry, agriculture, etc [1]. The most famous method of thiazole construction is the interaction of thioamides and haloketones [2]. In continuation of our interest for the synthesis of the bis(heterocycles), we decided to use this approach to obtain bis(thiazoles).

Started bis(hydrazonothioamides) **2** were prepared according to well-known procedure for the synthesis corresponding mono(hydrazones) [2]. Reaction between bis(hydrazonothioamides) **1** and bromoketone **3** was studied under various conditions. As a result of this investigations we obtained a series of bis(thiazoles) **5** and proposed convenient scheme for the preparation of this compounds.



Base: N(Et)$_3$; N(i-Pr)$_2$Et; DBU; t-BuOK; KOH; K_2CO_3; $CsCO_3$

The structural determination of synthesized products **5** was achieved following by their spectral (NMR ^{1}H; NMR ^{13}C; IR) and elemental analysis data.

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O-7. THE INVESTIGATION OF GAS PERMEABILITY THROUGH THE GLASS-CRISTALLINE SHELL OF HOLLOW ALUMINOSILICATE CENOSPHERES

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Helium is main component in many modern high-tech and science-intensive industries such as superconductivity, atomic industry, rocket engineering, detection of microleaks etc., which require of production of high-purity helium (99,9950 vol. %). The actual industrial technology for obtaining of high-purity trade helium is based on its release from the natural and oil gases using cryogenic process. This process involves following stages: preparation of natural and oil gases to the low-temperature condensation, the low-temperature condensation with the formation of a helium concentrate containing approximately 80 vol. % He, multistage purification of helium concentrate from impurities (CH_4, H_2, O_2, N_2, Ar and Ne) and liquefaction of helium, that make a very energy-intensive cryogenic separation method [1].

An alternative way for obtaining of high-purity trade helium is diffusion-sorption technology combining pressure swing adsorption (PSA) and membrane separation. To realize the membrane separation in practice is necessary to use materials with high helium permeability and selectivity, high chemical and thermal stability, high strength, and low cost. Such materials as different polymers, metal-organic frameworks (MOF), zeolites, glasses can be considered as the potential membranes due to their high permeability to helium. However, the selectivity for He/CH_4 of different polymers, MOFs, zeolites change in the range 2 -92 [2-5], and in rare cases, values are 10^3 [6] while this index for glasses reaches a level of the order of 10^4 - 10^6 [7-10]. This fact makes the most suitable silicate glasses for selective extraction of helium

The use of hollow glass-crystalline aluminosilicate cenospheres as membrans is one of the ways to improve of membrane technologies [11].

The narrow fractions of nonmagnetic nonperforated aluminosilicate cenospheres (fig. 1) with low-density, with globules size -0.063+0.050 mm, obtained from cenosphere concentrates of fly ash from burning coal were used in this study.

The extraction of cenosphere narrow fractions was carried out with the use of a technological setup[12],which included the stages of magnetic separation, granulometric classification with the subsequent hydrostatic isolation of the perforated globules and the destroyed particles. The average diameter of cenospheres in the obtained fraction -0.063+0.050 mm is equal to 58-61 µm, with the dense nonporous shell thickness being 2.5-3.1 µm.

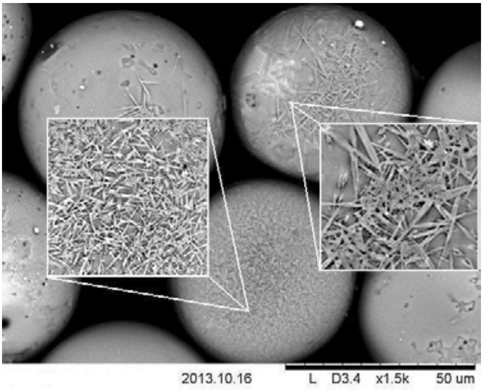

Fig. 1 SEM images of cenosphere narrow fraction about thermal treatment at 1273 K, O_2

According to the chemical analysis, the narrow fraction of cenospheres are multi-component system of SiO_2 - Al_2O_3 - Fe_2O_3 – CaO – MgO - Na_2O - K_2O - TiO_2 with the contents of the major components SiO_2 and Al_2O_3 in the ranges of 58.1-58.3 and 32.1-36.6 wt %, respectively. According to the quantitative X-ray analysis, the phase composition of cenosphere shell consists of the glass phase and crystalline phases includes of mullite, quartz, and calcite crystallites. To increase the content of crystalline phases the samples were subjected to thermal treatment at temperatures of 1273 and 1373 K in an oxygen or argon atmosphere. According to the data obtained as a result of heat treatment, the part of glass phase in samples decrease due to formation of an additional mullite (I) phase in an amount of 5.9 to 23.6 wt. %. The mullite (I) phase is different from the original mullite (0) by smaller crystallite sizes and different lattice parameters. The increase of mullite (I) lattice parameters is observed by thermal treatment in an oxygen atmosphere. This is due to the oxidation of Fe^{2+} ions to Fe^{3+} and their introduction into the crystal lattice of mullite. The samples processed through the inert argon atmosphere opposite are characterized by lower values of mullite (I) lattice parameters. Thus it should be pointed that defective-free mullite phase is formed by thermal treatment of samples in argon atmosphere unlike treatment in an oxygen atmosphere.

The permeability of the cenospheres to single gas He, H_2, and Ne was investigated in a vacuum apparatus under the conditions of gas diffusion from the reactor volume into globules at a pressure of $3{\cdot}10^4$ Pa in the temperature range from 298 to 623 K for helium and from 553 to 773 K for hydrogen and neon. The diffusion of gases through the globule shells occurred as a result of the difference between the gas partial pressures outside and inside the globules. The gas permeability *Q* [mol/(Pa·s·g)] determination is based on the measurement of the pressure drop time-dependence after the gas injection into the reactor filled with the sample. The relative error in the determination of the permeability does not exceed 10%. The permeability coefficient values K [(mol·m)/(m^2·s·Pa)] for the cenosphere shells were calculated according to basic equation for gas diffusion through a membrane

$$K = Q{\cdot}\delta/S, \qquad (1)$$

where *Q* is the gas permeability of cenosphere shells[mol/(Pa·s·g)]; δ is the apparent shell thickness [m], *S* is the geometrical surface of the sample particles, which is calculated as the sum of the surfaces of identical spheres with diameter D_{av} [m^2/g]. The selectivity was defined as ratio of K for single gases.

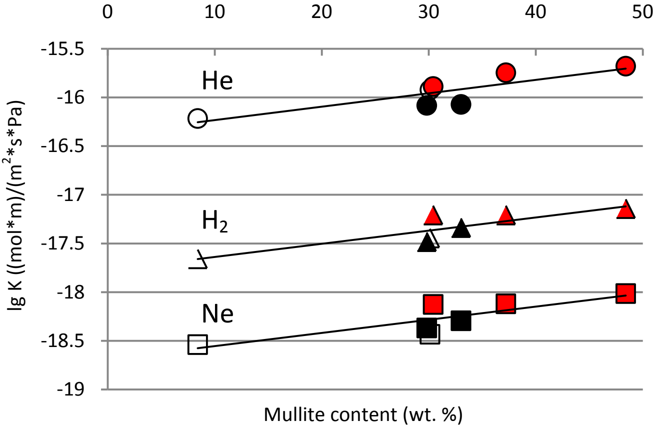

Fig. 2 Dependences of permeability coefficients to He, H_2, and Ne at 553 K on the content of mullite formed during thermal treatment in O_2 (red symbols), Ar (black symbols) and without thermal treatment (open symbols)

It was found the permeability of glass-crystalline shell of cenospheres increase with increase of mullite phase content for the studied gases over the entire temperature range. The sample of cenospheres processed through the inert argon atmosphere are exception. A subsequent additional thermal treatment in an oxygen atmosphere does not improve the diffusion properties. Figure 2 shows the dependences of the permeability coefficients K_{He}, K_{H2}, and K_{Ne} at 553 K on the mullite phase content in the cenospheres.

The cenospheres with the maximum mullite phase content (48.4 wt %) are characterized by the highest level of permeability for all gases studied. The values of the selectivity for He/H_2 and He/Ne for this sample at a temperature of 553 K are equal to 29 and 217, respectively.

The results of the study indicate the possibility of using cenospheres as membranes for helium capture during of diffusion-sorption technology

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O-8. ONE-POT, SEQUENTIAL FIVE-COMPONENT SYNTHESIS OF NOVEL SPIRO[INDENO]QUINOXALINE-PYRANOPYRAZOLE DERIVATIVES

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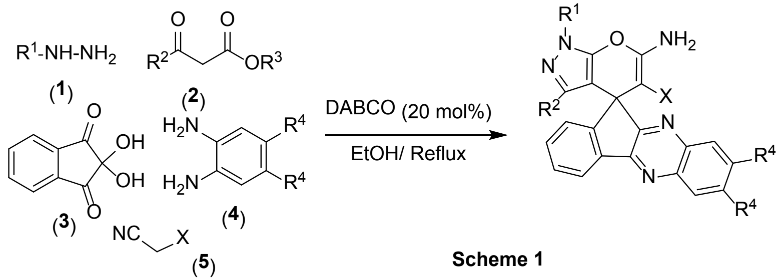
Multi-component reactions (MCRs), in which multiple reactions are combined into the synthetic operation, have been used extensively to form carbon-carbon bonds in the synthetic chemistry [1,2]. These reactions are economically and environmentally very advantageous because multi-step synthesis produce considerable amounts of waste mainly due to complex isolation procedures often involving expensive, toxic and hazardous solvents after each step. MCRs are now being tuned for synthesizing various heterocyclic compounds due to their diverse biological activities [1-3].

Functionalized nitrogen- and oxygen-containing heterocycles play important roles in medicinal chemistry [4]. Amongst them, quinoxalines [5], indenoquinoxalines [6], pyranes [7], pyrazoles [8] and their spiro compound [9] are an important class of biologically active heterocycles.

On the basis of biological studies, the existence of two or more different heterocyclic moieties in a single molecule often enhances the biological activity remarkably [10]. In continuation of our recent studies on green chemistry protocols, multi-component reactions and synthesis of quinoxalines, pyranes, pyrazoles and their spiro compounds [11-19], herein we report a sequential one-pot, five-component method for the synthesis of novel spiro[indeno[2,1-*b*] quinoxaline-11,4′-pyran]-2′-amines from hydrazine derivatives (**1**), β-ketoesters (**2**), ninhydrin (**3**), 1,2-diaminobenzenes (**4**) and alkylmalonates (**5**) in the presence of DABCO as a non-toxic and effective solid base catalyst (Scheme 1).



Scheme 1

For the synthesis of the titled compounds, at first, hydrazine derivatives (**1**) (1 mmol) and β-ketoesters (**2**) (1 mmol) were added to a 25-mL round-bottomed flask containing DABCO (0.2 mmol) in ethanol (10 mL). The flask was fitted with a condenser, and the resulting mixture was heated to reflux under stirring. After the required time for the formation of corresponding pyrazolone (0.2 -2 h), ninhydrin (**3**) (1 mmol), 1,2-diaminobenzenes (**4**) (1mmol) were added in to thr reaction mixture to form the corresponding indenoquinoxaline (0.2 h) and then alkylmalonates (**5**) (1 mmol) was added to this reaction mixture under reflux conditions. Upon completion of the reaction (monitored by TLC), the reaction mixture was allowed to cool to room temperature. The solid product was filtered, dried, and subsequently recrystallized from hot ethanol.

In conclusion, we have developed a clean, simple, one-pot, sequential five-component method for the synthesis of new spiroindenoquinoxaline–pyranopyrazole derivatives catalyzed by DABCO in ethanol under reflux conditions. This method is bestowed with several unique merits, such as high conversions, simplicity in operation, multi-component synthesis and cost efficiency and thus significantly contributes to the practice of green chemistry.

Acknowledgment

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O-9. SPARK PLASMA SINTERING OF SIC POWDERS PRODUCED BY DIFFERENT COMBUSTION SYNTHESIS ROUTES

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Ceramic materials based on silicon carbide (SiC)have a set of unique properties, such as thermal and chemical stability,refractoriness and high hardness. Due to these properties, SiChas a wide range of applications, including abrasivesand cutting materials, structural ceramics and crystalsfor microelectronics, catalysts, and coatings.

The traditional method of manufacturing SiC is theprocess invented by E. Acheson in the 19th century and is based on the reduction of silica SiO_2 with carbon. The method requires high temperatures (above 2000 K) and long durations (30 - 150 h), which makes difficult a production of nanosized silicon carbide powders. A modern alternative to the Acheson process could be self-propagating high temperature synthesis (SHS), which is based on the use of the heat of an exothermic chemical reaction for production of various advanced compounds.

In the case of combustion synthesis of silicon carbide from elements the reaction can be written as follows:

$$Si + C = SiC + 73 \text{ kJ/mol} \qquad (1)$$

The reaction (1) has a moderate enthalpy of product formation (compared to H_{273} = -230 kJ/mol for Ti-C system) and thus has relatively low adiabatic combustion temperature (T_{ad}=1860 K; compared with 3290 K for Ti-C reaction). Thus it is not easy to accomplish a self-sustained SHS process in this system. However, almost all available literature on CS of silicon carbide is related to this chemical pathway. Several approaches have been developed to enhance the reactivity of Si-C system. They can be sub-divided in five major groups:

(a) CS with preliminary preheating of the reactive media;

(b) CS with additional electrical field;
(c) Chemical activation of CS process;
(d) SHS synthesis in Si-C-air/nitrogen systems;
(e) Mechanical activation of the initial mixture.

The use of one or another approach depends on the desired product properties, e.g. purity, particle size distribution, morphology and yield, as well as cost considerations.

The other way to synthesize SiC in combustion way is to use reduction route. The overall combustion reaction for reduction synthesis of SiC, when magnesium (Mg) is used as a reducing element, can be written as follows:

$$SiO_2 + 2Mg + C = SiC + 2MgO \qquad (2)$$

The thermodynamic analysis allows calculating the adiabatic combustion temperature (T_{ad}) and equilibrium products composition for reaction (2) as a function of the inert gas (argon) pressure (P) in the reaction chamber. It was shown that T_{ad} increases and the amount of gas phase products decreases, with increase of inert gas pressure. Also the absolute value of T_{ad} exceeds 2000 K, which is above melting (m.p.) and boiling (b.p.) points of magnesium (922 K and 1363 K, correspondingly), as well as m.p. of silicon (1683 K) and silicon oxide (1923 K), but well below m.p. of MgO (3073 K) and carbon (4093 K). It was also proved that the amount of gaseous products (which includes Mg, CO and SiO) can be significantly decrease by increase of inert gas pressure in the reaction chamber, since higher P suppresses the metal -gasification processes.

In this work silicon carbide (SiC) powders were synthesized by four different combustion-based routes: (i) chemical activation of reaction by adding of polytetrafluoroethylene (Teflon); (ii) mechanical activation of Si-C powder mixture; (iii) in ternary Si-C-N_2 system and (iv) by reduction reaction (2).

Second, to obtain a compact material used spark plasma sintering techniques, homogeneous micro- structures of silicon SiC ceramics were obtained by four different combustion-based routes. The results show that an additional electric current is essential for achieving a large number of evenly distributed ignition points that ensure that the self-propagating reaction simultaneously takes place within the entire volume. The effects of the electric current and the heating rates on the resulting SiC ceramic densities and microstructures are discussed.

However, in the past, SiC ceramics have been difficult to sinter by traditional sintering techniques to an adequate density, e.g., hot pressing of SiC-based materials does not give a density over 70% of the theoretical value even despite using high pressures.

In addition, one of the aim of this work is to examine the influence of electric current on the self-propagation reaction Si-C using reaction mixtures after HEBM. Studied the effect of DC current under SPS conditions on nonconductive reactants. The resulting solidification and microstructures of the SiC ceramics formed were studied.

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O-10. SMILES REARRANGEMENT IN THE SYNTHESIS OF THE CONDENSED 3-CYANOPYRIDINES

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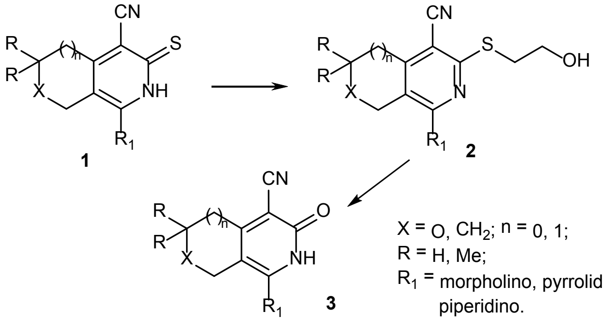
The 3-cyanopyridin-2(1*H*)-ones are of both theoretical and practical interest. In particular, they are synthons for annelated heterocyclic systems [1-4] while 3-cyanopyridin-2(1*H*)-ones show cardiotonic and inotropic activity as phosphodiesterase inhibitors [5-7].

We have previously prepared 5-cyanopyrano[3,4-*c*]pyridin-6(7*H*)-ones which contain alkyl and aryl substituents in position 8 [8]. With the aim of introducing cyclic amine fragments into the pyridine ring, we have developed a method for preparing condensed 3-cyanopyridin-2(1*H*)-ones through Smiles rearrangement.

We have used the condensed 3-cyanopyridin-2(1*H*)-thiones **1** [9, 10] as starting materials. This task was achieved using the 2-hydroxyethylsulfanyl derivatives **2** which underwent a Smiles rearrangement using sodium hydroxide under analogous conditions to give the 3-cyanopyridin-2(1*H*)-ones **3**. Structure of the synthesized compounds was proved IR, ^{1}H NMR spectroscopy and X-ray structural analysis.



X = O, CH_2; n = 0, 1;
R = H, Me;
R_1 = morpholino, pyrrolidino, piperidino.

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O-11. INTERACTION NATURE IN TI-NI SYSTEM AT FAST HEATING CONDITIONS

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In this workthe kinetic features of Ti-Ni heterogeneous exothermic reaction were investigated at fast heating conditions (from 60 to 2600 ^{o}/min). For this purposeHigh-Speed Temperature Scanner (HSTS-1) was used. HSTS-1 was designedto characterize the exothermic solid-state chemical reactions taking place in powder mixtures at rapid heating [1].

For investigations 50-100 mg samples were placed into the heater (Ni-foil with 100 □m thicknessas a mini envelope). Then the heater with reactive powder mixture isplaced into the reaction chamber and heated up directly by electrical current following the programmable steps (fig.1). The experiments were done at 1 atm Ar environment. Alumel-chromel thermocouple is used to monitor and record temperature during the experiment. The method allows heating rate of sample from 60 to 10^{4o}/min and temperature range of scanning: from room temperature to 1300^{o}C.

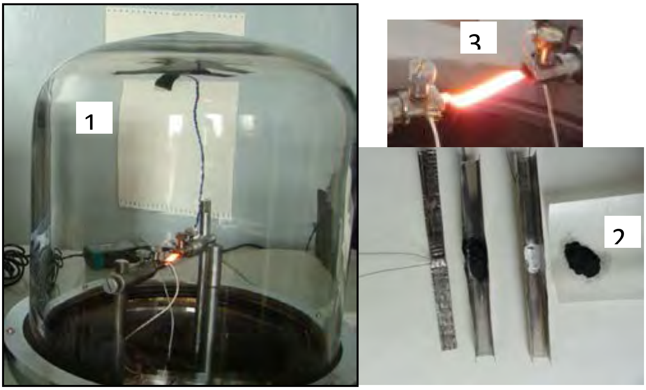

Fig.1. Experimental reaction chamber (1), reaction mixture and Ni-foil envelope (2) and heated sample (3)

Two different reaction systems were studied: initial powder mixtures and the same powder mixtures after mechanical activation (MA). The obtained results depend on heating rate and activation time show that:

- The self-heating increases upon heating rate.
- The reaction onset temperature for Ti-Ni non activated mixture is about 1000-1040 °C and does not display significant changes upon rising heating rate: from 60 to 2600 °/min.
- After 3 min MA an intensive interaction starts at almost twice lower temperature than for non activated mixture (fig.2).

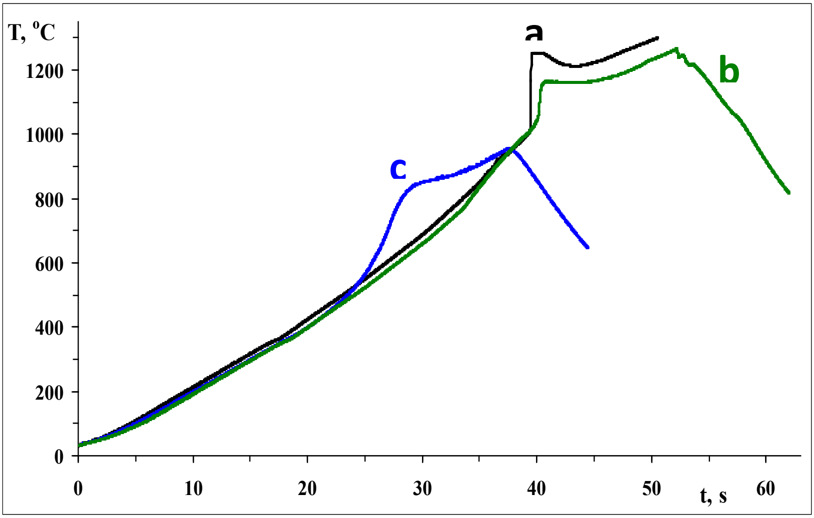

Fig.2 Ti + Ni interaction thermograms depending on MA duration: a – 0, b – 1 and c – 3 min.

(V_h = 1300 °/min)

This work is partially supported by SCS RA and RFBR joint Armenian Russian research Grant AR 13RF-057 // 13-03-90604.

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O-12. INVESTIGATION OF CHEMICAL COMPOSITION AND STRUCTURE OF THE SHELL OF CENOSPHERE FLY ASH PRODUCED FROM THE COMBUSTION OF THE EKIBASTUZ COAL.

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Fly ashes produced from the pulverized coal combustion contain a few microspherical components with valuable characteristics that determine the possibility of their use in different fields of industries. Among microspherical components of fly ashes are hollow aluminosilicate microspheres with a low bulk density (0.2-0.8 g/cm^3), namely, cenospheres. The formation of cenospheres occurs as a result of thermochemical and phase transformations of the mineral components of coal during combustion process. Their granulometric, chemical, and phase compositions depend on the composition of the original coal, the type of combustors used, and the conditions of cooling of the melt drops.

Cenosphere narrow fractions with certain composition and specific shell structure with predictable properties are very interesting to create new functional materials [1-3]. Hollow aluminosilicate cenospheres are valuable because of high strength, thermostability, acid resistance, and regular porosity of glass-crystal shell.

Earlier studies cenospheres allowed to determine the main stages for separation narrow magnetic and nonmagnetic fractions of cenospheres obtained from the concentrates Moscow Electric Power Plant No.22 and Novosibirsk Electric Power Plant No.5 [4].

In this work as a raw material used cenospheres fly ash from pulverized combustion Ekibastuz coal at a temperature of 1600°C (ReftinskayaThermal Power Plant). Narrow fractions of cenospheres were obtained by the scheme, comprising the steps of magnetic and particle size separation followed by hydrostatic branch destroyed globules. To obtain samples with low bulk density used separation in hexane.

Using the described separation schemes [4] two types of cenosphere fractions with a narrow distribution of the globules in size, thickness and porosity of the shell were obtained from cenosphere concentrate. The first type includes non-magnetic fraction of cenospheres with Fe_2O_3 content from 0.9 to 1.8 wt.%, and the variation of the content of Al_2O_3 and SiO_2 in the range of 33-38 and 56-61 wt.%, respectively.

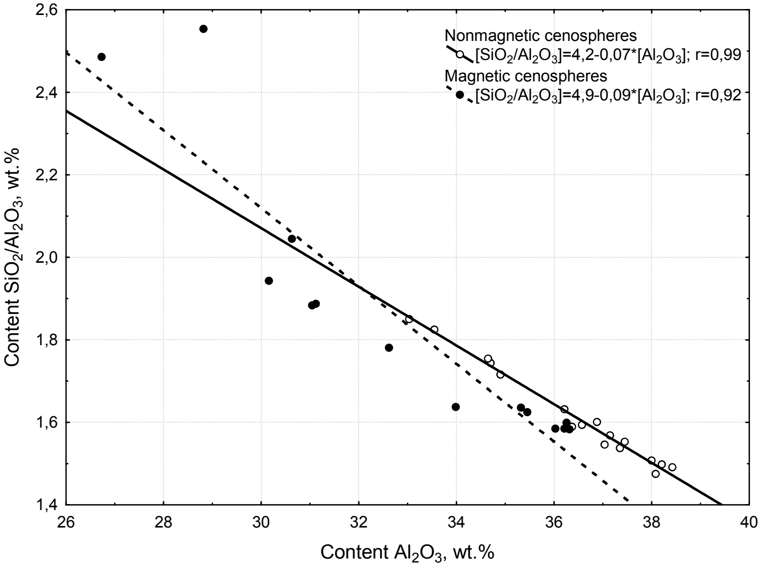

Fig.1. Dependence of the SiO_2/Al_2O_3 ratio on the Al_2O_3 content for two series of cenospheres – magnetic and nonmagnetic.

For the magnetic type fraction Fe_2O_3 content ranges from 1.90 to 8.07 wt.%, Al_2O_3 - from 24.74 to 36.32 wt.% and SiO_2 - from 55.64 to 64.20 wt.%. Figure 1 shows the dependence of the ratio SiO_2/Al_2O_3 on Al_2O_3 content obtained for narrow fractions of magnetic and nonmagnetic cenospheres.

Investigation of morphology shows the presence in nonmagnetic type ring structure and network structure globules (Fig.2). Magnetic type of cenospheres consists of globules with a regular spherical shape ring structure and contains heterogeneous regions with extended linear inclusions of ferrospinel (Fig.3). From the literature it is known that content of network structure particles are increase with increasing diameter of the cenospheres [5]. Cenospheres with ring structure formed by complete melting process, whereas cenospheres with network structure formed from droplets greater melt viscosity and/or cooled faster [5]. It was found that content of cenospheres with network structure in a fraction of the particles sizes -250+200 µm was 57%, in the sample with particle sizes -160+125 µm was 20%.

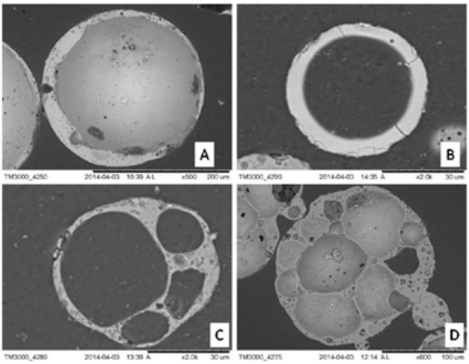

Fig.2. SEM images of ring structure (A, B) and network structure cenospheres (C, D)

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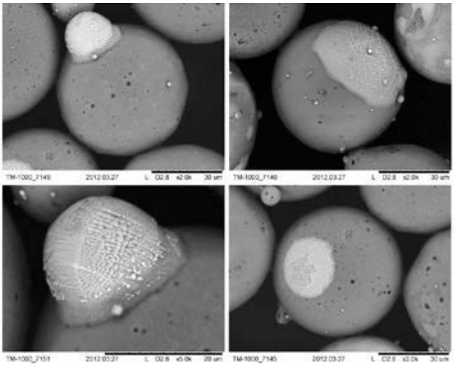

Fig.3. SEM images of magnetic cenospheres

Network structure particles are completely absent in fraction with globules sizes from 63 to 50 μm. The structure of cenospheres - one cavity or multiple - depending on the viscosity of the melt, surface tension, residence time in the melting z one temperature.

Thus, it was found that a sieving step and magnetic separation allows obtaining samples of cenospheres of different structure and chemical composition, which is important in the future practical application.

This work was supported in part by the Russian Foundation for Basic Research (Project No. 14-03-31471) and Siberian Branch of the Russian Academy of Sciences (Interdisciplinary Integration Project No. 91).

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O-13. MAGNETIC PROPERTIES OF IRON NANOCOMPOSITES OF ARABINOGALACTAN

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The magnetic properties of nanocomposites based on natural polysaccharide arabinogalactan and iron oxides (magnetite nanoparticles), that, being covered by natural high molecular polymer arabinogalactan, form stable aggregation magnetic nanomaterials, have been investigated.

It is shown that all the nanocomposites to a greater or lesser extent possess the ferromagnetic properties at room temperature that has been confirmed by measurements of their magnetization. Prolonged storage of the nanocomposites has shown that at least a year there are the stable metal nanoparticles, maintaining the EPR characteristics. The similar characteristics of FMR spectra of the investigated nanocomposites are the asymmetric broad absorption lines, indicating small changes in size and shape of the nanoparticles formed (for the nanocomposites containing iron from 3.5 to 6.4%). The greatest change in the magnetic properties of iron-containing nanomaterials is connected with the change of the domain structure of magnetic-ordered systems at increasing particles' sizes. Dramatic changes in the spectra character are observed at increasing iron content up to 9.2-12.5%. The appearance of several absorption lines, which position varies at different amount of microwave power, testifies the substantial change of nanoparticles' distribution, the increasing of the latter sizes and the possible change of domain structure. It accords with the appearance of inflection point at iron content 6.4% in the nanocomposites on the dependences of g_{eff}-factor and width of EPR signal, magnetization parameters and nanoparticles' sizes on percentage iron content in the nanocomposites and with the found relation of magnet-activity to the sizes of the nanoparticles.

This work was supported by the Russian Foundation for Basic Research (Grants 11-03-00022 and 14-03-00859_a).

O-14. PREPARATION OF HYBRID RASPBERRY-LIKE COMPOSITES USING DIFFERENT MORPHOLOGIES OF SILVER NANOPARTICLES AND COMPARING THEIR CATALYTIC PROPERTIES

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Introduction

The interest and need for hybrid particles with complex shapes that combine both properties of organic and inorganic parts, has increased considerably in the last decade. Due to their extraordinary properties and their ability to perform in different fields, hybrid nonspherical composite particles are utilized in applications like catalytic systems, drug delivery systems, light-scattering, biomedical devices, coating and etc. [1]. In this work, different morphologies of silver nanoparticles were obtained at room temperature, using tannic acid aqueous solution. These nanoparticles have exceptional physical and chemical properties; as a result theyhave wide applications in different [2-4]. Here, to determine their potential for improved catalytic activity, the rate of a reduction reaction for different morphologies of silver nanoparticles was compared with each other and their poly styrene (PS)-hybrid raspberry-like composites.

Experimental

Materials. Styrene monomer was purifiedunder vacuum to remove inhibitors. Reagent grade of 2, 2′-azobis(isobutyronitrile) (AIBN) (Acros Organics, Belgium) was dissolved in water and re-crystallized and was dried under vacuum prior to use. All other materials, including poly (acrylic acid) (Simab Resin, Iran), and guaranteed reagent grade of methanol were used as received.Silver nitrate, tannic acid and potassium carbonate (all from Merck Chemical,Germany) were used in synthesizing of silver nanoparticles. Methylene blue trihydrate (MBt; 373.9 g/mol) and sodium sulfide (Merck Chemical, Germany) were utilized as dye and reducing agent respectively.

Preparation of PS particles. Dispersion polymerization of Styrene was carried out using tumbling method under specific conditions. The morphology of produced particles was observed directly by scanning electron microscope (Seron Technology, AIS2100) [1].

Preparation of silver nanoparticles with different morphologies. Synthesis of silver nanoparticles was done following studies of Yi et al [5]. Different concentrations of silver nitrate and tannic acid solutions were mixed in room temperature, in order to obtain different morphologies (Table 1). This process was done using magnetic stirring for four hours in a dark room. The final nanoparticles were obtained after precipiting with centrifuge and washing the precipitate twice with ethanol and homogenizing in de-ionized water using ultrasound. The morphology of produced nanoparticles was observed by field emission scanning electron microscope (Zeiss SIGMA/VP, Oxford Instruments, UK).

Preparation of raspberry-like Hybrid nanoparticles.PS particles (600-700 nm) dispersion was diluted with deionized-water and was subjected to dilute ultrasonicated aqueous dispersion of silver nano-particles for four hours, while stirring.

Results and Discussion

The SEM micrographs of silver nanoparticles showed different morphologies for samples N1, N2 and N3 (Figure 1-A, B). Generally, the nano-metal particles, which are used as catalysts in reactions, would coalesce during the catalytic processes due to their van der Waals forces and high surface energy unless they are protected. For this reason, in this study PS micro-particles were used as a substrate to avoid the coalescence and increase the catalytic properties of silver nanoparticles [6]. The SEM micrographs of PS particles that were produced by dispersion polymerization, showed mono-dispersed particles (Figure 1-C). The particle size/coefficient variations of these particles were 0.74µm/3.3% and were calculated using ImageJ software. Centrifuged particles were subjected to diluted dispersion of silver nanoparticles.

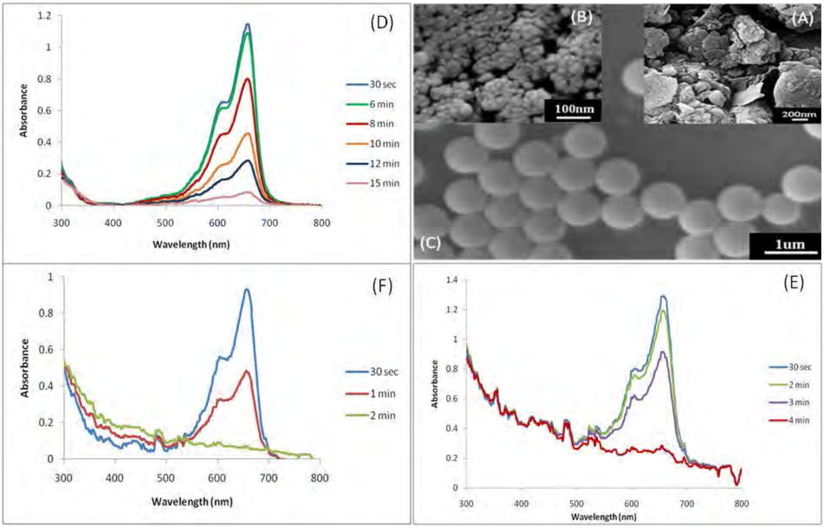

Figure 1: SEM micrographs of (A) planar silver nanoparticles - sample N2, (B) spherical silver nanoparticles - sample N3, (C) PS particles produced by dispersion polymerization. UV-Vis spectra for (D) blank sample, (E) sample N1, (F) catalyst.

Table 1: General information for different morphologies of silver nanoparticles.

Sample Name	Ingredients(mM)		pH	Morphology	Reduction Time (min)
	Silver Nitrate	Tannic Acid			
N1	20	16	5	Rod-shape	4
N2	20	16	7	Planar	2
N3	20	4	7	Spherical	3

In order to decrease reduction time for N1, these nanoparticles were absorbed on the surface of PS particles, forming a hybrid raspberry-like catalyst. To prepare a blank sample, a portion of dye was dissolved in de-ionized water and injected with Na_2S solution (Figure 1-D). The change in color of the system could be indicated by the variation in optical density at the wavelength of the maximum absorbance (λ_{max}) of the dye. As the spectrophotometer results showed, the reduction time for blank sample was approximately 15 minutes. However, when synthesized raspberry-like hybrid nanoparticles were used as catalyst, the solution turned colorless, in about two minutes (Figure 1-F). Results indicate the fact that in case of sample N1, these raspberry-like nanoparticles can perform remarkably as a reducing agent, by reducing the time of reduction reaction into a half [6].

Conclusion

In this work silver nanoparticles with different morphologies were prepared and their catalytic properties were studied in a typical reduction reaction. Rod-shaped nanoparticles showed weaker catalytic properties and in order to improve their catalytic activity, were used to prepare hybrid raspberry-like catalysts. The results indicated that these hybrid particles reduced the time of reaction into a half.

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O-15. EFFECT OF AMINO ACIDS ON AGGREGATION BEHAVIOR OF NONIONIC SURFACTANT HEXADECYL(POLYOXYETHYLENE (20)) ALCOHOL IN AQUEOUS SOLUTIONS

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The study of interactions between nonionic surfactant and AAs has a great importance, because the systems, containing both surfactant and AAs can be viewed as models for understanding the interactions and action mechanisms in multicomponent biological systems.

One of the most important parameters characterizing the structure of micelles is the mean micellar aggregation number N_{agg}, surface area per headgroup a_0, micellar radius R_0 and critical packing parameter*P* ($v/a_o l_c$).

The fluorescence quenching method was used to determine the aggregation parameters of micelles. This method first proposed by Turro and Yekta [1] is based on the quenching of a luminescence probe by a known amount of quencher species and was successively applied to the determination of mean aggregation numbers of $C_{16}A_{25}$ micelles in water and in the presence of additives. In our quenching studies we used pyrene as a luminescence probe and hexadecylpyridinium bromide as a quencher. There has been revealed that these donor-quencher pair is suitable for determining the aggregation number of nonionic surfactants in micellar solutions. The ratio of fluorescence intensities I_0/I without and with the quencher, Q, is related to the micelle concentration by the equation given in [1]:

$$\ln\frac{I_0}{I} = \frac{N_{agg}}{S - CMC}[Q] \qquad (1)$$

where S is the total surfactant concentration, CMC is the critical micelle concentration, and N_{agg} is the micelle aggregation number. It has been demonstrated that the surface area per headgroup (a_0) or its inverse the surface charge density is the most important controlling factor for micelle size [2]. In accord with Tanford [3] the hydrophobic chain volume of the micelle (υ) and the critical chain length (l_c) were obtained from:

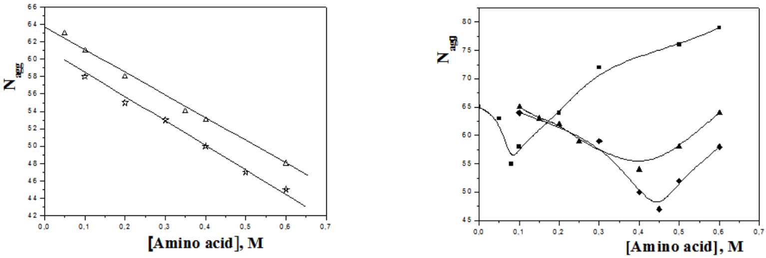
$$\upsilon = 27.4 + 26.9n \ (\text{Å}^3) \qquad (2)$$

$$l_c = 1.5 + 1.265n \ (\text{Å}) \qquad (3)$$

where n is the number of carbon atoms of the chain.

In the case of serine and lysine N_{agg} decreases with the increase of AAs concentration (Fig. (a)), while in the case of glycine, alanine, leucine and aspartic acid the first addition of additives decreases N_{agg} before it increases once again (Fig. (b)). This fact can be interpreted according to the demicellization property of AAs. But as the solvent structure is affected by the presence of AAs (both water structure making and structure breaking occur simultaneously), it is difficult to pin-point exact reason for the decrease in N_{agg} before the increase.

From the study of the micellar properties of the $C_{16}A_{25}$-AAs-water systems it can be assumed that in case of serine the behavior of N_{agg} is different than in the case of other studied neutral AAs (glycine, alanine, leucine). It can only be suggested that this is because of the existence of polar $-OH$ group in the molecule of serine, which is favored to additional electrostatic interactions between oxyethylene end of polyoxyethylated group of surfactant and $-OH$ group in the molecules of serine as well as water structure specific changes due to the possibility of formation of additional hydrogen bonds. We must note that similar behavior of serine was obtained when the volumetric properties of $C_{16}A_{25}$-AAs-water system had been studied [4].



(a) (b)

Fig. Aggregation number of $C_{16}A_{25}$ versus amino acids concentrations: (a) serine ☆, lysine Δ ; (b) glycine ■ , aspartic acid ◆, leucine ▲

It is also obtained that the shape of aggregates of $C_{16}A_{25}$both in pure water and solvent mixtures is spherical [2]. It means that the aggregates of $C_{16}A_{25}$both in pure water and solvent mixtures are very stable.

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O-16. DOUBLE CYCLIZATION ISOMERIZATION POLYMERIZATION OF VARIOUS TRIENES BY PD COMPLEX

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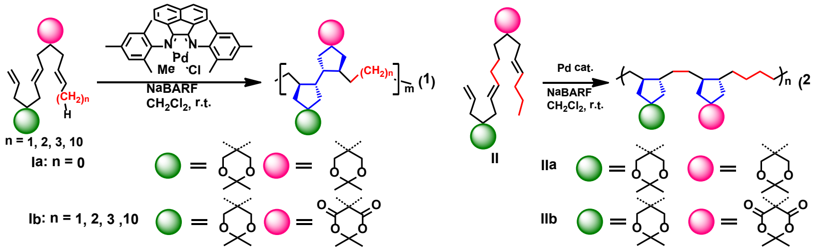
Cyclopolymerization of non-conjugated dienes is one of the methods to synthesize polymers with cycloalkane groups on the polymer chain. It has been difficult to control the stereochemistry of the cyclic structure by using conventional catalysts. Recently, we have found that Pd complexes with diimine ligands promote stereoselectivecyclopolymerization of trienes to afford polymers with *bis*-cyclopentane ring in one repeating unit[1]. Herein, we report double cyclization isomerization polymerization of various functionalized trienes by Pd complexes.

DiiminePd complex in combination with NaBARF (BARF = $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$) promotes polymerization of 1,6,11-dodecatriene (**Ia**) with quantitative double cyclization of the monomer (eq. 1). The polymer contains two *trans*-fused five-membered rings in every repeating unit, which are controlled in *racemo*-configuration selectively. 12-alkyl-1,6,11-trienes (**Ib**) are also catalyzed by the diiminePd complexes to produce the polymer with bis-cyclopentane rings and oligomethylene groups. The density of the bis-cyclopentane rings can be regulated by the length of alkyl chain of the monomer.

The cyclopentanes with cyclic acetal and cyclic ester groups can be placed alternatingly along the polymer chain. 1,6,13-Heptadecatriene (**IIa**and**IIb**) also



undergoes double-cyclopolymerization accompanying isomerization to afford polymers with two functionalized cyclopentane groups in less density along the polymer chain.

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O-17. REACTION OF ARYLHYDRAZONOAMIDINES WITH ACYL CHLORIDES

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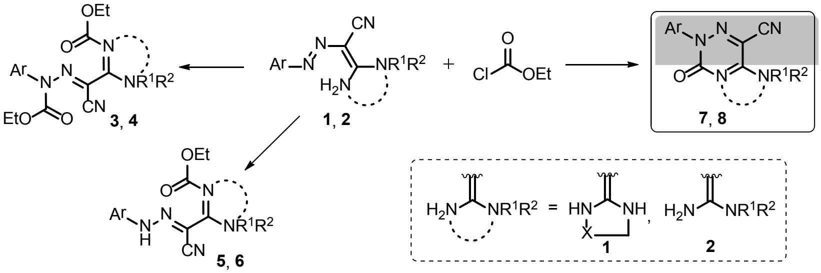
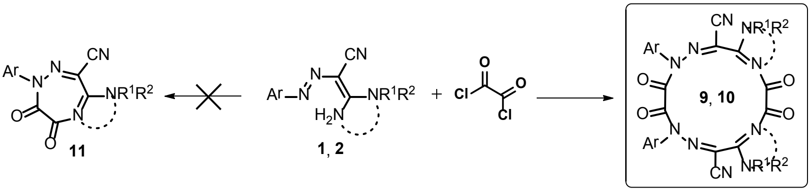
The arylhydrazones**1** and **2** containing linear or cyclicamidinemoietyare convenient building blockfor the synthesis ofheterocyclic compoundsdue to the several activenucleophilic centers including in their structure[1]. The purpose of ourresearch was the investigation ofthe reactions of hydrazonoamidines**1**,**2** with oxalyl chloride and ethyl chlorofomate.

It was found, that depending on thestructure of the startingcompoundsand reaction conditions, in the reaction of arylhydrazonoamidines**1** and **2** with ethyl chloroformate may beformed the linear and cyclic products**3**-**8**.



Reaction of amidines**1**and**2**withoxalyl chloride led tounexpected result. Instead of desirable1,2,5-triazepines **11** it were obtained the products of 2+2 condensation:hexaazacyclotetradeca-6,8,12,14-tetraenes **9**, **10**.



Thestructure of the synthesizedcompoundswas confirmedby theNMR data, IR spectroscopy and massspectrometry.The electronic characteristicsof the reaction products were studiedby theUV spectroscopy.

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O-18. INVESTIGATION OF THE PHASE FORMATION MECHANISM OF FLUOPHLOGOPITE IN CONDITIONS OF SHS USING TIME-RESOLVED X-RAY DIFFRACTION

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Synthetic micas can be obtained by various methods (hydrothermal synthesis, pyrogenic synthesis) [1]. Quartz powder, potassium fluorosilicate, magnesium oxide and aluminium oxide, are used as a raw materials. Synthetic mica morphologically does not differ from natural one, but even considerably surpasses the natural one in the field of exploration features. Mica-crystalline products are successfully applied as corrosion resistance and refractory materials, reliably working in aggressive environment of non-ferrous metals at the temperatures up to 1373 K. Casted mica-crystalline materials are used as channels of magneto-dynamic pumps, substrate for melted non-ferrous metals, apparatus for low-pressure casting, details of metallurgical furnaces, electric insulators, crucibles, tips of thermocouples, etc. Mica-crystalline materials are easily processed by the machine tools, possesses high thermal and chemical stability [1].

When the synthetic mica $KMg_3[Si_3AlO_{10}]F_2$ (fluophlogopite) is obtained by pyrogenic method with crystallization from the melt, even significant deviation from the stoichiometric composition does not inhibit crystallization of fluophlogopite [1].

Self-propagating high-temperature synthesis (SHS) can become an alternative method for obtaining of synthetic micas [2]. SHS allows to carry out the synthesis in air environment without significant power inputs and expensive equipment when the certain composition of initial mixture.

The purpose of the present work is investigation of the phase formation mechanism of fluophlogopite in SHS conditions directly during combustion process using time-resolved X-Ray diffraction (TRXRD) method.

TRXRD method [3] is based on recording of sequence of XRD patterns in a wide angular range during material synthesis with the determined time exposition (from 100 ms). The method allows to carry out *in situ* registration of changes of phase composition (from initial components up to final products throughout the intermediates) and to determine the sequence of phase transformations during combustion.

TRXRD setup is based on DRON-2 diffractometer with standard X-Ray tube, the specific is the using of high-speed one-coordinate position-sensitive X-Ray detector "LKD-4". Method TRXRD allows to carry out material synthesis directly in TRXRD setup with synchronous registration of X-Ray spectrum and temperature.

In experiments we used quartz powder (SiO_2), aluminium, magnesium, magnesium oxide, cryolite Na_3AlF_6, potassium perchlorate $KClO_4$. The samples were prepared by compression into rectangular rods ($30\times13\times5$ mm^3) with relative density of 0.55.

Time-resolved XRD pattern of process recorded during combustion of initial mixture (SiO_2–Mg–MgO–Al–Na_3AlF_6–$KClO_4$) is shown in figure 1. The image (representing a sequence of XRD patterns) is presented as a 2-dimentional graph in coordinates 2θ (x) – time (y), intensity of XRD peaks is proportional to degree of coloring of the field. Temperature profile of combustion is also present in figure 1. The heating of the sample is taking place within the first 18 seconds after sample ignition. The temperature in area of XRD pattern registration increases due to combustion front approaching and reaches 900°C. The main XRD peaks on initial components are observed during this period (first 18 seconds).

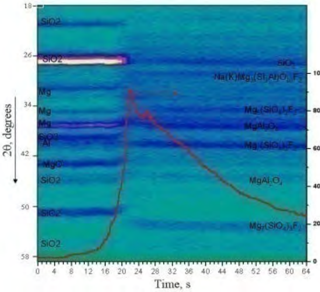

Figure 1. Time-resolved XRD pattern for combustion process of mixture SiO_2 – Mg – MgO – Al – Na_3AlF_6 – $KClO_4$ (the time of exposition is one second).

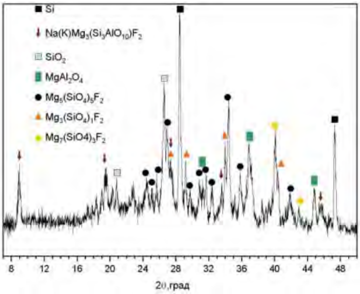

Figure 2. XRD pattern of final product for combustion of mixtureSiO_2 – Mg – MgO – Al – Na_3AlF_6 – $KClO_4$.

The front of combustion is passed throughout XRD registration area at 20 second of process. In this time there is a sharp decreasing of intensity of initial components lines (Mg, Al, MgO and SiO_2) and growth of the general background of XRD patterns. The first appeared phase is $MgAl_2O_4$ that is obviously caused by interaction between Mg, Al and SiO_2.

Magnesium oxide XRD peaks disappear at the moment of formation $MgAl_2O_4$, that is the MgO takes part in the formation of one of the final product phases. Occurrence of $Na(K)Mg_3(Si_3AlO_{10})F_2$ peak is observed at 22 second of experiment. The peaks of the phases based on $Mg_x(SiO_4)_yF_2$ are also observed on time-resolved XRD patterns after 22 seconds of experiment. It shows that the fluophlogopite and $Mg_x(SiO_4)_yF_2$ phases is occurring after passage of combustion front.

XRD pattern of final product after cooling to room temperature is shown in figure 2. X-Ray phase analysis of final product has confirmed the results of TRXRD and has shown that the synthesized product is multiphase: alongside with expected fluophlogopite $Na(K)Mg_3(Si_3AlO_{10})F_2$ the phases Si, SiO_2, $MgAl_2O_4$, $Mg_3(SiO_4)F_2$, $Mg_5(SiO_4)_2F_2$, $Mg_7(SiO_4)_3F_2$ are present.

Thus, the investigation of phase formation mechanism of SHS of fluophlogopite directly during combustion process using TRXRD method was carried out. It is shown that phase formation process has phasic character, and formation of the target product (fluophlogopite) occurs behind front of combustion.

This work was financially supported by Russian Fund of Basic Researches (RFBR), the project № 13-03-12061 ofi_m.

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O-19. COMBUSTION JOINING OFCARBON/CARBON COMPOSITES USING REACTIVE MIXTURE OF Ti AND MANi/Al POWDERS

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1. Introduction

Combustion joining (CJ) is an attractive method for joining of a variety of materials. Due to short (seconds) processing time, energy efficiency, simple technological equipment and the ability of producing joint layers with functionally-graded properties this method has proved as an effective tool for joining of refractory and dissimilar substances.

Combinations of properties of carbon/carbon (C/C) composites, such as low density, high strength-to-weight ratio, as well as high thermo-elastic stability at elevated temperatures, make it attractive material for a variety of applications. These characteristics allow using C/C composites for producing rocket nozzles, noses and leading edges of re-entry vehicles, as well as gas turbine engine components. As the demand for such materials increases, development of rapid and energy-efficient techniques for joining C/C composites are of great interest. White et al.[1], reported joining of refractory C/C composites via a class of refractory materials (carbides, borides, etc) by CJ. However, a short-term (~30 sec) but high-temperature (up to 2000 K) preheating of the joint stack was required in order to initiate the chemical reaction in the joint layer, which affected the composite properties.

Here is reported an improved combustion-based technique for bonding of C/C composites by using a CJ approach with a reactive mixture of titanium and mechanically activated Ni/Al powders. The present work focused primarily on validating the concept of low temperature joining of C/C composites with a reactive mixture of Ti powder and Ni/Al mechanically activated composites [2].

2. Experiments

Short-term (15min) high-energy ball milling (HEBM) of an equiatomic Ni + Al powder mixture (15g of Ni + Al mixture per batch) was carried out using a PM100 (Retsch,Germany) planetary ball mill with a 250 mL stainless steel jar and 2mm diameter stainless-steel balls as the milling medium in an inert atmosphere (argon).The ball-to-mixture ratio was 2:1. The rotational speed of the mill was 650 rpm. X-ray diffraction (XRD) analysis was performed to determine the phase composition of the initial Ni+Al mixture and after 15 min of MA. Results suggested that no new phases (NiAl, NiAlxsolid solution, etc.) were formed after 15min ball milling of Ni+Al powder mixture under the investigated conditions. It was shownthat such a mechanical activationtreatment allows one to significantly decrease the self-ignition temperature of Ni/Al reactive mixture.

Figure 1 demonstrates a scheme of the C/C joining configuration. The reactive medium stack, i.e. Ti+(Ni/Al)MA+Ti is placed between two C/C composites. Once triggered, the heat release and high temperature of the Ni/Al reaction facilitates the interaction between the Ti and the C/C composites, forming a TiC phase and simultaneously bonding the C/C composites. After the joining process, it is expected that a functionally graded joint layer (i.e., C/C-TiC-NiAl-TiC-C/C) will be produced.

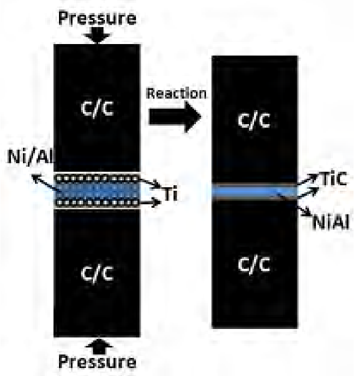

Fig. 1 Schematic illustration of the C/C joining

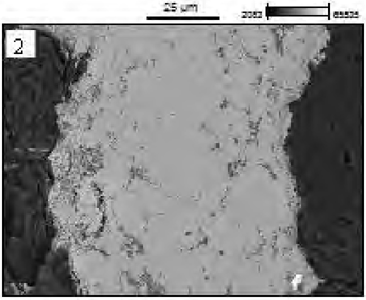

Fig. 2. Cross-sectional image of joined layer

3. Results and Discussion

Figure 2 shows typical back-scattered electron (BS) SEM images of a joined C/C sample cross-section near the joint layer. It can be seen at lower magnification that a crack-free joined layer ~75−100 µm in thickness was produced by the CJ method. Based on the joining scheme a three-step mechanism was suggested: (1) at an early stage the mechanically activated Ni/Al composite powders are rapidly initiated by direct heating of the C/C sample stack, forming NiAl solid solutions; (2) melting of the Ti powder (1900K) due to the chemical reaction of Ni/Al and the continued Joule heating of C/C sample; a minor part of the molten Ti diffuses into the NiAl solid solutions, while the majority of the mobile Ti stays active in the high temperature environment and is squeezed into the boundary of the intermediate layer and the C/C matrix; (3) the molten Ti reacts with the C/C composite and forms a TiCyphase.

Joined samples were machined to a configuration suitable for tensile-strength testing. As expected in brittle C/C materials, the rupture occurred without a pronounced strain difference (ε~0.04) in the course of elongation. In this typical case, the obtained ultimate tensile strength of a joined C/C sample was ~5.8 MPa. More importantly, the rupture occurred through C/C composite, indicating that the joined layer was stronger than the C/C matrix.

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O-20. BIOCHEMICAL RESPONSES OF THREE WHEAT CULTIVARS TO SALINITY STRESS

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For the purpose of studying the effect of different salinity levels on biochemical characteristics and yield three cultivars of wheat, an experiment on research greenhouse; Islamic Azad University, kermanshah ,was performed in 2007-2008. This factorial experiment of research was carried out 3 replication and in the form of the randomize complete blocks design. cultivars factor were placed in the blocks at 3 levels including Chamran,Marvdasht and Shahryar and salinity stress factors at 3 levels including 0.6(control) ,8 and16 dSm^{-1} in the blocks. The results showed that with increasing salinity, grain yield and relative water content were decreased but proline and water soluble carbohydrate were increased.The most this traits was observed at the Chamran cultivar.The most tolerant and stable was Chamran cultivar that had highest yield on salinity level of 16 $dSm^{-1}$to other cultivars.

Keywords: Salinity,Proline,Wheat,Yield,Relative water content

Introduction

Worldwide estimation, of land under cultivation is about 13%, of which 30-50% of irrigated land is salt affected [1]. In Iran about 12 % of the total land in under cultivation, about 50% of which is affected by salinity, sodicity and water-logged conditions to values degrees [2]. Afiuni et al [3] compared the response of 18 promising wheat lines with Kavir and Roshan cultivar, in saline conditions in which grain yields of the 8 promising lines were more than control [3]. Bao et al., [4] and Zhang et al., [5] reported that increase of free proline and soluble sugar in plants under salt stress is a ubiquitous phenomenon in nature; however, it could happen under osmotic stress.Proline is one of the well-known osmoprotectants and its accumulation is widely observed in various organisms under salt stress. High level of proline can be beneficial to stressed plants [6]. The objective of this study were to evaluate the response of grain yield and some biochemical characteristics of three wheat cultivars to three level salinity for selection of the most tolerant and stable cultivar.

Materials and methods

These studies were conducted at 2007 in the research greenhouse of the Islamic Azad University of Kermanshah, Iran (34º23' N, 47º8' E; 1351 m elevation). Ten seeds were planted in small pots filled with a clay loam soil .After germination three plants were retained in each pot. The experimental design was a factorial experiment based on Randomized Complete Block with three replicates. Three wheat cultivars(Chamran ,Marvdasht and Shahryar) were compared at 3 salinity levels [0.6 (control), 8 and 16 dSm^{-1}] for some biochemical characteristics(proline, water soluble carbohydrates and relative water content). Quantitative estimation of proline was done by the method of Bates *et al.,* [7] .In this extract, water soluble carbohydrates [8] was determined. Relative water content was determined by the method of Barrs and Weatherley [9].Statistical analysis including Analysis of variance (ANOVA), Duncan’s multiple range test was performed to study the significance of different salinity gradient on different parameters studied.

Results and discussion

The highest and lowest grain yield pertained to the salinity levels 0.6dSm^{-1}(control) and 16dSm^{-1}, respectively. also, the highest and lowest grain yield pertained to the cultivars of Chamran and Shahryar, respectively. Jafari-Shabestari et al [10] yield higher on salinity conditions have been considered as the best criterion for salinity tolerance. Cultivars Chamran and Shahryar had the highest and the lowest proline content, respectively With increasing salinity levels in comparison with control, proline content increased. Wang et al. [11] reported that during osmotic adjustment, many plants accumulate proline in response to salt stress widely believed to function as a protector against salt damage .Three of wheat cultivars in this study which had the highest water soluble carbohydrates in their flag leaves in salinity level 16 dsm-1 compared to control level. Cultivars Chamran and Shahryar had the highest and the lowest water soluble carbohydrates, respectively. Munns [12] reported that the amount of WSC increases with increasing salinity. The highest and lowest RWC pertained to the cultivars of Chamran and Shahryar, respectively. RWC on salinity stress of16dSm-1 decreased 25% to control. Fricke & Peters [13] reported that the amount of RWC decreases with increasing salinity. Our results are in agreement with those of Sairam *et al*. [14] who report a greater reduction in the RWC of salt sensitive wheat cultivar as compared with tolerant one under salt stress. Higher RWC in salt tolerant genotypes as compared to salt sensitive genotypes has also been reported in rice [15] and maize [16].

In general,This research showed that the content of proline and water soluble carbohydrates in wheat all increased with the increase of environmental stress intensity, indicated that the accumulation of proline and water soluble carbohydrates was an adaptation to ionic stress in plants.The most tolerant and stable was Chamran cultivar that had highest yield on salinity level of 16 $dSm^{-1}$to other cultivars.

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POSTERS

P-1. EFFICIENT COMPUTATIONAL PROCEDURE FOR THE CALCUALTION OF THE *p*Ka OF ORGANIC SYSTEMS IN THEIR ELECTRONIC EXCITED STATES

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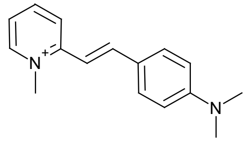
Photoacids have a stronger propensity to give protons in their excited state than in their ground state which is a key feature for developing new material properties. From an experimental point of view, the direct measurement of pK_a^* is hindered by the instrumental complexity, and therefore, most commonly, the indirect method, proposed by Förster[1] and Weller,[2] is employed for the (approximated) evaluation of the photo–acidity. This method is experimentally easier than direct measurements, but introduces some approximations being based on the knowledge of the pK_a and the measurement of the absorption (and/or emission) transition energies of AH and A^- forms. So, it does not account for the possible reversibility of the proton transfer process and neglects the difference of the vibrational pattern between the electronic ground and excited states. Experimentally the determination of the dissociation constants when the molecule is photo–excited remains challenging, because the lifetime of the photoacid, in its excited state, is generally very short. Computational methods can represent powerful and useful tools for the investigation and comprehension of the behaviour and mechanism of the photo–acids. Both from the experimental and computational point of view, two approaches can be basically followed for the evaluation of the pK_a^*, as hinted above, *i.e.* the methods employing the (thermodynamic) Born–Haber cycle, and those based on the (kinetic) Förster cycle. In the present work, we have set up a computational procedure in order to evaluate the pK_a of organic molecules in their electronic excited states. It is based on the employment of the state–of–the–art in the field of Quantum Mechanical (QM) calculation and computational techniques. In order to test this protocol, we have considered some methyl–pyridinium and methyl–quinolinium cation derivatives (see Chart 1). Comparing the obtained QM results with data from the Literature[3] a remarkable agreement has been found (see Table 1 and Figure 1).

Chart 1



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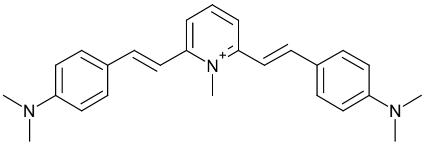

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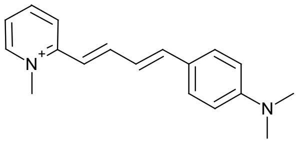

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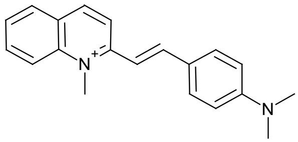

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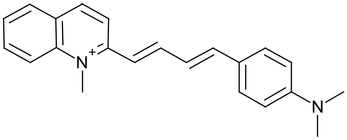

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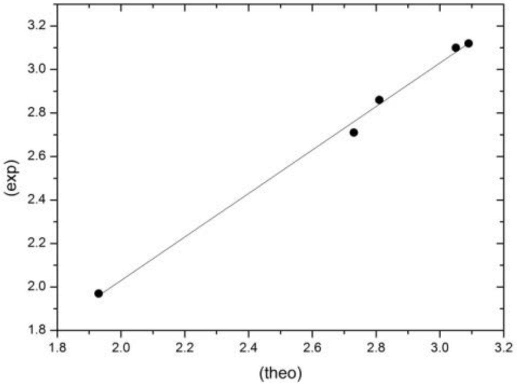
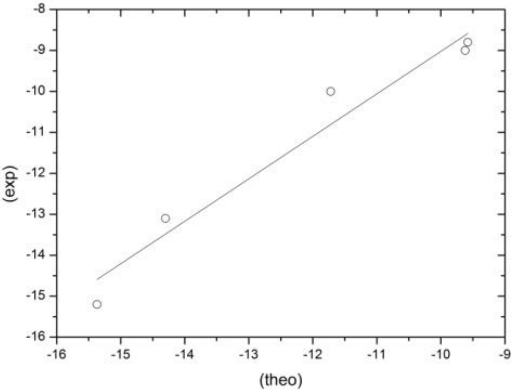
Table 1. Free energy differences (in kcal/mol) at 298.15 K and comparison between computed and experimental values of pK_a *and* pK_a^**. (The value of* $G_{(s)}(H^+)$ *is assumed −263.9 kcal/mol;* $\Delta G_{(s)} \equiv G_{(s)}(A^-) - G_{(s)}(HA)$*;* $\Delta G_{(aq)} = G_{(s)}(H^+) + G_{(s)}(A^-) - G_{(s)}(HA)$*).*

	$\Delta G_{(s)}$	$\Delta G_{(aq)}$	$pK_a^{(theo)}$	$pK_a^{(exp)}$	$G_{(s)}$	$\Delta G_{(aq)}^*$	$pK_a^{*(theo)}$	$pK_a^{*(exp)}$
1	268.06	4.16	3.05	3.10	242.94	−20.96	−15.37	−15.2
2	267. 73	3.83	2.81	2.86	250.78	−13.12	−9.62	−9.0
3	268.11	4.21	3.09	3.12	250.84	−13.06	−9.58	−8.8
4	266.53	2.63	1.93	1.97	247.93	−15.97	−11.72	−10.0
5	267.62	3.72	2.73	2.71	244.40	−19.50	−14.30	−13.1



slope = (1.00 ± 0.04) r^2 = 0.99486



slope = (1.04 ± 0.13) r^2 = 0.94314

Figure 1. Comparison between computed and experimental values of pK_a (left) and pK_a (right).*

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P-2. SYNTHESIS OF NEW HETEROCYCLIC SYSTEMS BASED ON PYRAZOLO[3,4-*C*]-2,7-NAPHTHYRIDINES

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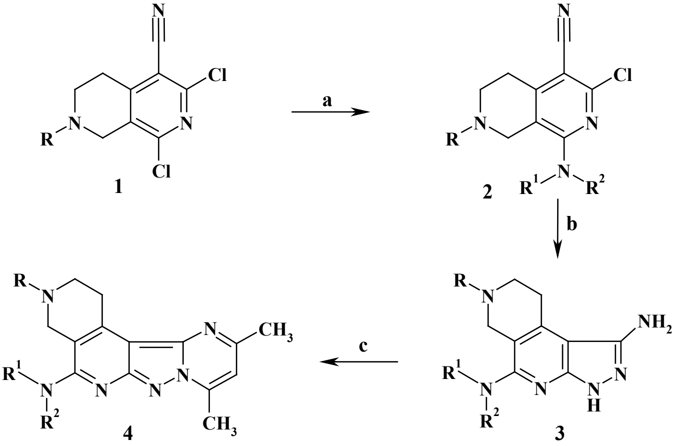
The study of the derivatives of five- and six-membered heterocycles containing nitrogen represents a ‘key’ field in the study of organic and biological chemistry [1, 2]. Their involvements in life processes, the pharmacological activities, the large use as intermediates in organic syntheses, and their variegated reactivity make the study of properties of these compounds an attractive research field. In this research line the derivatives of 2,7-naphthyridine occupy an important place.

As a continuation of our previous research [3–5] herein we report the synthesis of new heterocyclic systems – 3-alkyl-5-amino-9,11-dimethyl-1,2,3,4-tetrahydropyrimido[1',2':1,5]pyrazolo[3,4-*c*]-2,7-naphthyridines **4**. The synthesis was based on the 1,3-dichloro compounds **1**.



a: NHR^1R^2, CH_3OH, reflux 5 h; b: $N_2H_4.H_2O$, C_2H_5OH, reflux 4 h; c: $CH_3COCH_2COCH_3$, reflux 10 h.

R = alkyl; R^1, R^2 = H, alkyl, aryl; R^1+R^2 = cycloalkyl.

Using the different reactivity of the two chlorine atoms of the dichloro derivatives **1** we succeeded in obtaining 1-amino substituted derivatives of 2,7-naphthyridine **2** by conducting the reaction in methanol.

With the aim of annelation of pyrazole ring at the [*c*] side of the pyridine ring the synthesized compounds **2** were treated with hydrazine hydrate in ethanol. As a result of this reaction the relevant 1,5-diamino-6,7,8,9-tetrahydro-3*H*-pyrazolo[3,4-*c*]-2,7-naphthyridines **3** were obtained, which showed expressed anticonvulsant activity. Taking into account this circumstance, it was interesting from both biological and chemical point of view to synthesize new heterocyclic systems based on these compounds. Thus, reaction of pyrazolo[3,4-*c*]-2,7-naphthyridines **3** with acetylacetone leads to the formation of target products – pyrimido-[1',2':1,5]pyrazolo[3,4-*c*]-2,7-naphthyridines **4**.

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P-3. THE STUDY OF CONDUCTIVITY OF REVERSE MICELLAR SYSTEMS OF WATER+DIMETHYLSULFOXIDE OR DIETHYLSULFOXIDE/AOT/N-HEPTANE

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The electrical conductance of sodium bis (2-ethylhexyl) sulfosuccinate (AOT)/n-heptane/water-dimethylsulfoxide (DMSO) or diethylsulfoxide (DESO) reverse micellar systems has been studied at fixed ratio of molal concentrations of polar phase to surfactant (R). These systems are in the center of attention because they are considered to be models of membranes due to their structural similarities with biological membranes, they are using as microreactors for enzymatic reactions and for synthesis of nanoparticles.

The purpose of this work is to reveal the changes in the percolation of conductance when the mixed solvents DMSO-water (with different volume ratios) and DESO-water are used as a polar phase instead of pure water [1] as it is well known that conductivity of such systems is very sensitive to their microstructure [2,3].

The dependence of conductivity on temperature of AOT/n-heptane/water+DMSO (DESO) reverse micellar systems has been studied above the percolation threshold, which characterizes by sudden increase in electrical conductivity when either the temperature or the volume fraction of the dispersed phase reaches a certain threshold value.

It may be assumed from the results that the presence of mixed solvent has shown a decrease of T_p and tendency to transfer a system from percolating to non-percolating. The activation energy (E_p) for percolation of conductance has also been determined. The results show that E_p decreases with addition of both DMSO and DESO and with an increase of concentration of DMSO. It may be explained by the fact that in the presence of DASO the environment of micellar core becomes more rigid and the formation of aggregates takes place not immediately.

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P-4. STUDY OF THE INTERACTION BETWEEN DNA AND ETHIDIUM BROMIDE BY FLUORESCENCE ANISOTROPY

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The method of fluorescence polarization (anisotropy) is widely used in biochemical investigations [1, 2]. This method is informative for describing the binding process of various ligands to DNA and proteins. In fluorescence anisotropy measurements the sample is exposed to polarized light. The extent of polarization of the emission is described in terms of the anisotropy (*r*). When the emission polarizer is oriented parallel to the direction of the polarized excitation the observed intensity is called I_{VV}. Likewise, when the polarizer is perpendicular to the excitation the intensity is called I_{VH} (V-vertical, H-horisontal). These intensity values are used to calculate the anisotropy:

$$r = \frac{I_{\mathrm{VV}} - G I_{\mathrm{VH}}}{I_{\mathrm{VV}} + 2 G I_{\mathrm{VH}}} \qquad (1)$$

where G-factor is given by`

$$G = \frac{I_{HV}}{I_{HH}} \qquad (2)$$

where I_{HV} corresponds to horizontally polarized excitation and vertically polarized emission and I_{HH} corresponds to horizontally polarized excitation and emission.

In earlier literature the term polarization is used. The relationship between anisotropy and polarization is following:

$$P = \frac{3r}{r+2} \qquad (3)$$

The average angular displacement (θ) during excitation and emission processes is given by following equation:

$$r = \left(\frac{3 < \cos^2\theta > - 1}{2}\right) \quad (4)$$

The investigations of aqueous solutions of DNA at the presence of various biologically important substances have drawn considerable attention [3]. The solutions of DNA in citrate buffer were studied by means of fluorescence polarization (anisotropy). As a fluorescence probe the ethidium bromide was used. Fluorescence spectra of DNA-ethidium bromide complex at different orientations of polarizers are given in Figure.

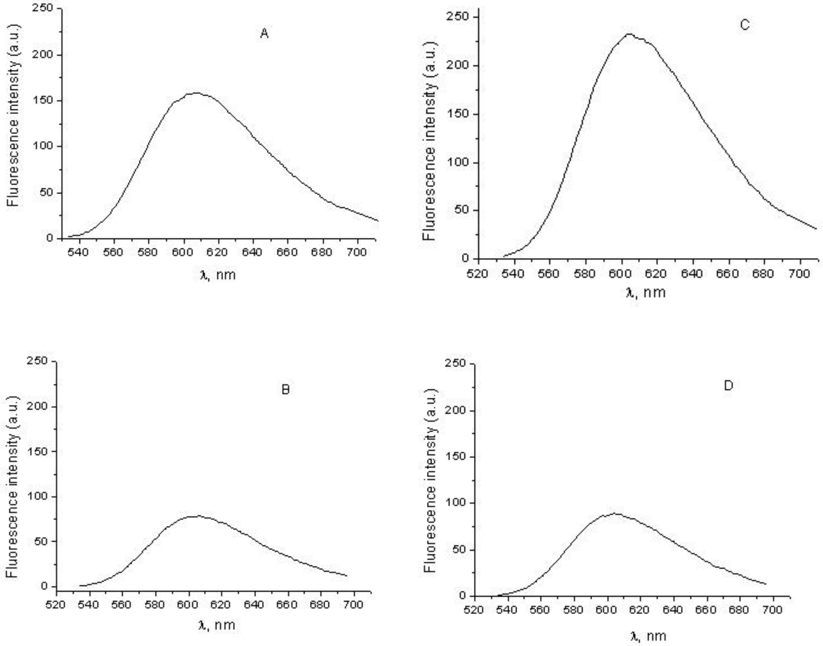

Figure: Fluorescence spectra of DNA-ethidium bromide complex at various orientations of polarizers: ***A.*** *HV,* ***B.*** *HH,* ***C.*** *VV,* ***D.*** *VH.*

The value of anisotropy of ethidium bromide bound to DNA was measured and it is equal to 0.09. Using this obtained value of fluorescence anisotropy the average angular displacement of transition moment was calculated according to equation 4 and was found to be 51^{o}. This angle describes the rotational diffusion of fluorophore's molecules and their motion in the internal hydrophobic region of DNA.

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P-5. LIQUID-PHASECATALYTICOXIDATION OF ALKYLARENE BY OXYGEN IN THE PRESENCE OF POLYMER-IMMOBILIZED COMPLEXES OF Co (II), Cu (II)ANDFe (III)

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Processes of catalyticoxidation of hydrocarbonsare among themost important both inthe petrochemicalindustry andin fine organic synthesis. As the oxidizing agentsare conventionally usedcompounds of chromium, manganese, nitric acid or chlorine-containing reagents. Typically, in these cases, the processes proceed under the strict conditions with a lower selectivity and often lead to the formation of large quantities of toxic byproducts. As an alternative to the use of stoichiometric oxidants is promising the use of oxygen what is effective and safe for an environment. Therefore, the problem of creating available catalytic systems for the selective oxidation of hydrocarbons and alkyl-aromatic compounds by oxygen retains its value. One way of solving this problem - is to use polymer-metal complexes as catalysts for the oxidation process. The method of fixation of metal complexes with ligands of organic and inorganic nature allows to create new improved catalysts. The LbL (layer-by-layer) deposition of polycations and polyanions on a solid substrate is a method of attracting the attention of many researchers as obtaining organized homogeneous coatings with controlled thickness.

The report presents the results of oxygenation of alkylarenes (toluene and o-xylene). As the catalysts was used polyvalent metals (M^{n+} – Co^{2+}, Cu^{2+}, Fe^{3+} and jointly Cu^{2+} / Fe^{3+}) embedded in the structure of thirty layers of copolymer polyethyleneimine - polyacrylic acid $(PEI / PAA)_{30}$ fixed on the glass plates.

The oxidation process of alkylarene by oxygen is carried out in manometric installation in acetonitrile medium at temperature 348 K and atmospheric pressure.Based on IR spectroscopy, GLC and chemical analysis is established that the products of oxygenation of o-xylene are o-toluic aldehyde and o-xylene hydroperoxide, and toluene are toluene hydroperoxide and benzaldehyde. The process proceeds according to the reaction:

$$2C_6H_5CH_3 + 2O_2 \rightarrow C_6H_5CHO + C_6H_5CH_2OOH + H_2O \quad (1)$$

Experimental data showed that the catalytic system[M^{n+} - (PEI / PAA)$_{30}$ - glass] ($M^{n+}$is Co^{2+}, Cu^{2+}, Fe^{3+}) allows to oxidize of alkylarenes without requiring additional activation. Oxygen absorption rate per hour is $1.54 \cdot 10^{-5}$, $2.20 \cdot 10^{-5}$ and $1.06 \cdot 10^{-5}$ mole / (l*s), respectively.

For the oxidation of toluene by oxygen in the presence of copper (II) and iron (III) clusters jointly incorporated into a polymer matrix [Cu^{2+} / Fe^{3+} - (PEI / PAA)$_{30}$ - glass] it is necessary additional activation of catalyst by carbon tetrachloride.

The comparison of the oxygen absorption rate (Wo_2), the degree of conversion of toluene per hour (α), and the induction period (τ_{ind}) depending from the metal and from the presence of carbon tetrachloride presented in Table.

Catalysts based on incorporated metal complexes [M^{n+} - (PEI / PAA)$_{30}$ - glass] were tested for reusability. It is established that in quadruplicate using the activity of the catalyst [Cu^{2+} - (PEI / PAA)$_{30}$ - glass] and [Co^{2+} - (PEI / PAA)$_{30}$ glass] in the process of oxygenation reduced. By the IR-spectral analysis of the catalyst established that the polyethylenimine and polyacrylic acid are not oxidized and do not undergo degradation. The activity of the catalysts [Fe^{3+} - (PEI / PAA)$_{30}$ - glass] and [Cu^{2+} / Fe^{3+} - (PEI / PAA)$_{30}$ - glass] is noticeably reduced at the secondary use. This is due to the fact that iron (III) ions form complexes of polymer matrix less stable compared with copper ions (II).

Table – Influence of metal M^{n+} on the oxidation of toluene in the system glass/(PEI/PAA)$_{30}$/ M^{n+}–O_2–$C_6H_4(CH_3)_2$–CH_3CN–CCl_4(348 K; Po_2 = 100 vol. %.)

Metal, M^{n+}	**$Wo_2 \cdot 10^5$, mol /(l·s)**		**α, vol. %**		**τ_{ind}, min.**	
	With CCl_4	**Without CCl_4**	**With CCl_4**	**Without CCl_4**	**with CCl_4**	**Without CCl_4**
Co^{2+}	**6,60**	**1,54**	**9,2**	**3,3**	**3**	**10**
Cu^{2+}	**5,30**	**2,20**	**8,3**	**4,2**	**3**	**10**
Fe^{3+}	**4,24**	**1,06**	**7,5**	**1,9**	**3**	**15**
Cu^{2+} / Fe^{3+}	**6,71**	**-**	**10,6**	**-**	**3**	**-**

P-6. ELECTRODEPOSITION OF TERNARY Fe-Mo-Re ALLOYS FROM AQUEOUS SOLUTIONS

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Modern scientific and technological progress as inextricably linked with the improvement of existing and development of new materials. In an emerging deficit valuable mineral with increasing demands for products quality is increasing need to develop new materials having a wide range of functional, mechanical and chemical properties [1].

Electroplated coatings of refractory metals are able to provide effective protection of parts and structures from heat, corrosion and chemical influences, to give a high hardness and abrasion resistance while maintaining the low cost of the final product, because of the small amount of metal consumption [2].Another important factor is the reduced weight of electrodeposited alloys in comparison with the alloys obtained by pyrometallurgical methods, through the use of substrates of various materials.

Molybdenum, rhenium and tungsten are difficult to deposit in alloy by the electrolysis of aqueous solutions because of the low overvoltage release of hydrogen on them. Additions of metals of iron subgroup into solutions containing molybdenum, rhenium or tungsten cause the codeposition of these elements. This mechanism called "Induced codeposition" [3]. When using pyrophosphate, citrate or gluconate electrolytes containing complex compounds of refractory metals can be obtained double, triple, and quaternary alloys.

Possibilities of combining of metals in alloys provide a wide range of functional properties and its potential application [4].

The aim of this research is to examine regularities of electrochemical codeposition of iron with refractory metals in ternary alloys from citrate-borate electrolytes.

The thermostaticelectrochemical cell, regulated power supplyand a liquidthermostat«LOIP LT-108a» used for investigation of processesof electrodepositionanddissolution of alloys. Recording of polarization curvesperformed inpotentiodynamicmode using potentiostat-galvanostat «IPC-

Pro»and«Autolab PGSTAT100». As the workingelectrodeused acopper electrode; auxiliary electrode and thereference electrodewereplatinumandsilver chlorideelectrodes. Corrosion testing of coatingsperformed byelectrochemical dissolution with recording anodic polarization curvesin the medium of solution of NaCl 3%. Control ofpH of the electrolytewas performedelectronicpH-meter"Aquilon I-500."

The electrolyticcodepositionof ternaryalloysperformed onthe copper substrateover 30minutes ata current density of25mA/cm^{2}andconstant stirring of electrolyte by a magnetic stirrer. Analysis of the compositionof the obtained alloys carried outby atomicabsorption spectrometer “AAnalyst400”.

Todetermine the effect ofconcentrationsof componentsused a seriesof electrolytes, which in turnchanges the concentration ofFe, MoandRe from 0.1 to0.8mol/dm^3. The concentration of$H_3BO_3$and$C_6H_8O_7$was 0.25and 0.40mol/dm^3 respectively.

The studies show with increasing concentration of Fe^{2+} has been a slight shift of the reduction potential to less negative values, followed by an increase in current density for the half-wave reduction from 15 to 50 mA/cm^2. Increasing the concentration of MoO_4^{2-} in electrolyte reduces the current density of reduction from 60 to 10 mA/cm^2 wherein the value of reduction potential is not changed (Figure 1 (a)).

With increasing the rhenium content in the electrolyte, observed a shift of the electroreduction potentials to the positive values up to 100 mV (Figure 1 (b)).

Whereas iron is the main component which involve molybdenum and rhenium in codeposition, increasing of its concentration naturally accelerates a chemical reaction of discharge cations on the electrode and increases the current density.

At the same time into the codeposition involve in more amount of hard-reducing complex ions of molybdenum and rhenium which are present in the electrolyte. This is affect on the shift of the deposition potential towards more positive values and facilitation of the deposition process.

Based on the results of the electrolytic deposition concluded that for deposition of quality coatings of Fe-Mo-Re alloys are optimal low concentrations of iron, molybdenum and rhenium in the electrolyte. Coatings obtained under these conditions characterized by high microhardness and the highest content of iron, molybdenum and rhenium, which indicates of the high efficiency of the process.

The corrosion resistance of alloys evaluated by anodic electrochemical dissolution in the medium of NaCl 3%.

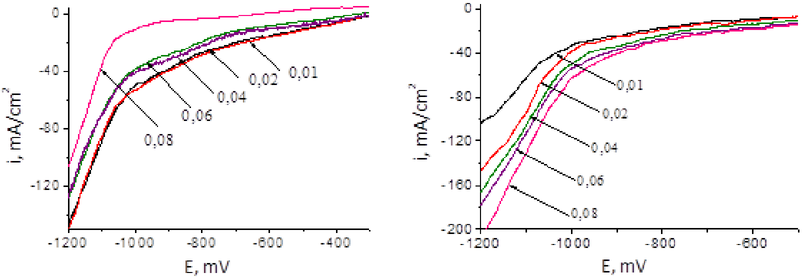

Figure 1– Polarization curves for electrolytes with differ concentration of, mol/dm^3:
a) - MoO_4^{2-} *b)* - ReO_4^-

Corrosion current density, the protective effect ‘Z’ and corrosion factor ‘γ’ calculated by extrapolation of the obtained anodic polarization curves. It is established that the range of optimal concentrations of metals for coating with maximum corrosion resistance is 0.1 - 0.2 mol/dm^3 for iron and 0.01 - 0.02 mol/dm^3 for molybdenum and rhenium.

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P-7. SYNTHESIS AND BIOLOGICAL ACTIVITY OF SOMEQUATERNARY AMMONIUM SALTSOF 3-(2-BROMOACETYL)-2-OXO-2,5-DIHYDROFURANS

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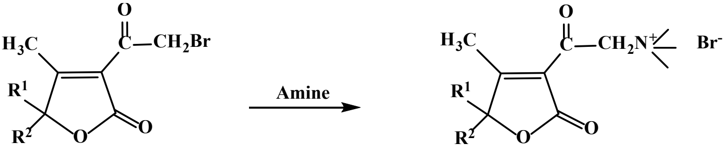
It is known that compounds containing in the structure a furan ring, have a wide spectrum of biological activity [1].With a view to the synthesis of new derivatives of the potentially active γ- lactones based on functionally substituted 3-(2-bromoacetyl)-(5*H*)-furan-2-ones (1a-e) we synthesized a series of quaternary ammonium salts (2a-h). As amines we used pyridine, 2,3-, 2,6- substituted pyridines and dimethylaminoethanol . Reaction was carried out in dry acetone at room temperature (in some cases at 40°C) at ratio bromolactone : amine - 1.2:1.



1a-h **2a-h**

$R^1=R^2=CH_3$; $R^1R^2=C_5H_{10}$:
Amine = pyridine; 2,3-dimethylpyridine; 2,6-dimethylpyridine; dimethylaminoethanol.

The anticholinesterase activity of synthesized salts (2a-h) towards human erythrocytic acetylcholinesterase (AChE) and plasmic butyrylcholinesterase (BuChE) was studied. Cholinesterase activity was determined by Ellman’s method [2]. Quantitative evaluation of the inhibitory properties was determined using values IC_{50}. It was found that all the compounds exhibit inhibitory properties both towards AChE and BuChE, but mainly they are AChE-specific inhibitors.

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P-8. THERMAL STABILITY OF HUMAN HEMOGLOBIN IN THE PRESENCE OF TANNIC ACID

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Tannic acid (TA) belongs to the class of hydrolysable tannins and is found in numerous plants and foods.It is known as an effective antioxidant, antimicrobial agent. It reversible binds to blood proteins(such as human hemoglobin (HHb) and human serum albumin) [1,2] and can stabilize or destabilize the protein structure.

We present results on thermal stability of HHb in the presence of TA studied by UV/vis and fluorescence (3D matrix method) spectroscopy in temperature range of 30.0– 66.0°C [3]. Temperature rise and the presence of TA cause denaturation of HHb (see Fig. 1).

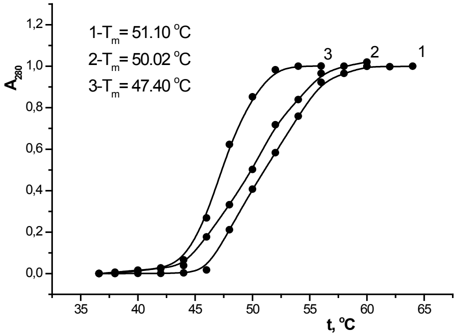


Fig. 1UV/vis profiles of HHb denaturing in the presence of TA.TA 1-0; 2-4.08.10^{-6}; 3- 8.17.10^{-6} M

Excitation/emission fluorescence matrix method has been used for detailed studying of structural changes in HHb molecule (3D spectra) caused by temperature rise(Fig. 2).

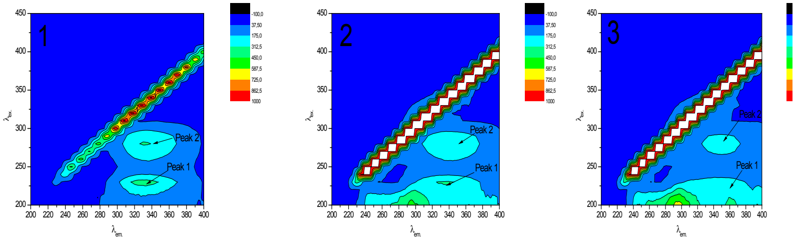
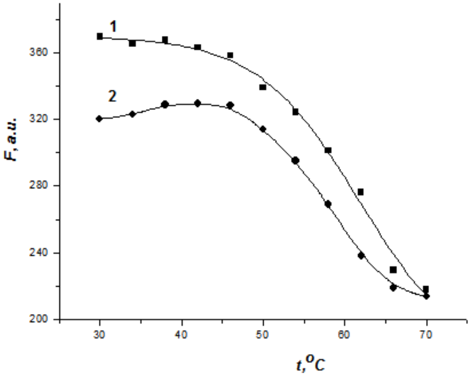


Fig. 2. Projections of3D HHb fluorescence spectra. HHb- 3.95·10^{-6} M, 1-t=30; 2-t=50; 3-t=66 °C

The fluorescence 3D spectra of HHb are described by two peaks: peak 1 at λex./λem.=230/335nm characterizes the fluorescence behavior of polypeptide chains of HHb and peak 2 at λex./λem.=280/339nm characterizes the aromatic amino acid residues Trp, Tyr and Phe. On the bases of 3D spectra we have constructed the fluorescent profiles of HHb thermal denaturating (Fig. 3), using intensities of peak 1 and peak 2.

Fig. 3. Fluorescent profiles for thermal denaturating of HHb: λex./λem.=230/335 nm (1) and λex./λem.=280/338 nm (2); C_{HHb} = 3.95.10-6 M



The curve 1 (λex./λem.=230/335nm) is shifted to higher temperature range compared with curve 2 (λex./λem.=280/339nm).The analysis of these facts revealed, that temperature rise causes more pronounced structural changes in the flexible areas of protein containing aromatic amino acids, than in the rigid α, β polypeptide chains.

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P-9. ELECTROPHILIC REACTIONS OF 1-(TRIFLUOROMETHYL)ALLYLALCOHOLS

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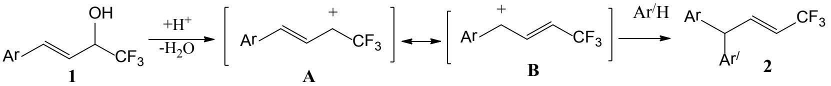
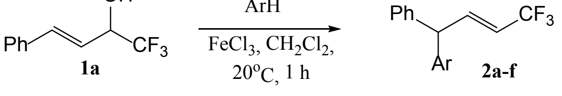
Fluoroorganic compounds are of great importance in chemistry, biology and medicine [1,2]. They exhibit a wide range of biological activities, and are used for preparation of new materials and substances.

In this paper we studied the reactions of CF_3-alcohols **1** with arenesin the presence of Brønsted and Lewis acids. Under the reaction conditions, alcohols **1** produceallylcations which exist in the resonance forms **A** and **B**. Only form **B** – where the positive charge, is stabilized by the presence of aryl substituent – react with arenes giving **2**.



Various protic acids (CF_3CO_3H, FSO_3H, CF_3CO_2H, H_2SO_4) and Lewis acids ($AlBr_3$, $AlCl_3$, $FeCl_3$, BF_3 × Et_2O) were studied in this reaction. The best yields of desired products **2**were obtained using $FeCl_3$. Thus, the reaction of 1,1,1-trifluorobut-3-en-2-ol **1a** with different arenesin the presence of $FeCl_3$-CH_2Cl_2 at 20°C for 1 h leads to compounds **2a-f** in 48-75% yields. ^1H, ^{13}C, ^{19}F and HH, HF-NOESY NMR data confirm the *E*-configuration of alkenes **2a-f**.

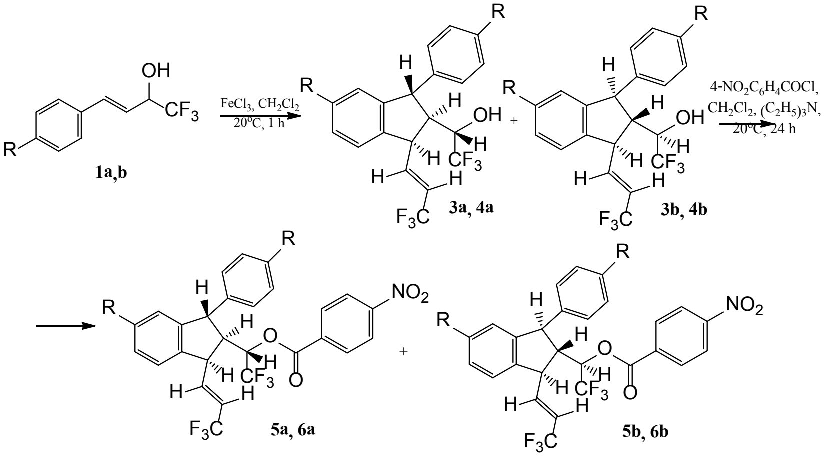


Ar = C_6H_nR, R = H (**a,** 65%), 2,4-Me2 (**b,** 56%), 3,4-Me2 (**c**, 75%), 3,4-MeO2 (**d**, 48%), 2-MeO (**e**, 14%), 4-MeO (**f**, 58%).

Table 1. Optimization of the reaction conditions.

Reaction conditions (molar ratio of reagents, temperature and reaction time)	Yield of product **2a**, %*
1a : C_6H_6 : TfOH = 1:15:50, 20°C, 1 h	–
1a : C_6H_6 : TfOH = 1:3:50, CH_2Cl_2, -35°C, 1 h	33
1a : C_6H_6 : FSO_3H = 1:3:86, SO_2, -75°C, 1 h	24
1a : C_6H_6 : CF_3CO_2H = 1:50:5, 20°C, 5 h	–
1a : C_6H_6 : H_2SO_4 = 1:16:268, 20°C, 1h	22
1a : C_6H_6 : $AlBr_3$ = 1:50:2, 20°C, 0.25 h	–
1a : C_6H_6 : $AlCl_3$ = 1:50:1, 20°C, 1 h	21
1a : C_6H_6 : $FeCl_3$ = 1:50:1, 20°C, 1 h	**65**
1a : C_6H_6 : BF_3×Et_2O = 1:50:1, 20°C, 72 h	32

Exposure of CF_3-alcohols **1a,b** in the system $FeCl_3$-CH_2Cl_2 at 20°C for 1 h bring about the formation of two diastereomeric "dimeric" compounds **3a,b** and **4a,b** in the ratio of 1: 1 with a total yield of 80%.



R = H (**1a, 3a, 4a, 5a, 6a**), Me (**1b, 2b, 3b, 4b, 5b, 6b**).

Indanes **3a,b** and **4a,b** are oily substances which give the solid esters of *para*-nitrobenzoic acid **5a,b, 6a,b** (Fig. 1, 2) suitable for X-ray diffraction study.

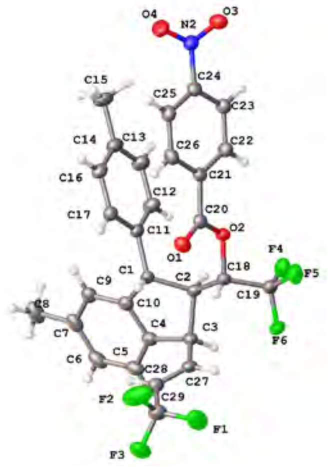


Fig. 1. Structure of compound **6a**.

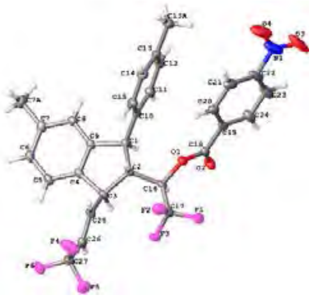


Fig. 2. Structure of compound **6b**.

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P-10. ELECTROPHILIC REACTIONS OF 4-ARYL-1,1,1-TRIFLUOROBUTENONES IN SUPERACIDS

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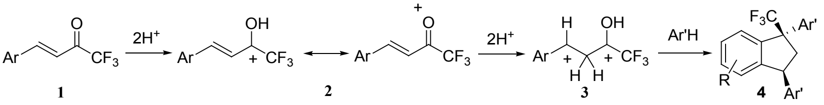
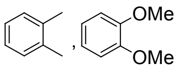
Indanes and indenes are compounds of great practical importance. They are used as biologically active compounds, ligands in metallocomplex catalysis etc. For this reason, the development of new synthetic routes for these compounds is an actual scientific goal.

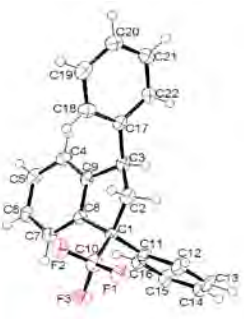
It was revealed that several 4-aryl-1,1,1-trifluorobut-3-en-2-ones (**1**) in superacids (CF_3SO_3H, FSO_3H) undergo SEAr reaction affording 1,3-diaryl-1-(trifluoromethyl)indanes (**4**). The active intermediates of reaction might be either monoprotonated (**2**) or diprotonated (**3**) form.

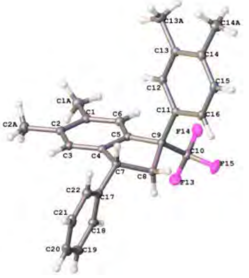


Ar = Ph, 4-MeC$_6$H$_4$,
4-ClC$_6$H$_4$

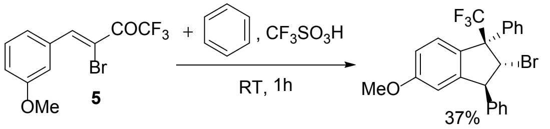
Ar'H = PhH,

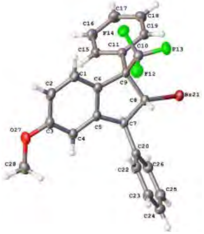


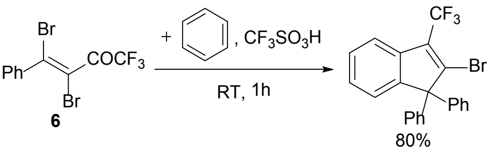


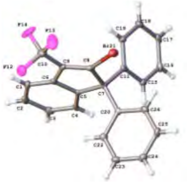


Some 3-bromo- or 3,4-dibromosubstituded trifluorobutenones (**5**,**6**) also showed similar reactions with arenes, but for dibromoketone, inlike many others, (**6**) reaction resulted in indene product.

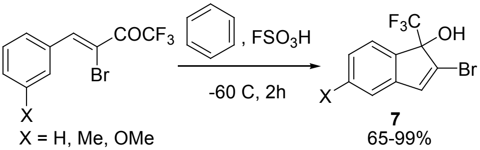


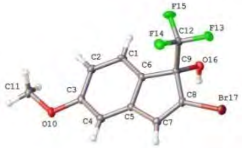


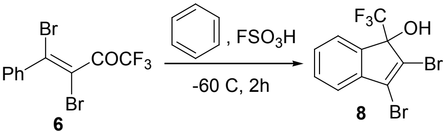




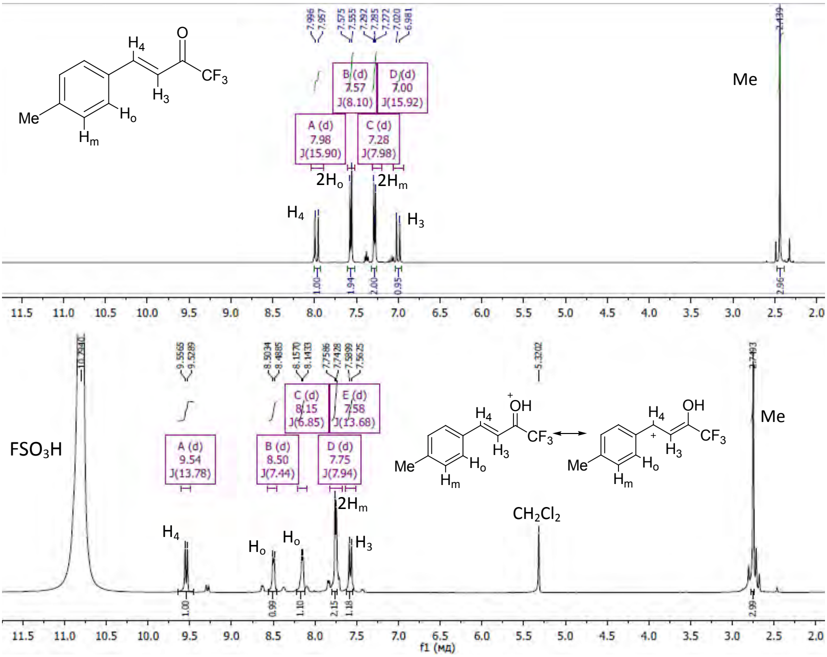
During further investigation of the reactions, it was found that in FSO_3H at -60°C in presence of benzene all bromoketones transform into 1-(trifluoromethyl)inden-1-ols (**7**,**8**).







However, non-brominated ketones don't form indenols at low temperatures, but remain unchanged at temperatures below -50°C. In order to investigate the mechanism of indenol formation, the series of NMR spectra of protonated forms in superacids was registrated. It was found that in conditions suitable for indane **4** formation there is no way to "catch" the active intermediate by NMR. But at lower temperatures it was possible to record NMR spectra of monoprotonated form (**2**). No trace of diprotonated form signal was detected.



^1H NMR spectra of starting ketone in $CDCl_3$ at 20°C (above) and of its protonated form in FSO_3H at -40°C (below).

P-11. "CHIRAL-AT-METAL" POSITIVELY CHARGED OCTAHEDRAL COMPLEXES OF Co(III) AS ASYMMETRIC CATALYSTS IN MICHAEL ADDITION AND OXIDATION REACTIONS

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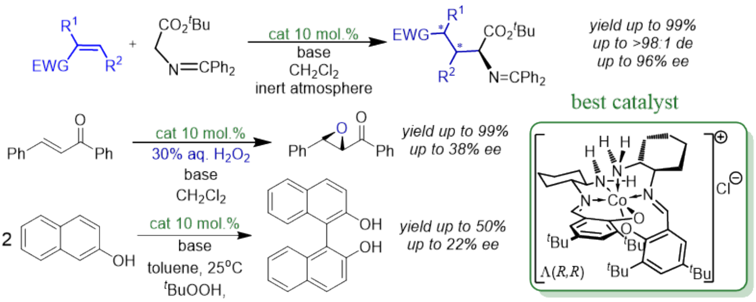
It is well known that Michael addition to activated olefins is a very convenient approach to the preparation of enantiomerically enriched biologically active compounds [1]. Also asymmetric oxidative coupling of phenols is a convenient and economic protocol for the synthesis of chiral atropoisomeric building blocks in asymmetric synthesis and catalysis [2].

Recently, "chiral-at-metal" positively charged Co^{III} complexes were developed by us as catalysts for the cyanosilylation of aldehydes (*ee* up to 27%) and for catalysis of asymmetric enolate alkylation (*ee* up to 92%) [3].



Herein we report the application of the complexes of Co^{III} as catalysts for Michael addition to activated olefins under PTC conditions with *ee* up to 96%. [4]. In addition, the epoxidation of chalcones can also be carried out under PTC conditions with moderate enantioselectivity. The catalyst can also be used for the asymmetric oxidative coupling of 2-naphthol leading to enantioenriched BINOLs with *ee* up to 22%.A plausible structure of the ion pair intermediate for the Michael addition was proposed on the bases of *ab-initio* calculations with different dispositions in the hypothetical ion pair of the complex cation and the amino acid generated carbanion.

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P-12. THE MATHEMATICAL MODELING FOR THE CONDUCTING POLYMERS’ SOLUBILISATION, MADE BY MEANS OF DERIVATIZING OR OVEROXIDATION

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Conducting polymers (CP), being capable to combine the properties of plastics (flexibility, light weight, tough, resiliency, versatility in shaping and corrosion resistance) with electron typeconductivity, and also being easily modified, have already received their use in corrosion protection, optoelectronics, light-emission diodes (LEDs), electrochemical cells (e.g., electrochromic and fuel cells), optoelectronics and sensors.

Most CPs are lyophobicin the majority ofsolvents. On the other hand, it is known, that the polythiophenes, substituted with acid groups (like - COOH or - SO_3H), capable to dope themselves (self-doped CP), are soluble, but the corresponding monomers are difficult to be polymerized, so the solubilisation is realized by polymeranalogic transformation of different nature and mechanism [1 – 3]. These transformations may be accompanied by electrochemical instabilities (oscillatory or monotonic behaviour) [3]and the most probable and theoretically based mechanism of their appearance may be given by the development and analysis of the mathematical model, capable to describe adequately the processes in the system. It is also capable to describe not only one concrete system, but also the similar ones.

To describe mathematically the polymeranalogic CP solubilisation, we introduce three variables:

c – monomer concentration in the pre-surface layer;
T – monomer coverage degree;
P – polymer coverage degree.

In order to simplify the modeling, we suppose that the reactor is intensively stirred, so we can neglect the convection flow. Also we suppose that the background electrolyte (containing the main dopant) is in excess, so we can neglect the migration flow. The concentration profile of the monomer and the alkali in pre-surface layer (with constant thickness, equal to δ) is supposed to be linear.

The balance equations' differential system, describing the process of the synthesis of soluble CP via polymeranalogical transformations may be represented as:

$$\begin{cases} \dfrac{dc}{dt} = \dfrac{2}{\delta}\left(\dfrac{D}{\delta}(c_0 - c) + r_{-1} - r_1\right) \\ \dfrac{dT}{dt} = \dfrac{1}{G_{max}}(r_1 - r_{-1} - r_2) \\ \dfrac{dP}{dt} = \dfrac{1}{\Pi}(r_2 - r_3) \end{cases}$$

In which D is the diffusion coefficient, c_0 is the monomer bulk concentration, G and Π are monomer and polymer maximal surface concentrations, r_1, r_{-1}, r_2 and r_3 are adsorption, desorption, polymerization and modification rates (the last reaction isn´t usually electrochemical). The balance equations describe the time evolution of the process by depicting the time change of the monomer concentration and coverage degree and polymer coverage degree.

By the analysis of the model, the steady-state stability requirementsare investigated with an emphasis on the verification of the possibility of surface, electrochemical and autocatalytic factors, which may destabilize the steady-state. The role of the mentioned factors in the realization of the oscillatory and monotonic instabilities is also evaluated.

By comparison of mathematical models, describing the cases of the absence of the solubilisation, with the given, the differences in behavior gain their theoretical explanations, confirmed by experimental data.

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P-13. SYNTHESIS OF THE DERIVATIVES OF GUTARIMIDE AND COUMARIN ON THE BASIS OF AMIDOESTHERS OF MALONIC ACID

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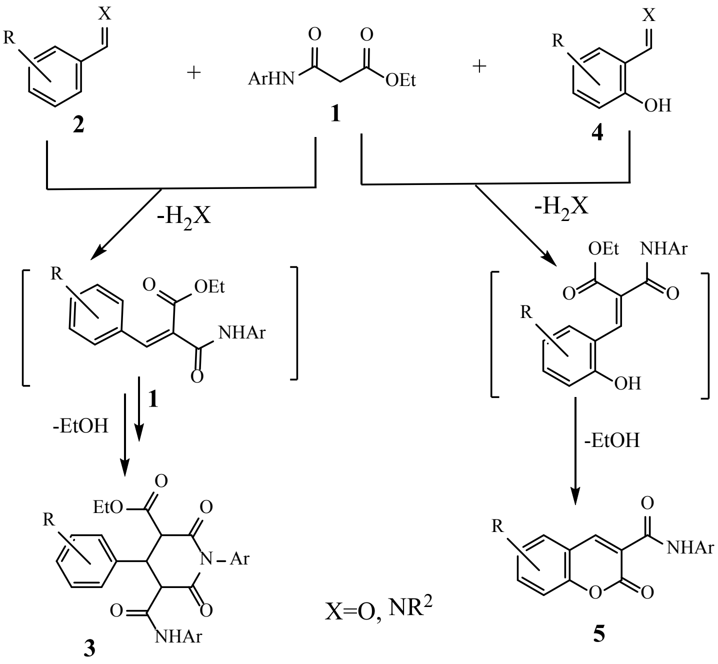
Development of the new methods for the synthesis of coumarins and glutarimides remain actual due to the fact that they reveal various biological activities [1,2]. Recently we have shown, that by the interaction of secondary arylamidoesthers of malonic acid (**1**) with the aromatic aldehydes (**2**) or their Schiff bases in the presence of piperidine in the boiling ethanol, the 3,4,5-trisubstituted glutarimides (**3**) are formed [3].



In current work, it was established that if the salycilic aldehyde is used in the mentioned interaction, instead of glutarimide derivatives, the arylamides of coumarin-3-carbonic acid (**5**) are formed, with the excellent yields 85-95 %.

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P-14. CYCLOPOLYMERIZATION OF DIENES WITH ACYCLIC FUNCTIONAL GROUPS BY Pd COMPLEXES

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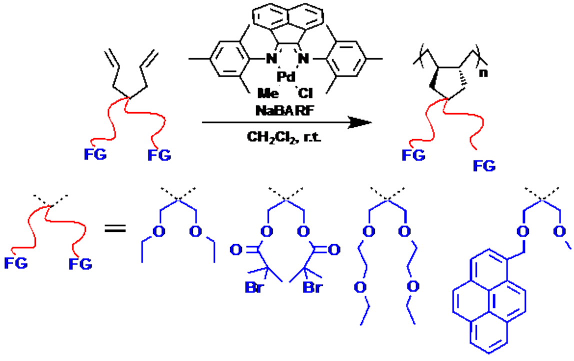
Cyclopolymerization of dienes is one of the methods to synthesize polymers with cycloalkane groups on the polymer chain. We have already reported that diimine Pd complexes promote stereoselective cyclopolymerization of dienes with cyclic functional groups to afford polymers with cyclopentane ring in one repeating unit. On the other hand, it is limited to polymerize acyclic dienes as a monomer. Herein, we report cyclopolymerization of 1,6-dienes with various acyclic functional groups by Pd complexes.

Diimine Pd complex in combination with NaBARF (BARF = $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$) promotes polymerization of 1,6-heptadienes (**1**) with various acyclic functional groups (**I** - **IV**) on the 4-position to give a polymer with cyclopentane rings in every repeating units. ^{1}H NMR spectra of the obtained polymers show the absence of olefin pendant. This indicates that reaction proceeds quantitative cyclization of the monomer during the polymerization. ^{13}C {^{1}H} NMR spectrum of the produced polymer show that the polymer contain *trans*- fused cyclopentane rings.



I **II** **III** **IV**

P-15. SYNTHESIS OF THE DERIVATIVES OF BIOLOGICALLY ACTIVE α,β-DEHYDROAMINO ACIDES WITH MICROWAVE IRRADIATION

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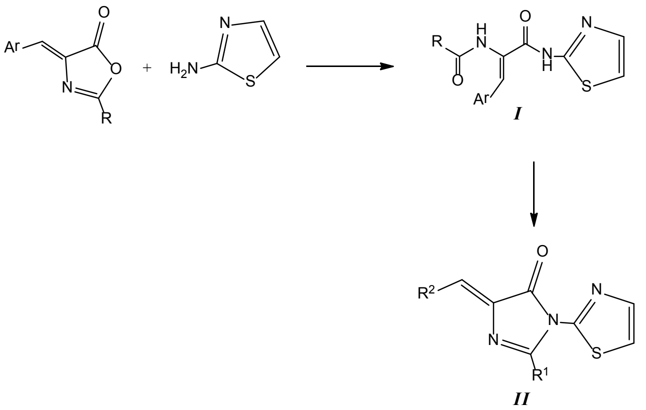
The aim of this work is to study the applicability of microwave irradiation for N-acylation of several amines with unsaturated 5(4H)-oxazolones. In connection with this work we have developed a new way of synthesis of unsaturated oxazolones which was used as raw material.

The applicability of zinc sulphate and acetate in the synthesis of unsaturated 5(4H)-oxa-zolones was examined. Investigation was carried out also for the catalyst, reactionary environ-ment, as well as the reaction conditions (room temperature or microwave irradiation) influence the outcome of target oxazolones. It was found that the best outcomes were from the presence of 0.3 equivalent of zinc acetate in the microwave radiation during five minutes. For comparison we should notice that the speed of synthesis with nitrobenzaldehyde in the microwave irradia-tion at least 300 times faster than in the room temperature.

It is also possible that zinc acetate can be used in the synthesis of saturated 5(4H)-oxa-zolones.

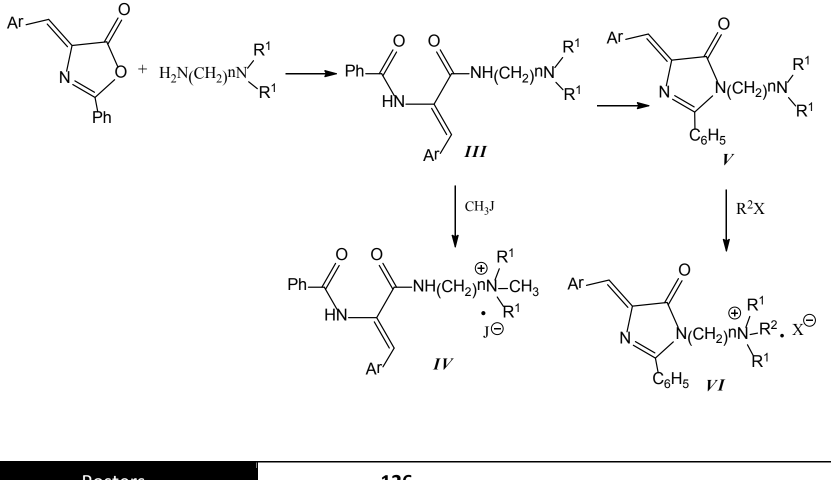
The synthesis of derivatives of α,β-dehydroamino acides, which contains aminothiazole residue (**I**), was carried out in different conditions (room temperature, boiling or microwave irradiation). The advantage of the method of microwave irradiation for synthesis of these comp-ounds was shown.

The NMR method indicated that the synthesized aminothiazole amides of N-substitut-ed α,β-dehydroamino acids have the Z-configuration. On the example of the thiazolyl amide of N-benzoyl α,β-dehydrophenylalanine the influence of a number of dehydration agents for the synthesis 5-imidazolon (**II**) was studied. In a number cases (acetic acid, acetic acid and sodium acetate or zinc acetate, as well as trimethylchlorosilane) the generation of oxazolone was observed. The relatively high outcomes of target 5-imidazolone obtained from participation of hexamethyldisilazane in the microwave irradiation conditions was shown.



For the determination of their configuration the NMR proton spectrum without hydrogen pressure was studied. In this spectrum the break of signal of carbon of carbonil group of imidazolon residue in the 5 Hz signal boundary was noticeable. Which is most likely the result of the interaction of that carbon and vinyl proton. So it is clear that the synthesized imida-zolones have the Z-configuration.

The synthesis of dialkylaminoalkyl amides of Z-N-substituted dehydroamino acids and their quaternery ammonium salts (**III, IV**) as well as their cyclic analogues: 1-dialkylamino-alkyl-2-aryl-4-aryliden-5-imidazolones (**V, VI**), was carried out. For the latter as dehydration agent is used trimethylchlorosilane. The X-ray study of 1-dimethyl-aminoethyl-2-phenyl-4-(p-methoxybenzylidene)-5-imidazolone was done. Results showed that the compounds have the Z-configuration.



Kinetic study of the cycle opening of the unsaturated oxazolones with dialkylamino-alkylamines in the pseudo first conditions was done. Obtained information suggested that in the dimethylaminoalkylamine the extension of methylene chain leads to acceleration of the reaction. Meanwhile the insertion of electron donor methoxy group in the aromatic side chains of oxazolone leads to the deceleration of the reaction.

The biological studies of the synthesized compounds have shown that they have antibacterial and anticholinesterase activity. Based on the results it was found that a variety of patterns between the structures of the synthesized compounds and anticholinesterase activity.

P-16. SYNTHESIS OF POTENTIALLY BIOACTIVE BISISOINDOLINIUM SALTS WITH PHENANTRENIC CYCLE

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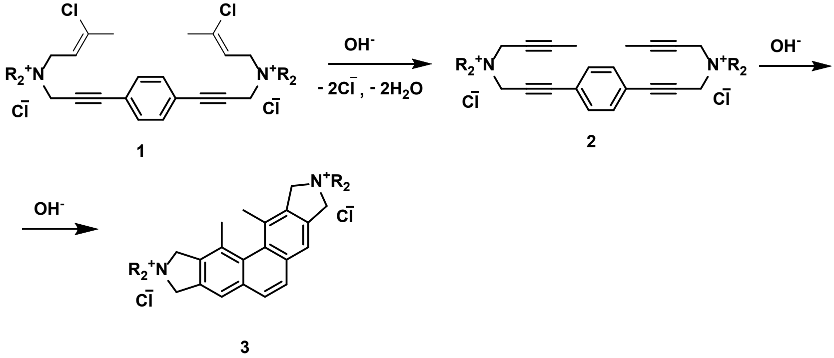
Earlier it has been established, that p-bis[3-[N-(3-chlorbuten-2-yl]pyrrolidino(pyperidino or morpholino)]propyn-1-ylbenzene dichlorides (**1**) in water-base medium undergo a double dehydrochlorination with formation of intermediate salts **2**, which undergo subsequent double intramolecular cyclization [1].



R_2= $(-CH_2-)_4$; $(-CH_2-)_5$; $(-CH_2-)_2O(-CH_2-)_2$

It was shown that by direct heating of water solutions of salts **1** at 80-85 °C within 6-7 hours in the presence of base in a molar ratio salt/base=3/1 the cyclic salts - benzo[5.6-5′.6′-a,c]bis[(2,2-tetramethylene)-4-methylisoindolinium, -(2,2-pentamethylene)-4-methylisoindolinium and benzo[5.6-5′.6′-a,c]bis(spiro-4-methylisoindolinium-2,4′-morpholinium dichlorides (**3**) were received with high yields (62-64%).

The conducted investigations except the theoretical have also applied significance. Among the earlier synthesized by us isoindolinium salts, containing a phenantrenic ring, there are representatives with high pharmacological activity: they possess the expressed hypotensive activity surpassing in the action a spasmolytic myotrophic preparation, applied now in medical practice papaverine, the activity is not only concerning the arterial pressure, but also concerning the cerebrovascular resistance of brain vessels, high analgetic activity of non narcotic character. The activities were defended by numerous copyrights of the Soviet Union [2,3]. There are representatives with complex pharmacological activity [4].

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[3] Copyright certificate (USSR) № 961310 “2,2-diethylnapht[f]isoindolinium) bromide, possessing analgetic activity (A.T. Babayan, E.O. Chukhajian, A.S. Saratikov, El.O. Chukhajian, K.G. Shahkhatuni, N.S. Livshits, L.V. Simak) - Priority of invention 16 of February 1981, isn't subject to the publication.

[4] Patent of the Republic of Armenia “2,2-diethyl-4-α-naphtylnapht[f]isoindolinium) bromide, possessing antianginal, cardiotonic, cholinolytic and hypotensive activity”. (E. Chukhajian, K. Shahkhatuni, El. Chukhajian, A. Babayan, V. Samvelyan, V. Hakobyan, E. Djhanpoladyan, E. Khoetsyan)

P-17. BASE CATALIZED INTRAMOLECULAR CYCLIZATION OF DIALKYL(3-PHENYLPROPEN-2-YL)(3-PHENYL- OR *p*-CHLORPHENYLPROPYN-2-YL)AMMONIUM BROMIDES

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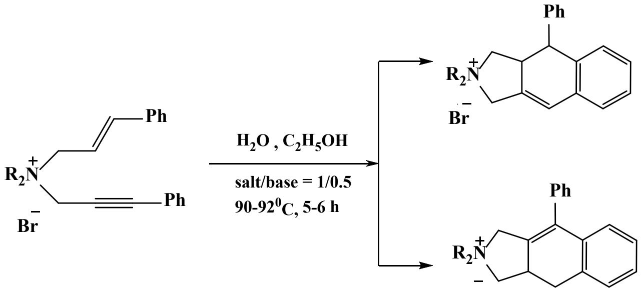
Base catalized intramolecular cyclization of ammonium salts containing β,γ-unsaturated groups alongside with 3-alkenyl(or aryl)propyn-2-yl group, discovered for the first time by A.T. Babayan, E. O. Chukhajian and coauthors, is absolutely new direction in Organic chemistry and includes enormous possibility for synthesis of bioactive di-, three- and polycyclic isoindolinium and dihydroisoindolinium salts [1,2]. The propargylic analogues are quantitatively undergo cyclization with self-heating in the water medium in molar ratio salt/base=5/1, while for cyclization of allylic analogues the reaction mixture was heated at 90 °C during 2-3 hours.

In 1973 by A. T. Babayan with coauthors was established that the salts with bis(3-phenylpropyn-2-yl) group undergo cyclization even in absence of base by heating of their water solutions [3]. On the basis of above-mentioned it can be assumed that the second phenyl group, apparently, facilitates the cyclization.



R_2= $(C_2H_5)_2$, $(-CH_2-)_5$

One may suppose that the second phenyl group, located in γ-position of allylic chain, should also promote cyclization. Contrary to our expectations the cyclization of salts, containing 3-phenylpropen-2-yl group alongside with 3-phenylpropyn-2-yl, proceeds in very hard conditions in comparison with allylic analogues.

Because of bad solubility of these salts in water their cyclization was carried out in water-alcohol medium. The cyclic products were formed with 62-72% yields. In the case of diethyl and pyperidinium analogues instead of 4-phenylsubstituted salts were obtained their 9-phenylsubstituted isomers with 65-68% yields [4]. As it was mentioned, because of bad solubility of initial salts in water the cyclization was realized in water-alcohol medium. Consequently, it was difficult to say that what was the cause of toughening of conditions of cyclization in comparison with allyl analogues [1]: the presence of alcohol during cyclization or the phenyl group, located in γ-position of allylic fragment. For elucidation of this fact the cyclization of dialkyl(3-phenylpropen-2-yl)(3-phenyl- or 3-*p*-chlorphenylpropyn-2-yl)ammonium bromides was carried out on the analogy of the cyclization of dimethylbis(3-phenylpropyn-2-yl)ammonium bromides [3] .

It was established that cyclization of above-mentioned salts in the water medium in presence of the base in molar ratio salt/base=5:1 at 40-50 ^{o}C heating during 5-10 min, in contrast to allylic analogues proceeds with self-heating and leads only to 2,2-dialkyl-4-phenyl-, -6-chloro-3a,4-dihydrobenzo[f]isoindolinium bromides in nearly quantitative yields [5].

On the basis of above-mentioned results and IR spectral investigations was established, that the phenyl group in 3-rd position of allylic fragment has a positive effect on cyclization.

The observed phenomenon is only in the field of cyclization of ammonium salts which contain allylic group alongside with 3-arylpropyn-2-yl fragment.

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P-18. SYNTHESIS OF THE NEW SPIROCYCLIC ANALOGUES OF ALKALOID "CERPEGIN"

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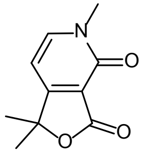
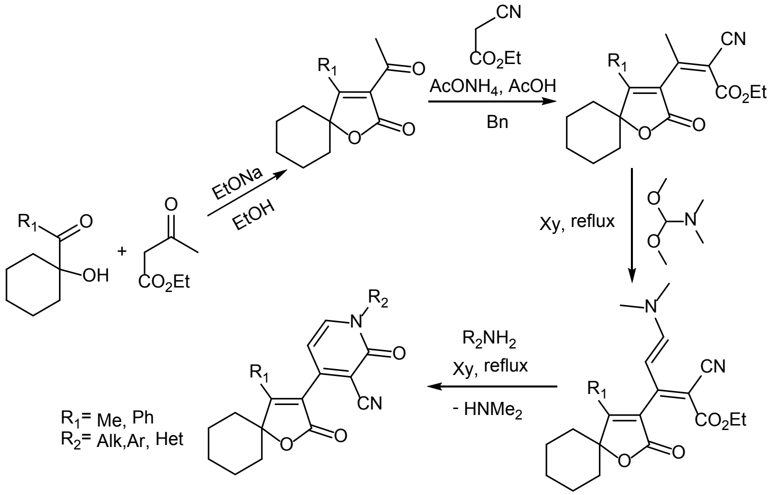


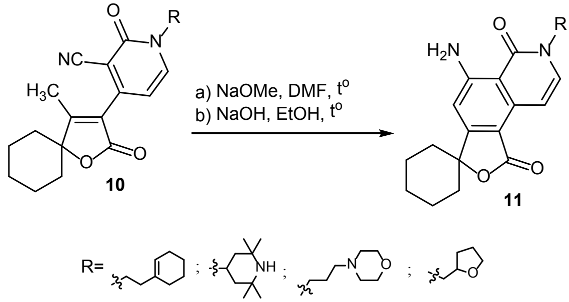
The natural alkaloid Cerpegin was isolated from the plant "Ceropegia juncea", which was used in the folk medicine and is possessing tranquilizing, anti-inflammatory and anestethic properties. Te structure of the cerpegin was estimated as a biheterocycle with condensed furanone and pyridine rings - 1,1,5-trimethylfuro[3,4-*c*]pyridine-3,4(1H,5H)-dione.

The synthesis of cerpegin and its derivatives bearing different substituents as in furanone ring as well as in pyridine ring was developed and published by the collaboration between Yerevan State University and the Paris-6 university [1,2].

Hereby we report a new investigation by which we have synthesized new type of



biheterocycles containing bonded pyridone and spirofuranone rings which can be considered as analogues of alkaloid cerpegin. The method allows to synthesize compounds in which the γ-lactone and pyridine moieties can contain various substituents.



In case when R_1 = Me the structural adjacent of the methyl group and the nitrile moiety of the pyridine ring allowed an assumption that the intramolecular nucleophilic cyclization is possible. The experimental data came to prove the assumption which allowed synthesizing a number of new tricyclic compounds.

Thus the method for the synthesis of new spirocyclic biheterocycles was developed and a number of derivatives were synthesized. The obtained compounds contain structural elements of alkaloid cerpegin. For some of the obtained compounds it was shown, that the structural properties of the molecule allow the intermolecular nucleophilic cyclization, leading to the spiro- substituted fused tricyclic biheterocycles.

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P-19. HYDROGENATION of TERMINAL HOMOPROPARGYL ALCOHOL 3 - METHYL-HEX -5- YN-3 -OL by LITHIUM ALUMINUM HYDRIDE

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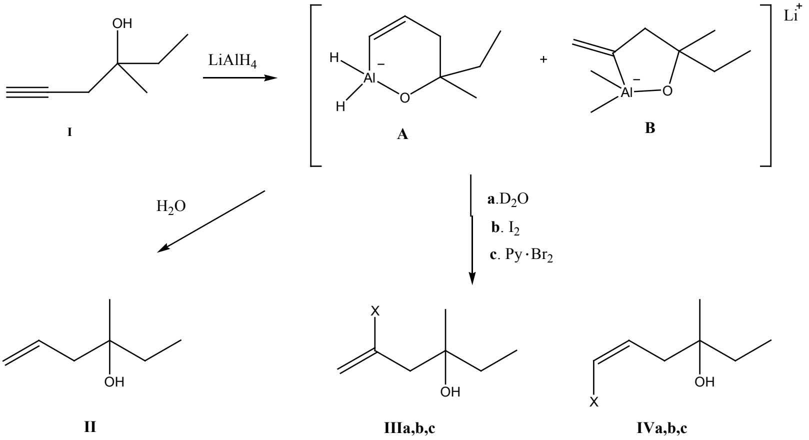
Information about reduction of the terminal triple bond in acetylene alcohols are limited. It is known that the triple bond in the α- acetylenic alcohols is easily hydrogenated by lithium aluminum hydride [1]. By halogenation of intermediate organoaluminum complex is recently shown us regioselectivity hydride attack on the triple bond [2,3], and is also we studied the hydrogenation of terminal triple bond in ethylene glikol monopropargyl ether [4] and 2-methyl-4,6-heptadiyn-2-ol [5]. We present here the results on reduction of 3-methyl-hex-5-yn-3-ol (**I**) - tertiary acetylenic alcohol containing a terminal acetylene group in β-position.



a. X=D, **b**. X=I, **c**. X=Br.

It is shown that boiling alcohol **I** with lithium aluminum hydride in dry THF in a ratio of alcohol: lithium aluminum hydride - of 1:4 leads to homoallylic alcohol 3-methylhex-5-ene-3-ol (I**I**) with 73% yield. In favor of the formation of the alcohol (II) is according to IR (3070 cm-1, CH2 =) and ^{1}H NMR [dt at 5.85 ppm (CH2 = CH);

doublets at 5.12 and 5.17 ppm (CH_2=)] spectra. To clarify the position of aluminum in the intermediate organometallic complex the last is decomposed by deuterium oxide , iodine and pyridiniumdibromide. In all cases it is obtained a mixture of alkenols **III** (**a, b, c**) and **IV** (**a, b, c**) in a ratio of 1:2. Individiual iodo- and bromoalkenols **III** (**b, c**) and **IV** (**b, c**) isolated by column chromatography. Using data of ^{1}H NMR spectra proved that the double bond in the compounds **IVa**, **IVb** and **IVc** has cis configuration (J = 8 Hz). Presence of atoms deuterium, iodine and bromine in the 3 and 4 positions as well as the cis - configuration of the double bond in the resulting products suggests that the hydride ion attack occurs simultaneously in two directions. Based on our results and published data reduction of α-acetylenic alcohols [6], we can assume that the reduction of homopropargyl tertiary acetylenic alcohol - 3-methyl-hex -5 - yn-3-ol (I), curries out via the cyclic organometallic complexes **A** and **B**.

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P-20. AZA-MICHAEL ADDITION OF AZOLES TO MVK

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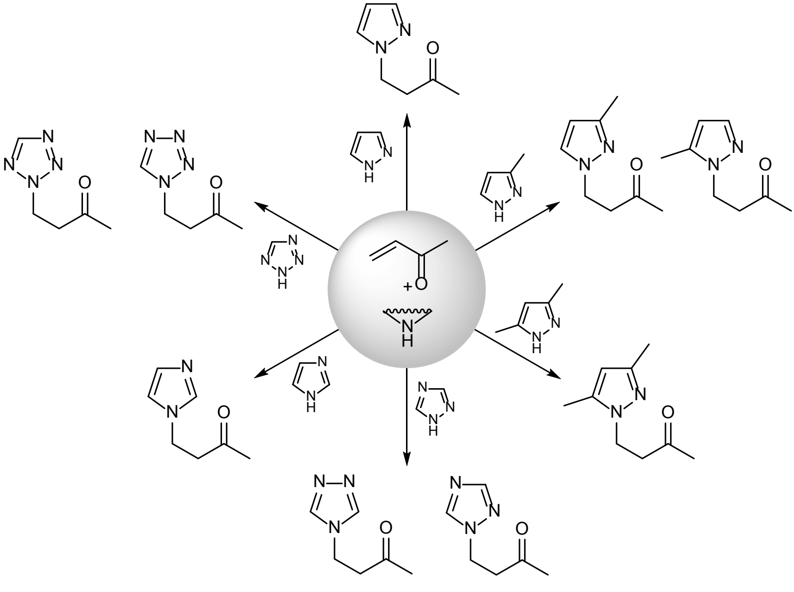
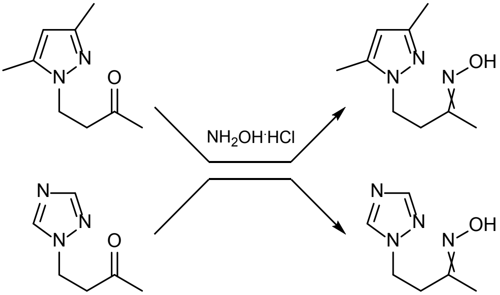
The thermal addition of nitrogen containing compounds to conjugated systems is known as a separate type of Michael addition. Particularly the addition of azoles to methyl vinyl ketone (MVK) is known from the literature to proceed in the thermal processes with the involvement of different Lewis acids.

Hereby we report the new and improved procedure for the addition of azoles to MVK, by avoiding of usage of solvents and catalysts, the reaction is held in sealed tube by heating of equimolar (or 10% excess MVK) amounts of azole and MVK at about the boiling point of MVK (80 °C). The reactions are finished in 3-15 mins with almost quantitative yields. As Michael donors substituted pyrazoles (I-III), imidazole (VII), 1,2,4-triazole (IX) and tetrazole (XI) are used.



The corresponding ketoximes of the obtained compounds were synthesized by the interaction with the hydroxylamine hydrochloride. The complexation properties of some of the obtained azolyl-butane-2-ones as well as their oximes were studied.



By mixing of the methanol solutions of ligands and metal salts ($NiCl_2$, $CuCl_2$) the corresponding complexes were formed as precipitates. The preliminary IR and UV investigations showed, that in case of the triazolyl-butanones, the azole ring is involved in complexaion, while its oxime acts as a bidentant ligand - with the cycle, as well as with the oxime moiety. Dimethylpyrazolyl-butanone was shown not to form complexes and its oxime is acting as a monodentant ligand by the oxime group. The further and complete investigations of the complexing properties of the mentioned ligands are on the stage of development.

P-21. COMPARATIVE INVESTIGATION OF FATTY OILS FROM SOME FABACEAE SPECIES

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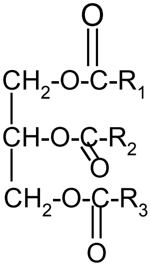
Fatty oils from plants are mixtures of triglycerides of fatty acids, common formula of mixture shown in pic. 1, R_1, R_2, R_3 in the picture are radicals of fatty acids.

Mostly, fatty oils separated from plants are liquids, and R_1, R_2, R_3 can be the same radical ($R_1= R_2= R_3$) or different radicals



Pic. 1. Common formula of fatty oil

Mixture of triglycerides of fatty acids often contains palmitic, stearic , oleic, linoleic, linolenic, arachidonic and other acids.Fatty acids have many properties that can be used either in medicine and pharmacy as a medical drugs, or food industry as nutritional supplements, and in cosmetology for its moisturizing, nourishing properties.[1]

We have isolated and investigated a fatty oils from a seeds of 10 species of Fabaceae . Shredded seeds from each species wehave fully extracted (~30-50 times) by dichloromethane in Soxhlet extractor.

The extracts were filtered, organic solvent was evaporated(in temperature 40-50^{0}C). After that the substances were warmed in a vacuum for 15-20 minutes (in 1-2 mm Hg pressure), then we have determined a weights and yields(%) of obtained oils.

The oils were compared by comparative thin layer chromatographic method and ^{1}H-Nuclear Magnetic Resonance spectra analysis.[2]

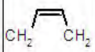
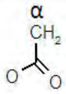
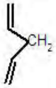
Thin layer chromatography (TLC) of fatty oils from 10 Fabaceae species was taken on Silufol UV-254 layers. Solvent system was hexane- diethyl ether (8:2). Spots was developed in 10% phosphoramolybdenic acid in ethanol.

^{1}H-Nuclear Magnetic Resonance spectra analysis was made using Varian Mercury-300 NMR spectrometr, using as a solvent $CDCl_3$.

Methyl groups signal of ω-3 fatty acids can be detected in a narrow area 0,85-1,05 p.p as a triplet (see table 1)

By investigation of signals of NMR spectra in area 0,85-1,05 p.p we have determined per cent of ω-3 acids in obtained oils [3]

Table 1.

^{1}H signal areas of oils(p.p.)							
0,85-1,05 p.p	1,22-1,40 p.p.	1,58-1,70 p.p.	1,98-2,20 p.p.	2,28-2,37 p.p.	2,70-2,82 p.p.	4,08-4,35 p.p.	5,20-5,30 p.p.
-CH_3	$(CH_2)_n$	β CH_2- CH_2- COO				glycerine 2CH_2-	glycerine CH,=

Results of NMR spectra analysis ,yields of oils and per cents of ω-3 acids in oils shown in table 2

Table 2.

^{1}H signal areas (p.p.) and intensity											
	Species	0,85-1,05 p.p	1,22-1,40 p.p.	1,58-1,70 p.p.	1,98-2,20 p.p.	2,28-2,37 p.p.	2,70-2,82 p.p.	4,08-4,35 p.p.	5,20-5,30 p.p.	yield of oils, %	% of ω-3 acids
1	Arachis hypogaea	9,2	80,59	6,46	9,8	6,46	2,15	4,0	7,68	29 %	-
2	Phaseolus vulg. black	10,4	39,1	1,55	11,0	6,44	6,2	4,0	11,1	1,5 %	45%
3	Phaseolus vulg. white	6,4	43,1	7,7	11,7	5,8	7,3	4,0	13	1,1%	43%
4	Phaseolus vulg. capras	6,81	40,8	7,44	11,0	5,9	7,4	4,0	13,6	1,6%	50%
5	Cicer anetium	8,86	50,6	8,3	10,3	5,7	2,6	4,0	8,3	1,2%	1%
6	Lens orientalis	9,7	38,2	8,0	8,58	5,72	3,4	4,0	6,86	1,1%	10%
7	Pisum sativum	10,6	43,8	7,0	9,2	6,2	3,4	4,0	8,0	1,4%	13 %
8	Phaseolus vulg. planae	12,0	51,4	6,8	10,4	5,8	3,4	4,0	8,8	1,2%	9%

9	Trigonella foenum-graecum	11,2	48,4	7,4	10,6	6,2	6,0	4,0	11,4	5,3% 27%
10	Lens culinaris	17,2	58,0	8,8	11,0	6,2	4,4	4,0	9,8	0,73% 14%

Results of this investigation one more time show that the some Fabaceae species can be used not only as a source of protein, but also as a source of important and necessary to human organisms ω-3 fatty acids.

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P-22. REDUCTION OF POLY(1.4-QUINONEDIIMINE-*N,N’*-DIYL-1,4-PHENYLENE)

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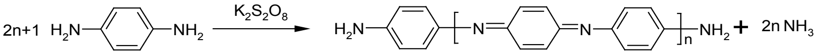
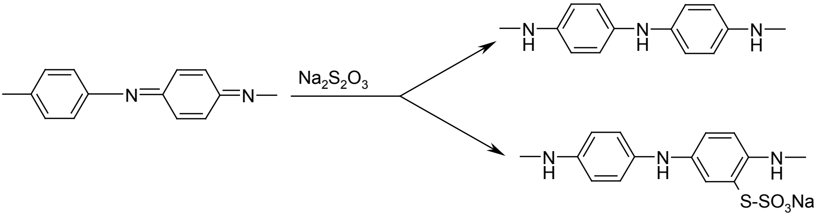
As we know polyaniline has a lot of properties which other polymers do not have. That is why this type of polymers have wide demand in technique. Depending on oxidation degree polyaniline has three different forms, which have different conductivities and properties and may be converted one to the other by the redox process. Since half-oxidized emeraldine form of polyaniline is more stable, the syntheses of other forms from emeraldine have been described [1].

On the base of p-phenylenediamine new one-step method of poly(1.4-quinonediimine-N,N’-diil-1,4-phenylene) – polymer with similar to pernigraniline structure, synthesis have been worked out[2].



The main goal of the present work is to obtain polymers with similar to leucoemeraldine and emeraldine structures by the reduction of poly(1.4-quinonediimine-N,N’-diyl-1,4-phenylene), dope obtained polymers with hydrochloric acid and compare conductivities with corresponding doped polyanilines. Reduction was carried out in formic acid and N-methylpirrolidone using potassium thiosulphate, ascorbic acid and hydrazine as reducing agents by similar procedure has been described for emeraldine [3,4]. It was established that1,4-addition of thiosulphate groups to quinonediimine groups of polymer proceeded simultaneously.



At first, it was shown, that during the reduction with ascorbic acid the reaction of solvent N-methylpirrolidone with reducing agent - ascorbic acid, occurred, as well. As a result of the reaction with hydrazine, completely reduction of quinonediimine units to phenylenediamine occurred and evidently, in UV spectrum the maximums of quinonediimine groups at 422 nm – 440 nm disappeared.

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P-23. COMBINED REDUCTION OF COPPER AND MOLYBDENUM OXIDES IN COMBUSTION MODE

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Mo–Cu alloys are of special interest in recent years because of their excellent physical and mechanical properties. Due to the combination of the metals' properties, these alloys show high thermal and electrical conductivity, low and alterable thermal expansion coefficient, nonmagnetic and well high-temperature behavior. They find wide applications as heavy-duty electrical contacts, welding electrodes in vacuum technology, in military, aviation fields and in many industrial leading areas.

A lot of researches were performed in the latest decade to synthesize Mo-Cu composites (and to improve their sintering behavior), such as mechanical alloying, hydrogen reduction of copper and molybdenum oxygen containing compounds, etc. These processes are energy-consuming and low efficient, besides the prolonged processes make copper grains to enlarge. The main goal of this work is to synthesize Mo-Cu alloys by self-propagating high-temperature synthesis (SHS), which has a lot of advantages (high productivity, energy-saving, ecologically harmless, etc.). SHS processes are perspective for synthesis of ultra-fine and homogenous alloys, which is effective for improving sintering behavior of powder mixtures.

The reduction of the copper monoxide and molybdenum trioxide in the combustion mode have been realized by (Mg+C) combined reducers. Either the molybdenum or copper oxides' reduction processes by magnesium are high exothermic processes and the reaction temperature is very high (3000^oC and more), so the evaporation of MoO_3, Mg and Cu, and partial reduction of molybdenum oxide take place. To reduce both oxides at lower thermal conditions and to avoid from above mentioned difficulties, as well as to provide complete joint reduction of oxides we suggest to substitute part of magnesium with low active reducer – carbon.

For exploration of the combustion possibility in the MoO_3-CuO-xMg-yC system, estimation of the adiabatic combustion temperature and equilibrium composition products, thermodynamic calculations were applied. It was found, that copper-molybdenum bimetallic system can be synthesized at amount of magnesium x=1-1.8 moles and carbon y=1-2.3 moles in wide temperature range (1200-2100°C).

The experimental investigations of phase- and microstructure formation at combustion of the system under study showed, that for the preparation of target alloy it is more preferable to mitigate the conditions of combustion wave propagation. As a result of such investigations, it was found the optimum composition of initial mixture: $CuO-MoO_3-1.2Mg-2.15C$. The microstructure and XRD pattern of obtained composite powder Mo-Cu is shown in Fig.1.

However the high velocity of SHS processes makes certain difficulties for study the reactions' mechanism. So the exploration of interaction mechanism has been realized at low heating rates by thermal analysis method.

From the results of thermal analysis it was ascertained, that in the $CuO-MoO_3-Mg-C$ system the reactions' sequences and reduction degree mostly depend on the heating rate of reaction mixture. It was shown, that only at relatively high heating rates (≥50°/min) it is possible to realize combined reduction of oxides, therefore the reduction process starts with low exothermic reducer (carbon) and ends with the reaction by the high exothermic reducer (magnesium).

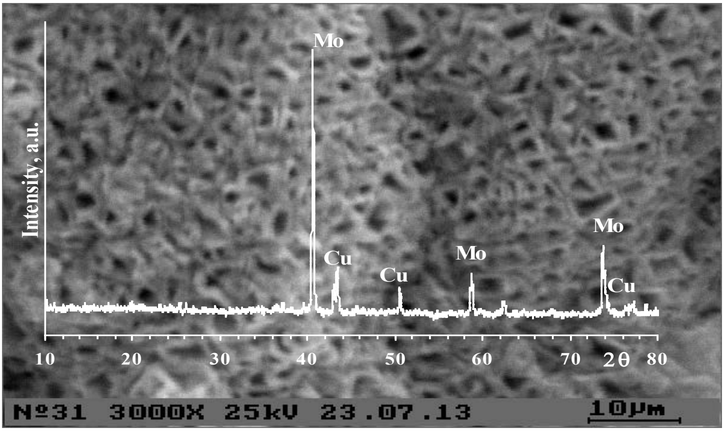

Figure 1. XRD and SEM analyses results of Mo-Cu composite powder

References

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P-24. MAGNESIOTHERMIC REDUCTION OF SILICA'S OF VARIOUS ORIGIN AND PREPARATION OF SILICON

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Silicon is the second most common element in the Earth by mass, but very rarely occurs as the pure free element in nature. Pure monocrystalline siliconis used to produce silicon wafers for the semiconductor industry, in electronics and in high-efficiency photovoltaic applications. Pure silicon has too low conductivity and for application in electronics it is doped with small amounts of certain other elements and used fortransistors, solar cellsand other semiconductor devices[1].

The main goal of the present research was to study and compare the magnesiothermic reduction peculiarities of silicon oxides of various origins at high and low heating rates, such as by self-propagating high-temperature synthesis (SHS) method and thermal analysis technique. Eghegnadzor's quartzite [A], silica obtained from sodium silicate, [B], and silica obtained from serpentine mineral [C] were used as precursors. The choice of magnesium as a reducer isn't casual, because it is well known that magnesiothermic reduction is characterized by high exothermicity and allows to perform reduction process in the combustion mode, in contrast of carbothermic reduction. Besides, the magnesia formed during the reduction process can be easily removed from the main product by acid treatment.

Experiments showed that silicon oxides exhibit different activities both in reduction patterns and products composition at high temperature conditions and also they show drastically different behavior at low heating rate processes. It should be mentioned that silica obtained from serpentine mineral is characterized by highest activity - combustion temperature exceeds adiabatic temperature about 150°C, and combustion velocity 2-3 times higher than in the case of other types of silica (Fig.1).

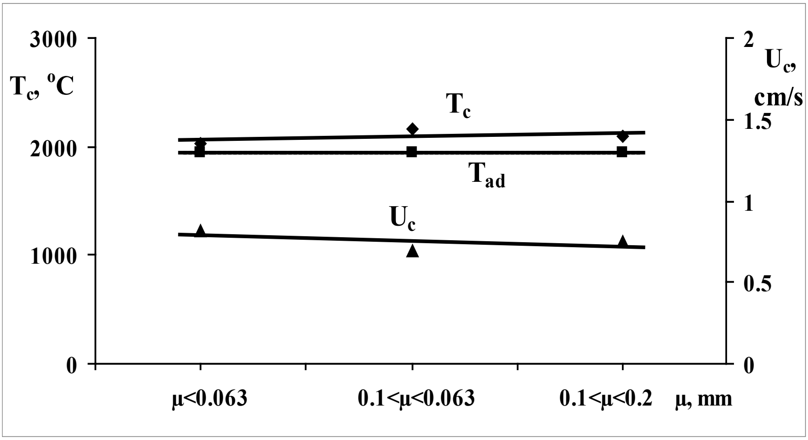

Figure 1. Combustion parameters vs. particle size of silica for the SiO_2[C] +2Mg mixture, P=10 atm.

This phenomenon can be explained with the presence of additional energy of Si-O bonds, which is accumulated in the compound during sequential acid-base treatment of serpentine. It should be noted that combustion parameters for SiO_2[C] +2Mg mixture practically don't depend on SiO_2 particle size because of high porosity of silica (specific surface area: S=560 m^2/g).

According to SEM analysis, the reduction products of silica's types [A] and [B] contain coarse particles, meanwhile in the case of [C] type silica, fine grained silicon forms.

Thermal analysis results certified that magnesium reduction of all three type silica's is one-stage process and proceeds in the solid phase (before magnesium melting). For the [C] type silica the maximum self-heating was observed compared with [A] and [B]. Activation energy calculated for the SiO_2[C]+2Mg interaction by Kissinger's method [2] amounts about 43 kcal/mol (Fig.2).

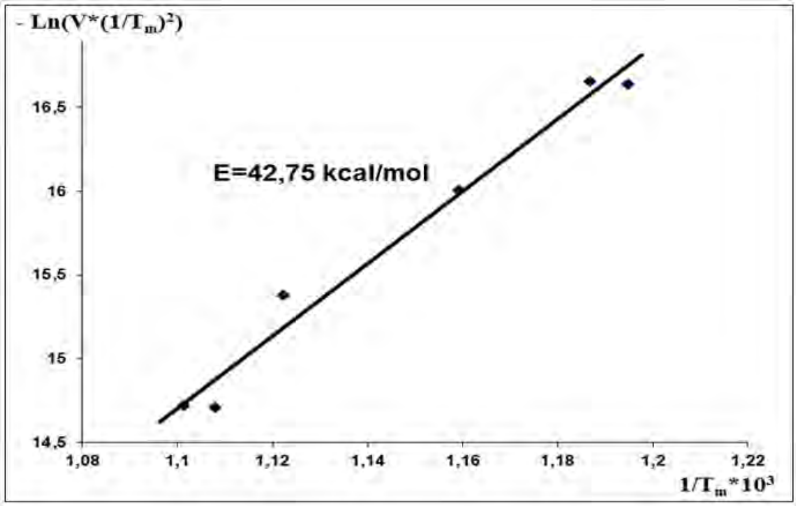

Figure 2. Determination of activation energy for SiO_2[C]+2Mg reaction by Kissinger's method

The latter establishes a relationship between the heating rate (V_h) of reaction mixture and maximum temperature deviation on the DTA curve $\left(T_{\max}^{DTA}\right)$.

$$\ln\left(\frac{V_h}{\left(T_{\max}^{DTA}\right)^2}\right) = \ln A - \frac{E}{R}\left(\frac{1}{T_{\max}^{DTA}}\right)$$

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P-25. DEVELOPMENT OF A COLORIMETRIC SENSOR FOR FISH SPOILAGE MONIRORING

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Literature review

Due to the increased demands for safe and high quality products and changes in consumer preferences, the food packaging industry has rapidly developed to meet and satisfy consumer expectation. Traditional packaging just contains and protects its content, but innovative development in packaging materials led to packages that do more than just preserving the product. They prevent or delay undesirable changes to the product, inhibit undesirable enzyme activities, protect the product against environmental effects, communicate product information, history and condition with the consumer, indicate seal leakage, confirm product authenticity and act to control theft. Packages with the ability to detect changes occurring in the environment inside or outside of them and respond by changing their properties or by producing a signal to inform consumers about quality changes, are referred as “Smart or Intelligent” packaging. Development of a color indicator as an intelligent packaging for evaluating kimchi fermentation based on bromocresol purple that changes from blue to light green by pH changes of kimchi fermentation [1], is an example of smart packaging. The fish industry and retailers need methods that are objective, cost effective, rapid, reliable, on-package and non-destructive to determine fish freshness during distribution and selling. Fish species skin contains some microorganisms known as specific spoilage organisms (SSO) which increase gradually after death. These microorganisms breakdown the aminoacids and release volatile amines such as trimethylamine, dimethylamine and ammonia, which are known as TVB-N. TVB-N level has the potential to be used as fish spoilage indicator. A pH sensitive dye can monitor the TVB-N level of headspace that shows the freshness of packaged fish. Development of a volatile amine sensor for monitoring of fish spoilage based on bromocresol green which changes from yellow to blue by pH increasing [2] is an approach to meet fish industry demands.

This paper reports use of a pH sensitive dye for monitoring fish (rainbow trout) spoilage based on bromothymol blue that changes color from yellow to blue, easily visible to the naked eye and following the mechanism of color changing shown in Fig.1.

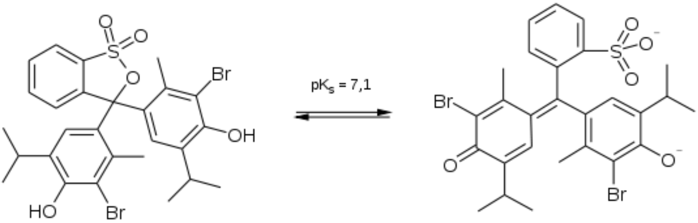

Fig 1: Mechanism of bromothymol blue changing color

Experimental

A solution containing agar-agar gel and bromothymol blue was prepared and coated on optically clear polyethylene sheet by K Control Coater (model K202) in 100 micron thickness. The films were then air dried and cut in 2×2 cm pieces and attached to cotton gas permeable membrane. The tag was installed on the inner part of the package where 15 g of fish tissue was packed. Samples were allowed to spoil in room temperature and the color was evaluated by spectrophotometer at each time interval. Fig 2 illustrates changes in Hunter color values of tags during storage.

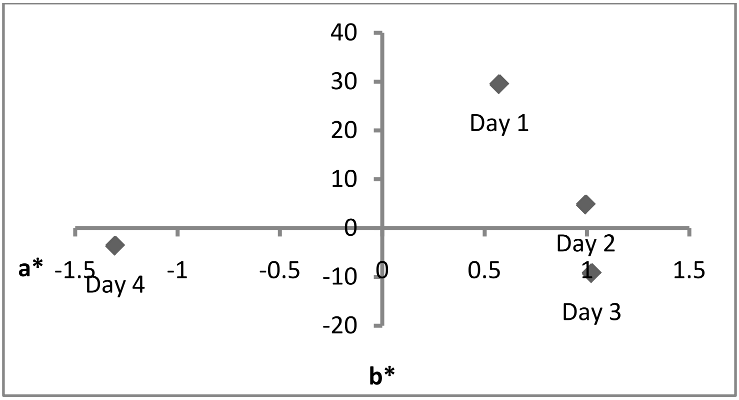

*Fig 2: Changes in La*b* values of tags during storage*

Conclusion

We have developed a simple sensor that monitors and informs food spoilage by a visible change in color from yellow to blue. Smart packaging is essential for having safe and high-quality products to satisfy consumers’ needs.

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P-26. COMPARISON OF ANTIBACTERIAL PROPERTIES OF NEEM SEED OIL AND ETHANOLIC NEEM EXTRACT

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Introduction

Due to sicknesses caused by bacteria which exist in environments around human, preparation of antibacterial agents for antibacterial finishes of fabrics has engaged scientists’ attention. Since natural antibacterial agents are biocompatible, natural, especially herbal, bioactive agents are one of the universal interests. Neem extracts are one of these natural antibacterial agents [1].

Neem is an evergreen tree which is mostly found in Middle East countries. Extracts provided from different parts of Neem has various bioactive properties including antifungal, antifeedant, antimalarial and antibacterial properties [2]. Different researchers have studied these bioactive properties and some have used the extracts gained from leaves and seeds of Neem for antibacterial finishing of cotton fabrics. Anderson et al. have studied the antifeedant properties of Azadirachtin (one of the compounds identified in Neem extracts) and they observed that this property is due to presence of tricyclicdihydrofuran ring in azadirachtin structure [3]. Joshi has studied antibacterial properties of polyester/cotton blend fabric which was finished using methanolic extracts of Neem seeds. He observed that finished fabrics showed up to 80% antibacterial activity against P. Vulgaris, a gram negative bacterium [4].

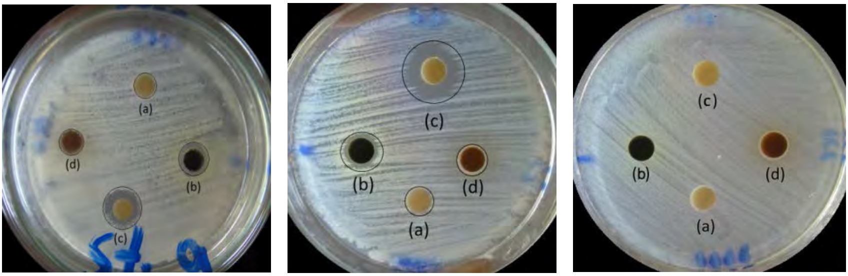
In this study, antibacterial properties of ethanolic extraction of Neem seeds, barks and leaves were studied against two gram positive and one gram negative bacteria using disk diffusion method. It was observed that extract provided from Neem seeds had the most antibacterial properties. Thereafter antibacterial properties of Neem seed extract and Neem seed oil was studied using minimum inhibitory concentration (MIC) method.

Materials and Methods

Neem seeds, leaves and barks were provided from Bandar Abbas, one of the southern cities of Iran. Materials were washed carefully three times with water and dried in room temperature till they became crispy. Leaves and barks were grinded and turned into powder. Seeds were put in oven for one hour in 50 °C and then turned in to past. The materials then were put in ethanol with the ratio of 1:3 and were stirred for 30 minutes with rate of 1000 rpm and were kept in room temperature for 48 hours. After 48 hours, the mixtures were filtered and extractions were prepared. Soxhlet extractor was used for preparation of Neem seed oil and acetone was used as the solvent with the ratio of 1:5 (W/V). Extraction was completed in eight hours.

Results

Inhibition zones of Neem extracts are shown in figure 1. Control sample, Neem leaf extract, Neem seed extract and Neem bark extract are marked with a, b, c and d respectively. As it is perceived from the figure Neem seed and Neem leaf extracts have great antibacterial properties against B. Subtillis and S. aureus which are gram posetive bacteria but no antibacterial activity against E. coli, a gram negative bacterium. Neem bark extract showed no antibacterial activity against any of tested bacteria. Differences between antibacterial properties of these three extracts are caused by proportion of functional groups in their structures.



(1) (2) (3)

Figure 1: Zones of inhibition of Neem seed, leaf and bark extracts against: (1) S. aureus, (2) B. Subtillis and (3) E. Coli

By comparison of inhibition zone of Neem seed and leaf extracts, it is indicated that both extracts show better antibacterial properties against B. Subtillis and Neem seed extract show the most antibacterial activity.

Thereafter antibacterial activity of Neem seed extract was compared with Neem seed oil using MIC method. Results of MIC studies are shown in table 1.

Table 1: MIC values of Neem seed oil and Neem seed extract

Bacteria strain	MRSA	S. epidermidis	M. luteus	P. aeruginosa	S. aureus	E. coli
Gram	+	+	+	-	+	-
Neem seed oil	0.00625	0.0125	0.025	0.025	0.025	0.05
Neem seed extract	0.00625	0.05	0.05	0.05	0.025	0.05

As it is indicated in the table both Neem seed oil and Neem seed extract have equal antibacterial activity against MRSA, S. aureus and E. coli. But Neem seed oil showed better antibacterial properties against S. epidermidis, M. luteus and P. aeruginosa. The MIC value for Neem seed oil against these three bacteria strains is one half of MIC values for Neem seed extract, meaning Neem seed oil inhibits the growth of this bacteria in lower concentration. Because of high hydrophilic nature of Neem seed oil, its compounds could permeate through bacteria cell membrane. So ions and other contents in bacteria cells would leak out. This would affect the viability of bacteria and as a result causes the death of bacteria. So in general antibacterial properties of Neem seed oil is higher than antibacterial properties of ethanolic extract of Neem seed.

In conclusion Neem seed oil showed better antibacterial properties against different kinds of bacteria strains in comparison to ethanolic extracts of Neem seed. So Neem seed oil could be modified to forms that could be used as an antibacterial agent for finishing of fabrics in textile industry.

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P-27. ASYMMETRIC SYNTHESIS OF NEW ENANTIOMERICALLY ENRICHED α-AMINO ACIDS CONTAINING SUBSTITUTED THIADIAZOLE SUBSTITUENTS IN THE SIDE CHAIN OF RADICAL

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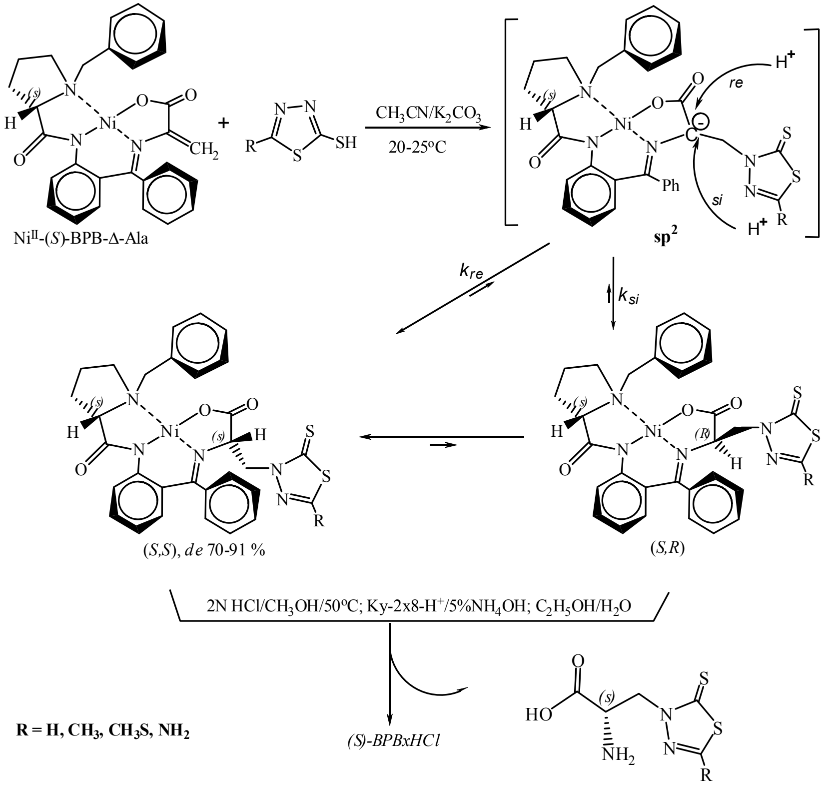
During recent years there has been intense investigation of different classes of thiadiazole compounds, many of which were found to be pharmacologically active. Substituted thiadiazole derivatives exhibit different biological activities. In particular there were found to have effective anti-inflammatory, analgesic, antibacterial, antihypertensive, antidepressant, anxiolytic, anticonvulsant actions [1-3].

Our work is devoted to the development of efficient methods for biomimetic asymmetric synthesis of new enantiomerically enriched non-protein *(S)*-α-amino acids containing substituted thiadiazole substituents in the side chain of radical with the use of square-planar Ni^{II} complexes of Schiff's bases of dehydroalanine with chiral auxiliaries *((S)*- BPB) as model systems of pyridoxalphosphate-dependent enzymes.

As a result, effective methods (*de* 70-91%) for asymmetric synthesis of new heterocyclic substituted nonprotein *(S)*- α-amino acids have been developed, particularly alanine analogs containing thiadiazole substituents in the side chains were synthesized (*ee* > 97%).



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The work has been carried out in the frame ofNational Foundation of Science and Advanced Technologies, Youth Foundation of Armenia (2013 Young Scientists Support Program (YSSP-13-40)). Also the work was realized partly by a research grant from the Armenian National Science and Education Fund (ANSEF) (chemorg-3477).

P-28. NOVEL SULFUR-CONTAINING DERIVATIVES OF BIS-1,2,4-TRIAZOLE: SYNTHESIS AND TRANSFORMATION

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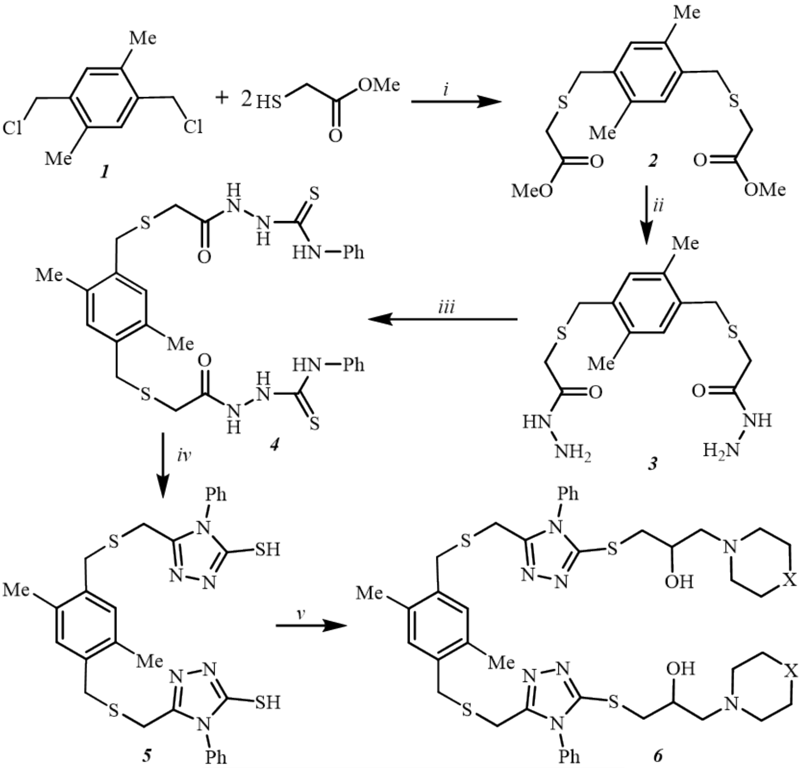
One of the most interesting classes of organic compounds are nitrogen- and oxygen-containing heterocycles having a wide range of practical applications. They are used as biologically active substances - drugs, pesticides, plant growth stimulants, and in various branches of engineering - optoelectronics, as anticorrosion agents, dyes, etc. The aim of our work is the synthesis of molecules having in their composition analogous functional groups in the two fold amount. In particular, 1,2,4-triazole ring is part of various various biologically active substances with anticonvulsant, antifungal, anticancer, anti inflammatory and antibacterial activities. In this study, 1,2,4-triazole derivatives based on 2,5-bis-(chloromethyl)-p-xylene were synthesized. The synthetic route of 2,5-bis-(((4-phenyl-3-(3-(N,N-di-substituted)amino-2-hydroxypropylthio)-4*H*-1,2,4-triazole-5-yl)-methylthio)-methyl)-p-xylenes is shown in the scheme.

The key compound *5* was prepared in four steps. Interaction 2,5-bis-(chloromethyl)-p-xylene with methyl thioglycolate in methanol in the presence sodium methylate obtained ester *2*. The hydrazide *3* was obtained by reaction of the ester *2* with 85% hydrazine monohydrate in ethanol. The reaction of hydrazide *3* with phenyl isothiocyanate produced thiosemicarbazide *4* that then cyclised intermolecularly in alkaline medium to transform into the corresponding key compound *5*. It was found that the cyclization should be carried out in aqueous KOH (10%). The reaction was completed quickly and provided high yield of the desired product.



X = O(*6a*), NMe(*6b*), $(CH_2)_n$ n = 0(*6c*), 1(*6d*), 2(*6e*)

Scheme. Synthesis of derivatives of bis-1,2,4-triazole. Reagents and conditions: (*i*) MeONa, MeOH, reflux 4 h; (*ii*) N_2H_4(aq), EtOH, 25°C 1 h and reflux 3 h; (*iii*) PhNCS, EtOH, 25°C 1 h and reflux 2h; (*iv*) step1: KOH, H_2O, 25°C 0.5 h and reflux 5 h, step2: HCl(aq) before pH ~ 4; (*v*) N-(oxiran-2-yl-methyl)amine, DMF/EtOH - 1:1, 25°C 1 h and reflux 5 h.

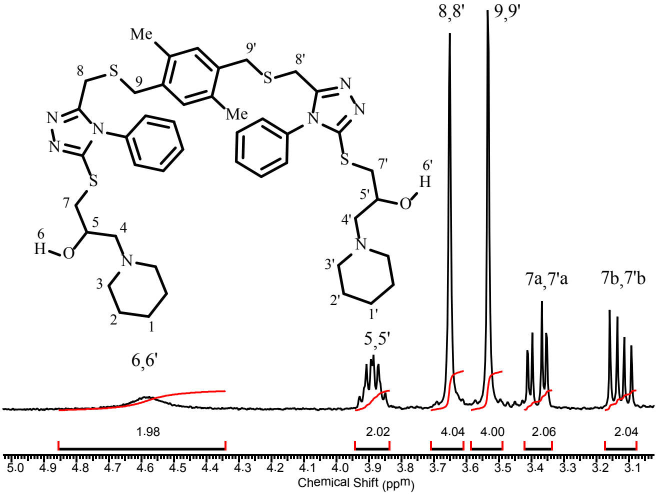


Figure. Partial spectra ^{1}H NMR of compound ***6d***(300 MHz,*MeOH*-d_6)

By condensation of key compound ***5*** with N-(oxiran-2-ylmethyl)amines [1-4] (reactant ratio is 1:2.1) in EtOH/DMF compounds ***6*** has been obtained as a mixture of diastereomers, but the ^{1}H and ^{13}C NMR spectra contain a single set of signals probably due to the remoteness of the asymmetric sites (Figure).

It should be noted that the disclosure of thiolysis oxide ring occurs Krasuskii rule, proof of which is the signal of CH groups in the range of 3.80-4.20 ppm in the ^{1}H NMR spectrum of compound ***6***.

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P-29. NOVEL 2-SUBSTITUTED-4-BUTANOLIDE DERIVATIVES AND THEIR SYNTHESIS

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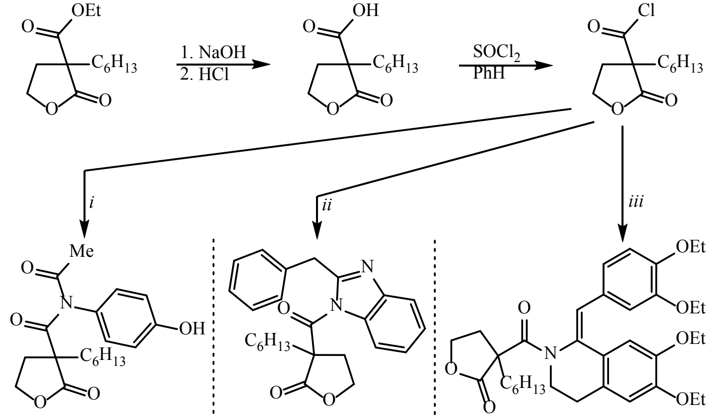
Drugs that contain a lactone ring moiety, such as Verospiron® (spironolactone) [1] and many others, have many diverse applications in medicine. In addition, there are a large number of analgesic and spasmolytic drugs that are not only important in chronic therapy, but are also important in acute conditions where drugs such as Tylenol® (acetaminophen), bendazol, No-spa® (drotaverine), and others are effective.

Lactone-ring integration into the molecular structure of drugs is a subject that is not well-studied [2]; however, research into this area can potentially yield new bioactive molecules that could result in the discovery of novel drugs.

Our objectives were to carry out the synthesis of new lactone-ring containing derivatives that contain an known bioactive (drug) moiety. In this study, we have synthesized 2-hexyl-2-carboxyl-4-butanolide, from which we then produced an acyl chloride intermediate that was ideal for coupling with the amine groups of acetaminophen, bendazol, and drotaverine.



i - 2eq. acetaminphen, PhH, 75°, 3h; ii - 2eq. bendazol, K_2CO_3, PhH, 75°, 4h; iii - 2eq. drotaverine, K_2CO_3, PhH, 75°, 3h

We have demonstrated that the reaction produced high yields of the respective lactone-drug derivatives, i.e., lactone-acetaminophen, lactone-bendazol, and lactone-drotaverine, which are complex molecules. The introduction of the lactone-ring in the structures of the drugs used in this study can lead to practical and theoretical applications for these novel derivatives.

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P-30. SYNTHESIS OF NEW HETARYL SUBSTITUTED QUINOLINES ON THE BASE OF BENZ-SUBSTITUTED 3-(BUTAN-3-ONE)QUINOLINES

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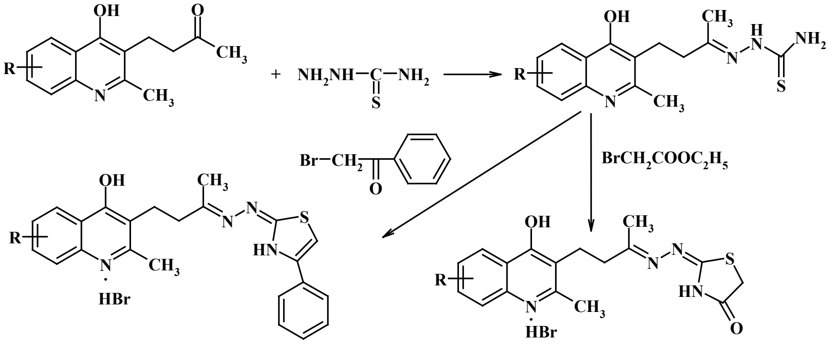
In recent years, thiazolidinones and their derivatives have become among the most extensively investigated compounds. They constitute an important group of heterocyclic, displaying a broad spectrum of biological activities, including anticancer [1], anti-inflammatory [1], anticonvulsant [2] and anti HIV [3,4].

In this work, new class of structurally novel 4-thiazolidine derivatives were synthesized with high yields on the base of previously obtained benz-substituted 2-methyl-4-hydroxy-3-(butan-3-one)quinolines [5,6] by incorporation of quinoline and thiazolidine nuclei. Firstly, for the synthesis of the target hetaryl substituted quinolines, corresponding thiosemicarbazones have been synthesized [7]. Taking into account the functionality of obtained thiosemicarbazones, the interaction with some electrophiles - in particular with bromoacetophenone and with ethyl bromo acetate, were carried out by refluxing of former compounds in ratio of 1:1 in presence of sodium acetate in ethanol medium. As a result, corresponding heterocyclic compounds were obtained.



R = H, 6(8)CH$_3$, 6(8)OCH$_3$, 6-OC$_2$H$_5$, 6-Br

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P-31. SYNTHESIS OF (2-METHYLQUINOLIN-4-YLTHIO)GLYCOLIC ACID AND ITS DERIVATIVES

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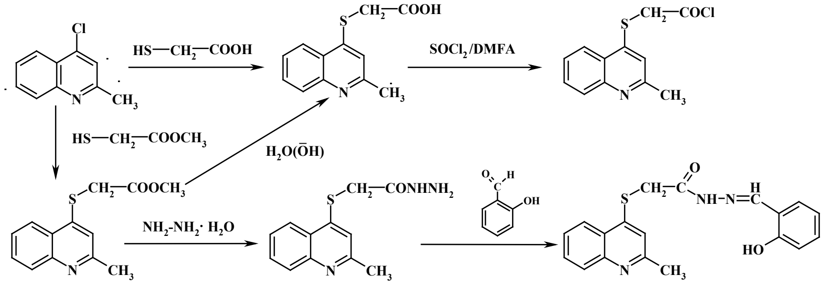
Quinoline and its derivatives have always attracted both synthetic and biological chemists because of its diverse chemical and pharmacological properties [1-4]. Moreover, the quinoline ring system occurs in various natural products [5], especially in alkaloids and is often used for the design of many synthetic compounds with diverse pharmacological properties. There are number of natural products of quinoline skeleton used as a medicine or employed as lead molecule for the development new and potent molecules [6]. From this viewpoint, especially chloride and hydrazide of quinolyl substituted carboxylic acids are of great interest [7].

In this work the interaction the substitution of 2-methyl-4-chloroquinolines with thioglycolic acid and methyl thioglycolate nucleophyls has been studied. Reaction was carried out with ratio of quinoline - nucleophyl equal to 1:1 at room temperature in acetone and affords in high yields the corresponding (2-methylquinolin-4-ylthio)glycolic acid and methyl (2-methylquinolin-4-ylthio)glycolate.

Scheme



Obtained quinolylsubstituted thioglycolic acid and its methyl esther then interacted with thionyl chloride in the presence of dimethylformamide in waterless benzene medium and with hydrazine hydrate, correspondingly. 2-Methylquinolin-4-ylthio)glycolic chloride and hydrazide of corresponding acid were formed as a result of the reactions. On the basis of hydrazide the appropriate Schiff base was synthesizeds (scheme).

Alkaline hydrolysis of the synthesized quinolyl substituted methyl thioglycolate leads to the formation of corresponding thioglycolic acids in quantitative yields.

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P-32. SYNTHESIS AND X-RAY INVESTIGATION OF SOME PYRIDO [2,3-d] PYRIMIDINES

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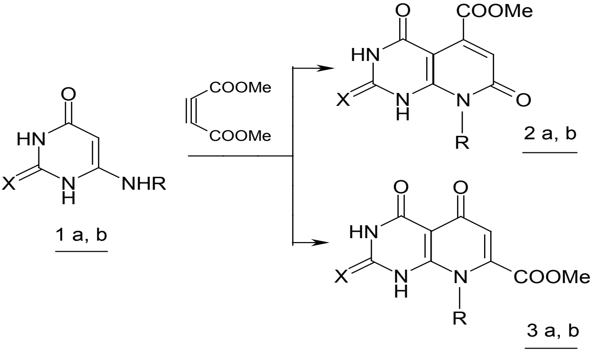
The present investigation of pyrido[2,3-d]pyrimidines was undertaken in connection with our prior studics of variouspyrimidines and condensed pyrimidine systems as antitumour and antiviral agents [1-3]. An this paper we studyed the reaction of substituted 6-aminouracils with dimethyl acetilendicarboxylate prompted to synthesize of isomeric pyrido [2,3-d] pyrimidines (2a, b) or (3a, b).



X=NH, R=H (a); X=O, R=$(CH_2)_3$OH (b)

An the NMR^{1}H spectraof the synthesized isomeric compounds [2] or [3] were observed signals confirming the pyrido [2,3-d] pyrimidines structures , however, based on them impossible accurately determine the position of a methoxycarbonyl group on the pyrimidine ring system. For the final confirmation of the obtained compounds the X-Ray diffraction analysis of compound (2b) has done.

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P-33. X-RAY DIFFRACTION STUDY OF THE METHYL 8-(3-HYDROXYPROPYL)-2,4,7-TRIOXO-1,2,3,4,7,8-HEXAHYDROPYRIDO[2,3-d] PYRIMIDINE-5-CARBOXYLATE

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For the diffraction experiment was selected purple-red monocrystal, size 0.4×0.35×0.32 mm. Diffraction measurements were performed on an Enraf-Nonius automated diffractometer CAD-4 (graphite monochromator, Mo-K_α radiation, $\theta/2\theta$-scan) at room temperature. Triclinic unit cell parameters were measured and refined with 22 reflections ($14.28<\theta<15.76$, a = 8.284(2)Å, b = 12.132(2)Å, c = 13.485(3)Å, α = 76.00(3)^o, β = 85.33(3)^o, γ = 77.06(3)^o, V = 1281.1(5)Å^3). During the diffraction experiment were measured 7926 reflections in the range $0\leq h\leq 11$, $-16\leq k\leq 17$, $-18\leq l\leq 18$, θ_{max} = 30^o. Statistical distribution of intensities in the experiment was given preference space group P-1. Array of experimental data contained 7448 symmetrically nonequivalent reflections (R_{int} = 0.011) of which 5492 observed with $I>2\sigma(I)$. The structure was solved by complex software package JANA2006 [4]. Hydrogen atoms partially located from difference Fourier maps. The hydrogen atoms of the methyl and ethyl groups were positioned geometrically and refined using riding model with C-H = 0.96Å, Uiso(H) = 1.2Ueq(C) for CH_3 groups and C-H = 0.97Å, Uiso(H) = 1.2Ueq(C) for CH_2 group. Structure was refined by full-matrix anisotropic approximation for non-hydrogen atoms and isotropic - for hydrogen atoms, the final divergence factor R = 0.0426, S = 1.96.

The full crystallographic data in CIF format available free of charge via internet at: http://www.ccdc.cam.ac.uk/products/csd/request/, deposition number: CCDC 943885.

A study of the structure of the compound revealed that in the unit cell there are two symmetrically independent molecules, and the total number of molecules in the unit cell is four. Analysis of anisotropic thermal vibrations ellipsoids and the difference Fourier electron density maps showed that the atoms C48, C49, C50 and O51 are disordered. Further analysis by splitting of atomic positions showed that occupancy disordered atoms make up the 81% and 19%.

The two type of hydrogen bonds: intramolecular (N1-H1·····O21 и N31-H31·····O51(A,B)) and intermolecular (O21-H21·····O43, O51(A,B)-H51(A,B)·····O13, N3-H3·····O37 and N33-H33·····O7) are observed as well(Table 1). Probably the both intramolecular hydrogen bonds play the same role in both independent molecules, while the roles of intermolecular hydrogen bonds differ essentially. Intermolecular hydrogen bonds N3-H3·····O37 and N33-H33·····O7 connect the independent molecules to dimmers (Fig.1). In 3D packing these dimmers arelinked into an infinite chain along [0 1 -1] with intermolecular hydrogen bonds between atoms O21-H21·····O43 and O51 (A, B)-H51 (A, B)·····O13 (Table 1, Fig. 2.).

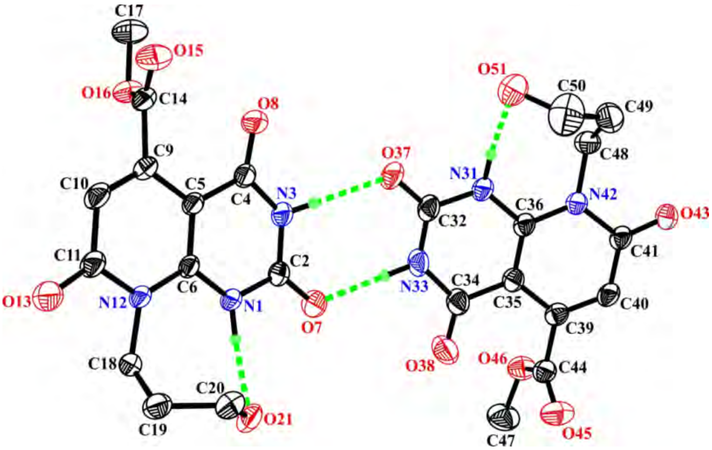

Fig.1. The dimeric pair of a compound methyl 8-(3-hydroxypropyl) -2,4,7-trioxo-1 ,2,3,4,7,8-hexahydropyrido [2,3-d] pyrimidine-5-carboxylate. Displacement ellipsoids drawn at the 50% probability level (H atoms are omitted for clarity).

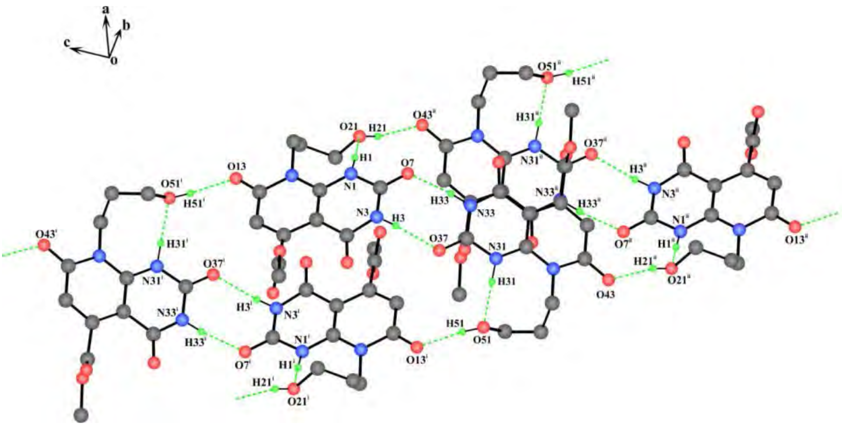

Fig. 2.Infinite chain along [0 1 -1]. Hydrogen bonds are shown by dotted lines. Symmetry codes: (i) 1-x; 1-y; 1-z, (ii) 1-x; 2-y;-z.

Refernces

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P-34. SYNTHESIS, MOLECULAR AND CRYSTALLINE STRUCTURE OF NEW 9,10- SUBSTITUTED 5-DEAZAFLAVINES

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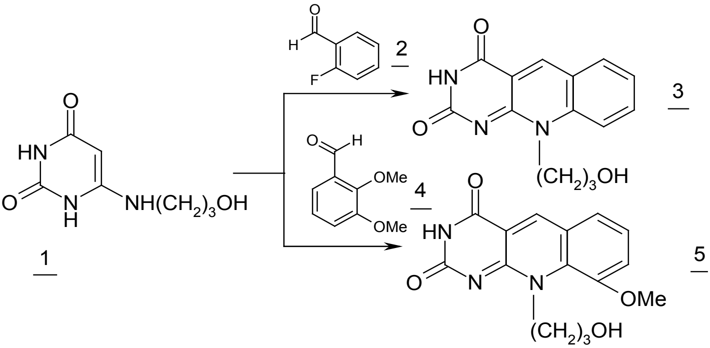
During the last years there has been considerable interest in synthesis and biological evalution of 5-deazaflavines . They have the potent broad –spectrum antitumor activities. Beside on these data and in the proposals of our research in the field of pyrimidine and its condensed system [1-3] in this work included the synthesis of some derivatives of 5-deazaflavin containing methoxy-, 3-hydroxy propyl substituents in the 9, 10- positions system (scheme 1).



For the final confirmation of the structure of the compound (5) from the standpoint of the intended mechanism of reaction studied its molecular and crystal structure by diffraction analysis.

Refernces

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P-35. X-RAY DIFFRACTION STUDY OF THE COMPOUND 10-(3-HYDROXY-PROPYL)-9-METHOXYPYRIMIDO[4,5-b]QUINOLONE-2,4(3*H*,10*H*)-DIONE

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The unit cells parameters of crystals of the compound 10-(3-hydroxypropyl)-9-methoxypyrimido[4,5-b]quinoline-2,4(3H,10H)-dione were measured on an Enraf-Nonius CAD-4 automated diffractometer at room temperature using the diffraction angles of 22 reflections. The diffraction experiment was performed on the same diffractometer using graphite monochromated Mo-K$_\alpha$ radiation, θ/2θ-scan. All calculations were performed using the crystallographic computing programs SHELXTL [4]. The initial structure model was determined by direct methods and the positional parameters of non-hydrogen atoms were refined together with anisotropic thermal parameters, the hydrogen atoms were positioned geometrically and refined using riding model. Molecular structure of compound 10-(3-hydroxypropyl)-9-methoxypyrimido[4,5-b]quinoline-2,4(3H,10H)-dione is shown in figure 1. The molecule of titled compounds contains flat tricyclic fragment, RMS deviations of atoms from the average plane does not exceed 0.053 (3)Å. The analyses of ellipsoids of anisotropic thermal vibrations and difference electron density Fourier maps showed that the atoms in hydroxypropyl group are localized in two positions. Further calculations were carried out by splitting of atomic positions of hydroxypropyl groups in two positions and the occupancies of disordered atoms were 0.642 and 0,358. In 3D packing the molecules

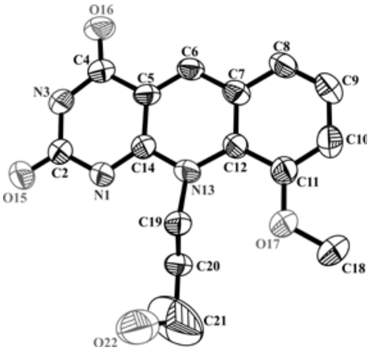

Fig.1. The molecular structure of 10-(3-hydroxypropyl)-9-methoxypyrimido[4,5-b]quinoline-2,4(3H,10H)-dione with displacement ellipsoids drawn at the 50% probability level (H atoms omitted for clarity).

of investigated compound forming dimer(fig. 2) linking via intermolecular hydrogen bond between atoms N3-H3·····O15(D-H=0.86Å,H·····A=2.03Å,D·····A=2.862Å,D-H-A=164°).

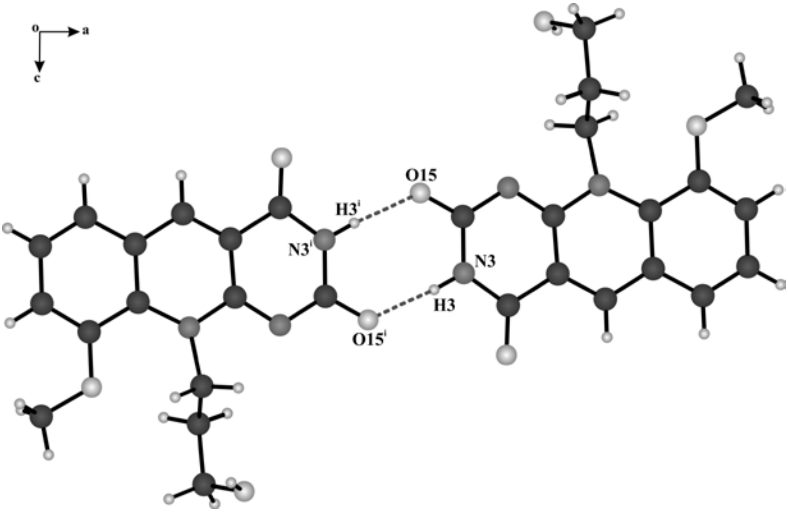

Fig.2. The dimeric pair of a compound 10-(3-hydroxypropyl)-9-methoxypyrimido[4,5-b]quinoline-2,4(3H,10H)-dione. Symmetry code: (i)=1-z; 1-y; 2-z.

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P-36. THE NEW DERIVATIVES OF CONDENSING THIAZOLO-TRIAZOLES

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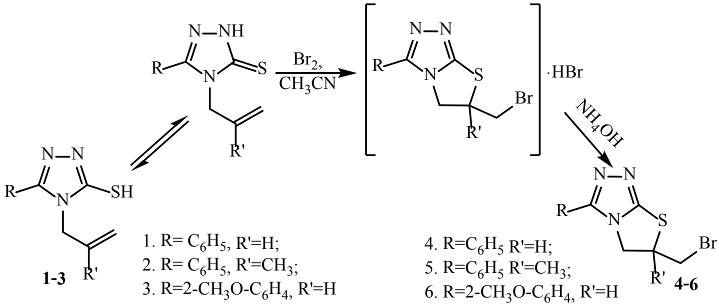
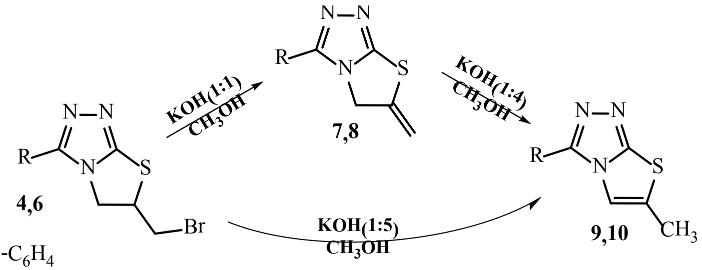
It is known that some of synthetic analogues of heterocyclic compounds widespread in animal and plant world, have shown wide range of bioactivity. In this series of particular interest are derivatives of 1,2,4-triazoles, which mainly are of synthetic origin. Some members of this class exhibit hypotensive effect [1] exhibit antitumor [2], fungicidal [3], antibacterial [4] and other types of activity. We have previously shown that the mercapto derivatives of 1,2,4-triazoles exhibit antioxidant and anti radiation activity and have a stabilizing effect on the membrane of red blood cells [5].Taking into account the fact that hetero combined 1,2,4-triazoles are the drugs acting mainly on the central nervous system (Brotizolam, Triazolam) [6] and thiazoles containing systems are used for treatment of serious infection diseases (Anabactyl, Azlin, Picillin) we design the compounds wherein the substituted thiazole ring is condensing with triazoles. To achieve our objectives accomplished bromination of 4-allyl(methallyl)-3-substituted-5-mercapto-1 ,2,4-triazole **1,2,3** and found that the resulting formed 6-brommethyl-(6-methyl)-3-substituted-5,6-dihydrothiazolo[2,3-c]-1,2,4-triazoles **4,5,6**.

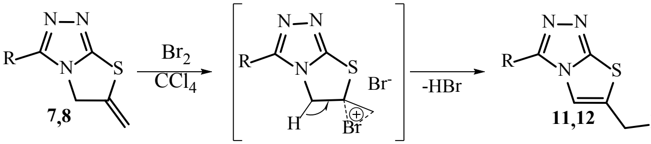


It is shown that the dehydrobromination of compounds **4,6** with a 5% methanolic potassium hydroxide solution, with different ratio of reagents, leads to various derivatives of condensing triazoles.



4. R=C_6H_5;
6. R=2-CH_3O-C_6H_4

In order to obtain new derivatives of heteryl combination 1,2,4-triazoles, which containing active bromine atom in allyl group we intended to brominates the compounds **7,8**. It has been shown that as a result of accession and simultaneous dehydrobromination obtained 6-bromomethyl-3-substituted thiazolo [2,3-c] -1,2,4-triazoles **11,12**, which can be used as starting compounds in a fine organic synthesis, to produce in particular an optically active no protein α-amino acids.



11. R=C_6H_5;
12. R=2-CH_3O-C_6H_4

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P-37. EFFECT OF STRUCTURE PECULIARITIES UPON CONDUCTIVITY VALUE AND NATURE OF SCHEELITE-TYPE TUNGSTATES $Me^{2+}[WO_4]$ (Me=AEM) AND THE SAME TYPE BUT DEFECT TUNGSTATES WITH STRUCTURE VACANCIES $Ln_{2/3}[V_{Ln}^{S}]_{1/3}WO_4$

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Tungstates $Ln_2(WO_4)_3$ [Ln = La – Dy] are crystallize in a structure type of so-called "defect" scheelite– 1/3 of positions in La sublattice are vacant: $Ln_{2/3}[V_{Ln}^{S}]_{1/3}WO_4$. These materials possesses perspective optic and laser properties. Charge transfer in this type compounds is not studied. At low T the V_{Ln}, are ordered, but at heating the structure rearranging take place to its statistical location. For majority of this type tungstates this change of structure is not known exactly – different techniques, HTXRD including, shows different T temperature, depending on purity and method of samples production. The single phase of $Ln_2(WO_4)_3$ (Ln = La, Sm) ceramic was checked by XRD. The relative density of samples after synthesis (500…1000°C) and further sintering was ≈ 0,85. σ_{total} measurements were performed using alternative current (1 kHz) and by impedance technique - $\sigma_{ac.}$ Conductivity on constant current – σ_{dc} was determined too. The dependences σ(T) are shown on fig. 1. By EMF technique (air/O_2) the sum of ionic transport numbers was shown - for $La_2(WO_4)_3$ and $Sm_2(WO_4)_3$ – $\Sigma t_{ion} \approx 1$, that means that σ_{total} is close to pure ionic. It was determined that σ_{ac} does not depend from a_{O2} in the range $a_{O2} = 0…10^{-20}$,fig. 2. In the Tubandt experiments in cells (–)Pt|$Ln_2(WO_4)_3$|$Ln_2(WO_4)_3$|Pt(+) the change of section mass was neglible, what mean that WO_4^{2-} and Ln^{3+} transfer is near to zero. This conclusion is directly supported by relation $\sigma_{dc} \approx \sigma_{ac,}$ Fig. 1. Thus, the set of experimental data shows that high temperature σ of $La_2(WO_4)_3$ and $Sm_2(WO_4)_3$ is O^{2-} ionic – $\Sigma t_{ion} \approx t_{O2-} \approx 1$. In solid electrolytes $Me_2(WO_4)_3$ (Me-Sc,In,Al) the main charge carriers are complex anions WO_4^{2-}. The strong difference in conductivity nature of these phases and "defect" shelties probably connected with following: subsystem of V_{Ln}^{S} opens the channels for predominant O^{2-} transfer and simultaneously blocks transport of WO_4^{2-}.

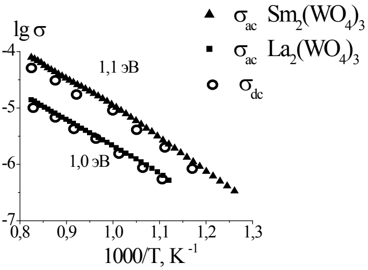

Fig. 1. The dependence $\sigma_{ac}(T)$ for $Ln_2(WO_4)_3$.

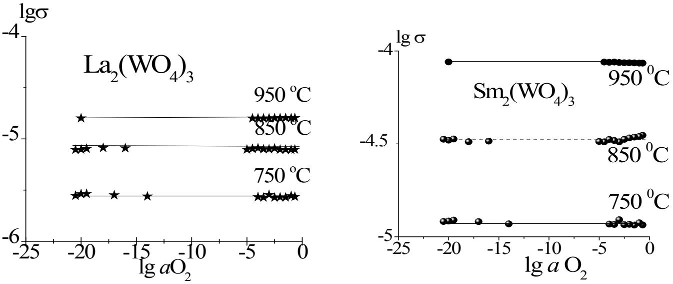

Fig. 2. The dependences σ_{ac} from aO_2.

This work was supported by RFBR 13-03-96114_ural, 14-03-00804_a and UrFU Development Program.

P-38. SYNTHESIS OF BICYCLIC SULFOPROPIONIC ACIDS CONTAINING OXAZOLE

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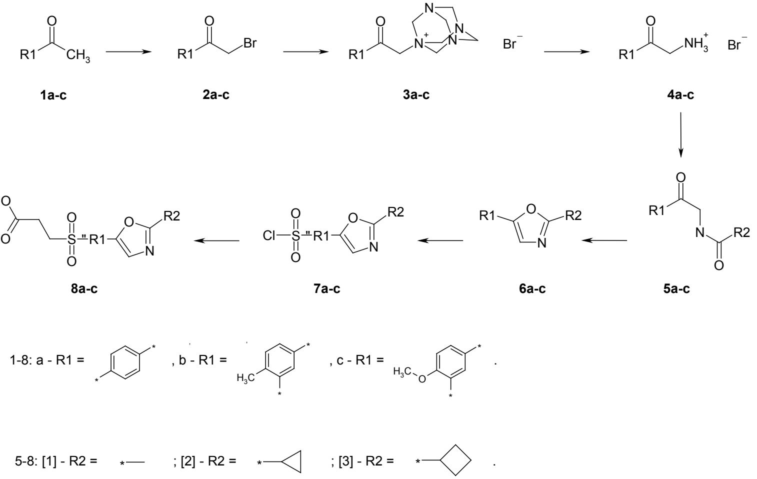
Structural fragments of sulfopropionic acids and their derivatives are promising pharmacophores and are of interest to medicinal chemistry in the search for new biologically active compounds. We developed the synthesis of bicyclic sulfopropionic acids containing oxazole.

Scheme 1



Compounds **4** were obtained by conducting a series of sequential reactions: bromination of acetophenones**1**, formation of the quaternary salt **3** with hexamine and acid hydrolysis (Scheme 1). After acylation of the compounds **4** with carboxylic acid chlorides in the presence of pyridine, amides **5** were obtained. Heating compounds **5**in excess of phosphorus oxychloride led to intramolecularcyclocondensation and obtaining oxazoles**6**.

Sulfochlorination of the compounds 6 was conducted in a tenfold excess of chlorosulfonic acid and in an equivalent amount of thionyl chloride. Substitution proceeded in the *p*-position of the compound **7a** and *m*-position of the compounds **7b,c** with respect to the oxazole. Position of the sulfonic group was determined by NMR - spectroscopy.

Next, chlorosulfonic group was restored by the sodium sulfite in the highly alkaline medium to the corresponding sulfinic acid. Nucleophilic addition took place on the activated double bond of acrylic acid to form sulfopropionic acids **8**.

The resulting acids **8** are of interest as building block for the synthesis of carboxamide derivatives and for search compounds with high biological activity.

P-39. NUCLEOPHILIC SUBSTITUTION IN A SERIES DERIVATIVES OF AMINO(HYDRAZINE)-1,2,4-TRIAZINES

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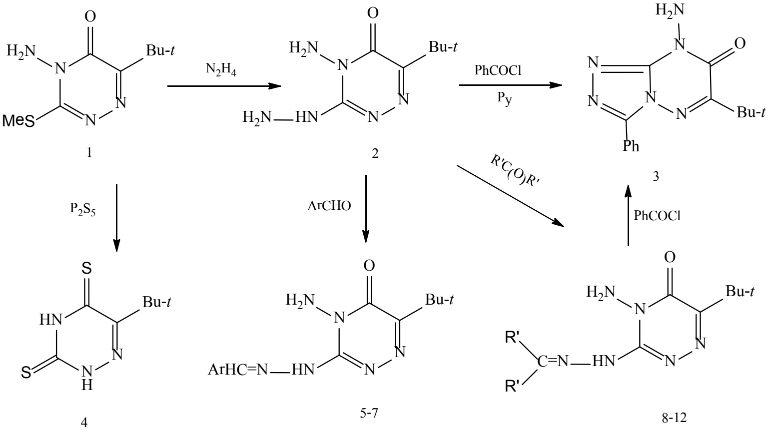
Nitrogen-containing heterocyclic compounds are compounds that lately attract the attention of organic chemists. Among them the compounds of the series 1,2,4-triazin are investigated quite intensively, due to their presence in a number of biologically active compounds, which have found practical application: pesticides (metamitron, metribuzin), pharmacological agents (ceftriaxone, lamotrigine, triazavirin).

Hydrazinolysis of 4-amino-6-*tert*-butyl-3-methylmercapto-5-oxo-1,2,4-triazine (1) was carried out with 100% hydrazine in a polar solvent at boiling and isolated 4-amino-6-*tert*-butyl-3-hydrazino-5-oxo-1,2,4-triazine (2). Boiling compound 2 with benzoyl chloride in a polar solvent, there is a hydrazine group by acylation, followed by intramolecular cyclization at the nitrogen atom at the 2-position of heterocycle with allocation of 1-amino-3-*tret*-butyl-2-oxo-5-phenyl[1,2,4]triazolo[4,5-*b*][1,2,4]triazine (3). Mass spectrum of the compound 3 confirms its structure: [M +] = 285.



When boiling the compound (1) with phosphorus pentasulfide in pyridine for 4 hours we isolated yellow crystalline solid (4). According to data elemental analysis, IR, ^{1}H NMR, mass spectrometry, instead of the expected 4-amino-6-*tert*-butyl-3,5-ditioxo-2*H*,4*H*-1,2,4-triazine we obtained 6-*tert*-butyl-3,5-ditioxo-2*H*,4*H*-1,2,4-triazine (4). The IR spectrum of the compound (4) shows absorption bands at 1230 cm^{-1} and 1125 cm^{-1} attributed to the stretching vibrations of the group C=S, which are absent in the spectrum of the starting compound (1).

The heating of the hydrazino-1,2,4-triazine (2) with ketones in dioxane results in the isolation of N-(R,R^1-methylidene)-N^1-(4-amino-6-*tret*-butyl-5-oxo-1,2,4-triazine-3-yl) hydrazines (8-12), which form the compound (3) under reflux in pyridine with benzoyl chloride. The boiling of the compound 2 with aldehydes leads to the aldimine (5-7).

The structure of compounds was determined on the basis of their elemental compositions and IR, NMR, and mass spectra.

P-40. THE NEW METHOD FOR THE SYNTHESIS OF MONTELUKAST USING ENZYMATIC SYNTHESIS

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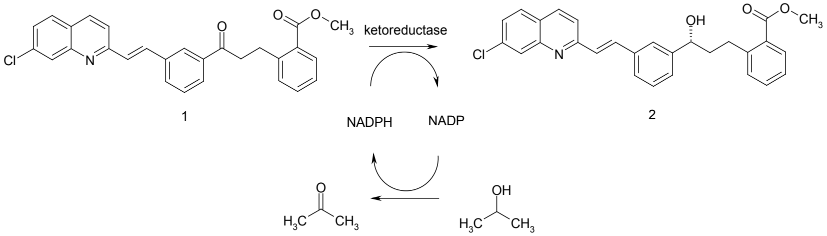
Montelukast - active pharmaceutical ingredient, which has antagonistic activity against a leukotriene receptor, is used in drugs for the treatment of bronchial asthma and allergic rhinitis[1]. It should be noted that a specific biological activity has only the R-form of the molecule. In an effort to develop an effective technology industrial production of the montelukast, we conducted a study on the synthesis of the key intermediate for the synthesis of the montelukast - the compound 2. S-form of the compound 2 is used to produce R-form of the montelukast as during the further multistage synthesis process the inversion of the stereocenter takes place as the result of a bimolecular nucleophilic substitution reaction[2]. The literature describes the chiral synthesis of the key intermediate 2 in S-form using the chemical reducing agent (-)-DIP chloride[3]. The disadvantage of using DIP chloride is its corrosive activity, high moisture sensitivity, complexity of the application and the large costs associated with losses and disposal.



We have developed the method for the synthesis of the compound 2 by enantioselective reduction of the ketone 1 using ketoreductase enzyme and co-enzyme NADP. As the co-enzyme regeneration system using isopropanol and formed in the process acetone was removed from the reactor by bubbling of the nitrogen. The optimized keto reductase by Chinese company EnzymeWorks was used for the reaction, which is active for biotransformation of bulky ketones. It is also known to use the keto reduktase CDX-026 by Codexis for this process, but its price is more than 10 times greater than that used by us[4]. The solvent used was a mixture of isopropanol and toluene, water and as buffer the mixture tris-(hydroxymethyl)-aminomethane and HCl. Advantages of developed enzymatic process are the high value of enantiomeric excess of the product 2 and the ease of isolation of the product as a precipitate due to degcrease solubility of the compound 2 in comparison to the compound 1.

This work performed under the Contract number 02.G 25.31.0019 on February 12, 2013 between company "R-Pharm" and the Ministry of Education and Science of the Russian Federation about conditions of granting and use of subsidies for the implementation of a comprehensive project to high-tech production, performed with the participation of the Federal state budget institution of higher professional education "Yaroslavl State Pedagogical University named after K.D. Ushinsky" and Contract number 121119 on November 19, 2012 between "R-Pharm" and "Yaroslavl State Pedagogical University named after K.D. Ushinsky" "Development of innovative technologies for import substituting of active pharmaceutical ingredients based on biological methods of catalysis and enzymatic synthesis".

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P-41. ADSORPTION OF FLUBENDIAMIDE IN TWO INDIAN SOILS VARYING IN PHYSICOCHEMICAL PROPERTIES

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Present study reports adsorption-desorption behavior of flubendiamide in two different Indian red soil and black soil varying in their physico-chemical properties. The soil sorption coefficient *K* and the soil organic carbon normalized sorption coefficient *K*oc are the two basic parameters used for describing adsorption-desorption of the insecticide. The adsorption data for the insecticide fitted well the Freundlich equation. Adsorption and desorption rates were calculated from kinetic studies. These values varied depending on the soil type and physicochemical properties. Freundlich adsorption equation described that the calculated K values from red soil was 2.13 and from black soil was 1.07. The distribution coefficient based on clay content *K*c values were 3.04 from red soil and 1.78 from black soil. The *K*oc values were 560.5 in red soil and 345.2 in black soil. Organic matter also played a significant role in adsorption and desorption of flubendiamide. Adsorption was lower at acidic pH and gradually increased towards alkaline pH, except in the range of pH 6-8. The study indicated that absorption of the insecticide was higher in red soil than black soil, which may be attributed due to different physico-chemical properties and thus contributing a significant role in flubendiamide adsorption and desorption.

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P-42. SYNTHESIS OF FLUORESCEIN-5-ISOTIOCYANATE THE UNIQUE NANOMARKER FOR LABELED IMMUNOGLOBULINES TO CREATE BIOSENSORS

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Currently, fluorescein and other xanthene-dyes are increasingly used both in traditional and in new areas of chemistry and neighboring sciences.In particular, the fluorescein dye using in sensor devices, monolayers and Langmuir-Blodgett films, in an immunoassay comprising microarray to produce molecular beacons in NanoChemistry in Supramolecular Chemistry. New prospects opening the using of photophysical and photochemical properties of the previously little studied fluorescein derivatives and analogs [1].

There are a lot of new work on the application of fluorescein dyes in biochemistry including immunological studies.

Infectious disease outbreak, the emergence of new types of infectious diseases, and recently returned so-called "old" infections determine troubled epidemic situation in the world.Genetic variability of circulating strains, nosocomial infections, bacteriocarrier, difficulties in application and immunobiological preparations required strengthening in the field of immunization and immunotherapy. Inadequate attention to these issues will inevitably lead to the rise of infectious diseases. For rapid diagnosis of viral infections applied Immunofluorescence staining.

Fluorescein-labeled immunoglobulins are widely used dye to the high quantum yields and resistance to photobleaching. Brightfluorescence ofthe conjugatesinthe region of maximum sensitivity of the human eye, color fluorescence contrast from autofluorescence of microorganisms and tissues, as well as the ability to dissolve in weakly alkaline solutions put forward fluorestseni-5-isothiocyanate (FITC) in the first place among the known protein labels. FITC properties allowed to use in a number of branches of medical science as a diagnostic tool: in immunology - evaluation of cellular cytotoxicity, in oncology-allows observation of patients at risk; in cytology - assessment activity of intracellular enzymes, in hematology - diagnosis of acute leukemia; and for identify a number of particularly dangerous infections.

In this regard, the aim of this work is the synthesis of fluorescein-5-isothiocyanate –the almost important fluorescent nanomarker.We developed a unique nontiofosgenic method, according to the scheme 1.

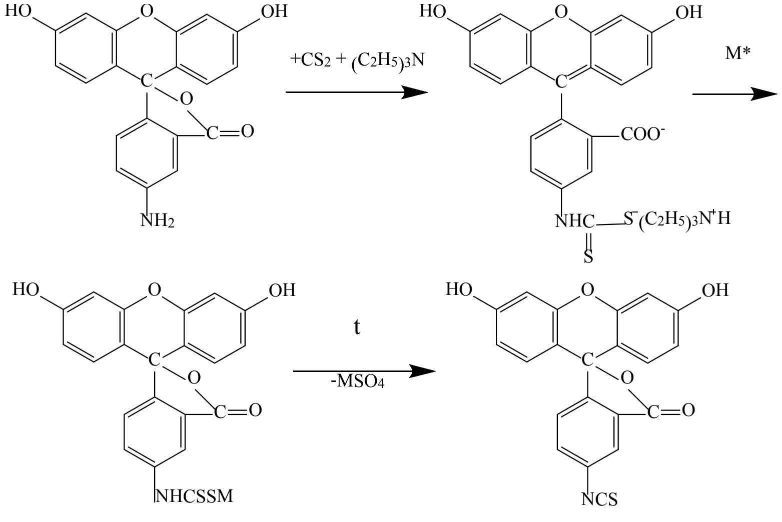
Studies had shown the best of our suggested methods of obtaining a neutral dye is a thermal decomposition reaction of salts of fluorescein-5-dithiocarbamic acid with heavy metals.

In the literature published many works, which emphasize the importance of using pure samples possible for FITC fluorescent label immunoglobulins [2-4].

At the same time, there are no reports of purification methods FITC, except fractional precipitation from acetone solutions of its petroleum ether [5,6].

However, this is cleaning an ineffective method could not always apply, because sometimes cleaning this method resulted in a decrease in the base material.

We succeeded for the first time show that FITC can be cleaned by various methods, such as reprecipitation from anhydrous solvents,recrystallization, but the most effective of the techniques used is chromatographed on silica gel using anhydrous solvents.Due to such a method was obtained with FITC main substance content of 99.8%.



Scheme 1.Synthesis of fluorescein-5-isothiocyanate.M- Pb(II), Cu(II), Co(II), Ni(II), Fe(II), Zn(II), Cd(II), Ag(I)*

So, the improved method of the synthesis of chromatographically pure fluoresciein-5-isothiocyanate nanomarkerfor labeled immunoglobulins allows to create high-quality biosensors was described.

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P-43. MEASUREMENT OF THE THERMAL STABILITY OF ENERGETIC COMPOUNDS AND COMPOSITIONS AT MAXIMAL LEVEL OF THE CONTAINER FILLING

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Oneof the most significant parameters applicable to high-energy components and compositions (gunpowder, propellants, explosives, pyrotechnics, etc) is a high level of their thermal stability. Otherwise even at relatively low decomposition degree (considerably lower than 0.1%) fundamental changes in thematerialstructure (cracking,even destruction, until thermal explosion) may occur. There are many methods for thermal stability of energetic condensed materials measurement, all of them are based on the decomposition rates determination as function of the temperature, the activation energy calculation and then one estimates the decomposition level under given temperature and the storage time. Usually the term "thermal stability" means ba property of an individual compound, while the term "compatibility" means the thermal stability of a mixture of a few compounds, when the reason of the decomposition is any interactions between components. The usage ofonlyone of the possiblemethods of investigation (volumometry, that is the total gas release measurement, analyses of decomposition products, heat release etc) can not give the appropriate data (e.g. the energetic material may decompose with no gas release or on the other hand with no heat release, or with an negligible heat release etc.). Besides, the condition of the investigation plays a great role too.

It is important that the degree of filling the sample under investigation into the reaction volume (m/V (m- the sample mass, V-the reaction vessel volume), where gaseous decomposition products are stored, would adequate to the values of m/V at which the real energetic material would be really stored. Otherwise the forecast will be wrong, e.g. if one of gaseous decomposition products is a gas that catalyses the decomposition (e.g. NO_2), the m/v decrease during the experiment increases drastically the seaming stability. If there is an equilibrium like that in onium salts (e.g. $NH_4X \leftrightarrow NH_3 + HX$) the m/v decrease decreases the seaming stability, and the salt under investigation seems less stable as it will be at real storage conditions at higher m/V values.

As mostly energetic materials are stored at high filling values, often close to m/V=ρ, where ρ - the sample density, one should test the samples in conditions when m/V→ρ , that is when the gas volume around the sample seeks to zero. Sure this method can investigate thermal stability level only at very low decomposition degree, but really namelythis is whatis required because compositions with the decomposition degree higher than 1-2% during the storage time are not interesting in reality.

The investigation is devoted to developing a method of determining the depth of the decomposition of energetic materials and compositions at a temperature 20-80 ˚ C at m/V values close to the density. A test procedure of samples being polymerized elastic integral composites (individual compounds or their mixtures) as well as being in in powder form is developed. If one tests powders the m/V values is about the bulk density. The procedure allows to determine the amount of gaseous decomposition products such as nitrogen, hydrogen, carbon monoxide, carbon dioxide, nitrous oxide, nitrogen monoxide) during the exposure at the predetermined temperature and time. A special device was developed (Fig.) for this task resolution. A steel cup (2) is completely filled with the test sample, this cut is placed into a special nest (1) that ensures the its vertical stability. Then one evacuates all the device through vacuum valve (5) at opened bellow valve (7-8), then one closes the bellow valve (7-8) for prevent gaseous decomposition products to leave the cup (2).

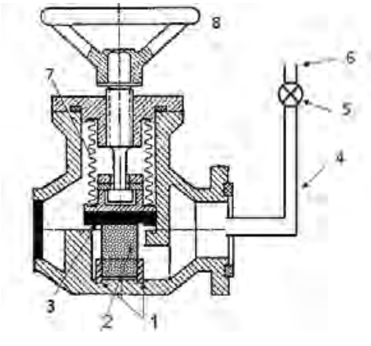

***Figure**. Principal schema of the device: 1 - the nest for the cup; 2 -a steel cap with the sample; 3 - packing plate. 4- thin branch tube; 5 - vacuum valve; 6 - exit to vacuum or an outside source of gas; 7 - bellow; 8- check valve*

Then the device is exposed at the given temperature and the predicted time. After this exposition the device is taken out from the thermostat, one evacuates all the device through vacuum valve (5) again (but at still closed bellow valve (9)), then one closes vacuum valve (5) and open bellow valve (7-8) allowing the exit of the gaseous decomposition products inside the cup to fill all the device volume. If the sample under investigation is a powder one may extract gases to chromatographic analysis just in a few minutes, bit if the sample is a polymerized elastic integral material it is necessary to keep the sample in the device up to four days - it was showed experimentally that in this case more than 90% of gaseous decomposition products leave the sample.

Appropriate materials for packing plates, type of bellow valve, allowing to keep the decomposition products inside the cup at pressure up to 50 atm, preventing the penetration of the outward air into the device have been found.

P-44. SYNTHESIS AND TOXICACTION OF DI-NA-SALT OF 2-(PYRIDINE-4-ILTIO)SUCCINIC ACID

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Introduction

Pyridine chemistry for the last decades grew into one of the widest division of chemistry of heterocyclic substances. The heterocyclic system of pyridine is basis of many medicinal facilities that have a wide spectrum of pharmacological action. Substances, that show an antioxidant, antimicrobial, fungicide and other types of activity, were found among them. The purposeful organic synthesis is the most perspective way to develop the pyridine chemistry. The research of biologically active substances in the rows of insufficiently known S-pyridinederivates is important and has the theoretical and practical value [1].

Succinic acid(butanediovic acid, ethane-1,2-dicarbonic acid) that is an universal energy source in an organism causes an interest the last time. This natural substance participates in the cycle of Кrebs and is present in all organisms. The physiology action of this acid on an organism is many-sided. Such effects of succinic acid are today known: organstimulating, cytoprotective, oncopreventive, immunemodulating, antistress, antiinflammatory, detoxication, vasoprotective,neuromodulating, cardioprotective [2].

Results of researches of the last years show that combination of nitrogen-containing heterocycle and mercaptocarbonic acids influence on strengthening of biological action or appearance of new effects, that conditioned, in particular, by influence on the processes of free-radical oxidation in tissues. Therefore a search of new bioactive substances containing in the molecule a heterocycle and a deputy with high antioxidant properties such as succinic acid is perspective. That’s why on the basis of those studies [3] the di-Na-salt of 2-(pyridine-4-iltio)succinic acid was selected for the deep research.

Purpose of the work was a study of sharp toxicity, antibacterial activity and cytotoxicity of new synthesized substance – di-Na-salt of 2-(pyridine-4-iltio)succinic acid.

Research materials and methods

Structure of the synthesized substance is confirmed by data of PMR-, IR-spectroscopy and element analysis, and the cleanness – by the method of thin-layer chromatography (TLC).

The sharp toxicity was studied on white intact adults bisexual mouse weighing 20±3,0 g by means of Prozorovsky V.B. tabular express-method to determinate middle effective measures of influence on biological objects [4].

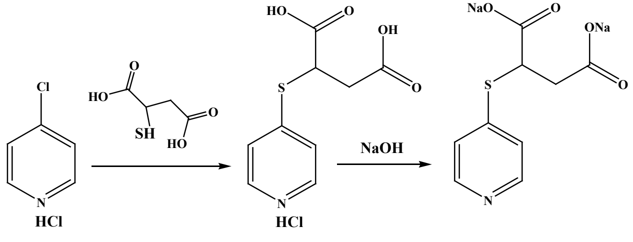
Researches of antibacterial activity of substance were conducted *in vitro* on methodology of the serial double breeding in a liquid nourishing environment (broth of Hottinger) [5]. Experiments executed on the 4 strain of bacteria, from that 2 cultures were gram-positive(*Bacillus subtilis, Staphylococcus aureus*), and other 2 – gram-negative(*Escherichia coli, Pseudomonas aeruginosa*). The estimation of results was carried out depending on intensity by oppressions of height of that or other culture of bacteria by a substance with a maximal concentration 500 mcg/ml.

The investigation of synthesized substance influence on a fission and cell growth(cytotoxicity) was done on a root test on the sprouts of *Cucumis sp*. (during experience used the cucumbers of sort "Competitor") [6]. Cytotoxicity of substance was estimated after reduction of the marked parameters in an experiment comparatively with control. Control(water) indexes are taken for a zero.

Results and discussion

Substance of di-Na-salt of 2-(pyridine-4-iltio)succinic acid was synthesized in the conditions of the extended laboratory synthesis on the following chart 1.

Chart 1



(80 %) (72 %)

Di-Na-salt of 2-(pyridine-4-iltio)succinic acid is the crystalline substance of lilac color with the temperature of melting of 238-240 ^{0}C, water and methanol soluble.

The studies of sharp toxicity proved that di-Na-salt of 2-(pyridine-4-iltio)succinic acid is more or less safe according to the classification of Sidorov at intra-abdominal introduction to the wide range of doses. Animals were put the dose 4000 mg/kg and they were alive and active through 12, 24 hours and on a 14 day. Reflex activity, breathing depth and frequency of mice was not damaged. The reception of water, meal, egestion were not changed. Weight was not changed in comparison with the control group of animals. LD_{50} of di-Na-salt of 2-(pyridine-4-iltio)succinic acidpresents 4960±66 mg/kg.

Research of antibacterial and cytotoxic action of di-Na-salt of 2-(pyridine-4-iltio)succinic acidconfirmed the absence of toxic effects. It is found out that investigated substance does not have antibacterial activity at concentrations 500 mcg/ml. Cytotoxic action of di-Na-salt of 2-(pyridine-4-iltio)succinic acid was not marked, but even for concentrations 500 mcg/ml this substance stimulates fission and cell growth of sprouts of *Cucumis sativus*.The prospect of further study will be a study of other types of biological activity of di-Na-salt of 2-(pyridine-4-iltio)succinic acid and creation new effective pharmaceutical preparations on its basis.

Conclusions

1. The preparation synthesis method of di-Na-salt of 2-(pyridine-4-iltio)succinic acid was developed, its physical and chemical properties were studied.
2. It is found out that di-Na-salt of 2-(pyridine-4-iltio)succinic acid is relatively safe at intra-abdominal introduction to the wide range of doses (her LD_{50} = 4960 mg/kg). Research of its antibacterial and cytotoxic action confirmed absence of toxic effects.
3. Methods of di-Na-salt of 2-(pyridine-4-iltio)succinic acid receipt are technologically accessible and economic, substance is untoxic and can come forward as a substance for further researches to create new effective pharmaceutical preparations on its basis.

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P-45. SYNTHESIS AND BIOLOGICAL ACTIVITY OF NEW AMINO ACID DERIVATIVES OF 9,10-ANTHRAQUINONE

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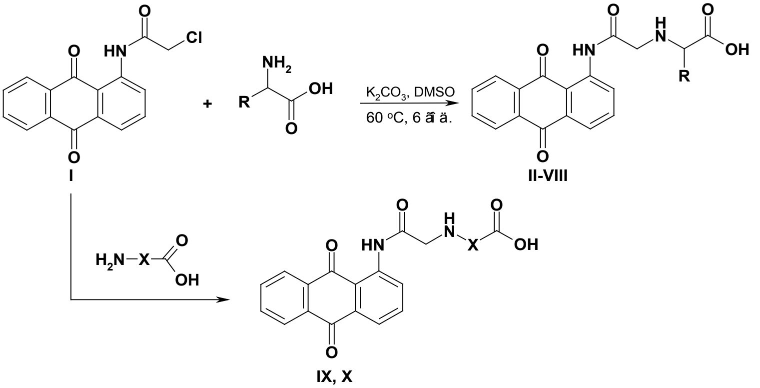
Chemistry of derivatives of 9,10-anthraquinone has long evolved in a separate section of organic chemistry. Among of these compounds are identified substances with a number of properties, including pharmacological [1, 2].In spite of the well-studied chemistry of dyes and anticancer drugs based on 9,10-anthraquinone, remain unknown other anthraquinone derivatives. Therefore, the aim of our work was synthesis and investigation of new amino acid derivatives of 2-chloro-N-(9,10-dioxo-9,10-dihydroanthracene-1-yl)acetamide **II**-**X**.



R = -H (II); $-CH_3$ (III); $-CH_2C_6H_5$ (IV); $-CH(CH_3)_2$ (V); $-CH_2CH(CH_3)_2$ (VI); $-(CH_2)_2SCH_3$ (VII); $-(CH_2)_2COOH$ (VIII)
X = $(CH_2)_2$ (IX); $(CH_2)_3$ (X)

The reaction of compound**I** [3] with anorder of amino acids was carried out in the presence of potassium bicarbonate in DMSO at heating. Targeted products **II**-**X** were isolated from the reaction mixture by fivefold water dilution, acidification with dilute hydrochloric acid and filtered.

The synthesized amino acid derivatives of 9,10-anthraquinone were tested for antimicrobial activity against strains of *Escherichia coliB-906, Staphylococcus aureus*

209-P, Mycobacterium luteum B-917, Candida tenuis VKM Y-70 and *Aspergillus niger VKM F-1119* by methods of diffusion and serial dilutions. In the studied concentrations 0.5% and 0.1% (diffusion method) compounds**II**-**X** have not shown activity against strain test culture *E. coli*. The bacterium *S. aureus* at studied concentrations proved insensitive to the action of compounds **II**, **V** and **VIII**. Others amino acid derivatives have showed a bacteriostatic effect at concentrations 0.5% to 0.1% (the diameter of inhibition zones of microorganism - 15.0-30.0 mm in 0.5% concentration of the substance and 10.0-18.0 mm at 0.1% concentration). *M. luteum* appeared not enough sensitive to the action of anthraquinone **II-X** (d = 7,0-14,3 mm at a concentration 0.5% and 0.1%). Strains of fungi *C. tenuis* and *A. niger* are insensitive to the action of the above compounds at these concentrations.

Antimicrobial activity of amino acid derivatives of 9,10-anthraquinone

Compound	Concentration, %	Diameter of inhibiton zone of microorganisms, mm					Compound	MIC, mkg/ml				
		E. coli	*S. aureus*	*M. luteum*	*C. tenuis*	*A. niger*		*E. coli*	*S. aureus*	*M. luteum*	*C. tenuis*	*A. niger*
II	0.5	0	0	0	0	0	**II**	+	+	+	+	1,9
	0.1	0	0	0	0	0						
III	0.5	0	16.0	12.0	0	0	**III**	+	+	+	125,0	31,2
	0.1	0	12.0	0	0	0						
IV	0.5	0	18.0	0	0	0	**IV**	+	+	+	250,0	31,2
	0.1	0	16.0	0	0	0						
V	0.5	0	0	0	0	0	**V**	+	+	125,0	+	+
	0.1	0	0	0	0	0						
VI	0.5	0	30.0	8.0	6.0	0	**VI**	+	+	15,6	+	125,0
	0.1	0	15.0	0	0	0						
VII	0.5	0	20.0	8.0	0	0	**VII**	+	+	31,2	+	15,6
	0.1	0	18.0	0	0	0						
VIII	0.5	0	0	0	0	0	**VIII**	+	+	250,0	+	+
	0.1	0	0	0	0	0						
IX	0.5	0	16.0	14.3	0	0	**IX**	+	+	7,8	+	+
	0.1	0	12.0	9.7	0	0						
X	0.5	0	15.0	11.3	0	0	**X**	+	+	15,6	7,8	1,9
	0.1	0	10.0	0	0	0						

«+» - growth of test cultures of microorganisms

The study of minimum inhibitory concentration (MIC) by serial dilutions of compounds **II**-**X** showed, that within the studied concentration (1,9-500 mkg/ml) inhibitory effect on the growth of test cultures of*E. coli* and *S. aureus* were not found. Growth of *M. luteum* is observed at an action of compounds **II**-**IV**, for other derivatives value of MIC is 7.8-250 mkg/ml. A MIC for compounds **III**, **IV** and **X** relative to test cultures of *C. tenuis* is 125, 250 and 7.8 mkg/ml, respectively.The amino acid derivatives **II**-**IV**, **VI**, **VII**, and **X** are showing antifungal action within 1.9-125 mkg/ml against strains of *A. niger*. For other compounds have been found inhibitory effect on the studied concentrations or occurred growth of microorganisms.

Thus, it was carried out directed synthesis of new promising amino acid derivatives of 2-chloro-N-(9,10-dioxo-9,10-dihydroanthracene-1-yl)acetamide. Carried experimental studies have identified compounds with antibacterial and antifungal activities in relation to the test cultures of *S. aureus*, *M. luteum* and *A. niger*.

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P-46. THEORETICAL INVESTIGATION OFNAPROXEN-METHYLPYRROLIDINE’S PHOTOTRANSFORMATIONS

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Chirality is very important property of bioorganic molecules. No one origin of life scenario can not be created without solving the problem of the mechanism of chiral purity. More than one half of all drugs are chiral compounds, but very often therapeutic effect has only one isomer. So, chiral systems are very important and perspective objects of investigation.

By the present moment many experiments were conducted with chiral compounds (in particular with naproxen-Methylpyrrolidine dyad (NPX-PYR)) [1,2]. The aim of these investigations was to determine an influence of chirality to reactivity of dyads. Theoretical study complements results of experiments and helps to understand a role of some parameters (as a constant of diffusion, thickness of the reaction layer, dielectric permittivity, temperature, rate constants, frequency of singlet-triplet conversion, constant of hyperfine interaction and etc).

In our work we offered an approximate model that describes relative motion of radical centers in Coulomb field near the stationary state. Constructed model accounts all physical effects very good. Applying the method of Green functions and density matrix’s approach made possible to find chemical polarization of nuclei.

$$\rho\left(\vec{q}\right)=\int G\left(\vec{q},\vec{q}',s\right)\rho_0\left(\vec{q}'\right)d\,\vec{q}'+\int G\left(\vec{q},\vec{q}',s\right)\hat{K}\left(\vec{q}'\right)\rho\left(\vec{q}'\right)d\,\vec{q}'$$

$$CIDNP=\sum_{i=1}^{n} m w_m,\, w=k_i\rho_i$$

These theoretical calculations were conducted in two different cases: radical pair (RP) in restricted volume and RP in unrestricted volume. More than that, we obtained a population of exciplex state in different polarities of a solvent.

Theoretical dependences of the exciplex concentration versus time for the two enantiomers were compared with experimental data. Calculations confirmed the results of experiments about small differences between exciplex’s kinetics curves for

(R,S) and (S,S) isomers of NPX-PYR. It is shown that an important role in the formation of the nuclear polarization plays dielectric permittivity of the medium and the mechanism of the relative motion of radical centers in the dyad.

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P-47. SYNTHESIS AND QUANTUM CHEMICAL INVESTIGATION OF NITROGEN-CONTAINING HETEROCYCLIC SYSTEMS, CONTAINING 3-[4-(2-BROMACETLY)PHENYL]COUMARIN MOIETY

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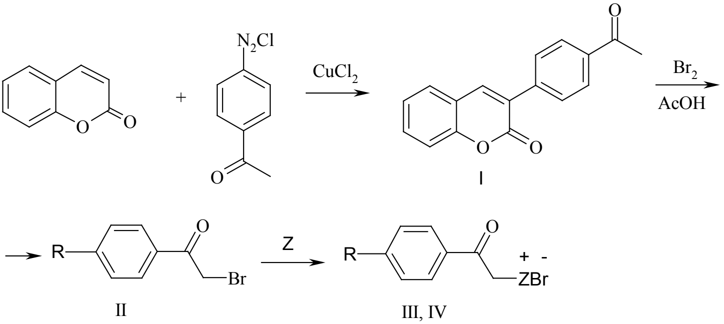
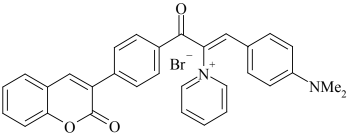
The novel derivative of coumarin: 3(4-acetylphenyl)coumarin (I) was obtained for the first time by using Meierwein reaction. Its bromation in acetic acid lead to 3-(4-acetylphenyl)coumarin (II). The reaction of the compound (II) with pyridine and 4-methylpyridine leads to the formation of quaternic salts (III, IV) [1].



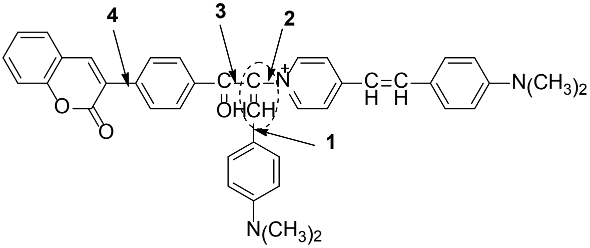
R= coumarin-3-yl; Z^+ = N-pyridinium (III), N-4-methylpyridinium (IV)

We have observed that the salt (III) enters the aldolic condensation by methylene group, and the salt (IV) – by methylenic and methyl groups with 4-dimethylamminebenzaldehyde, which leads to the formation of cyanine dies (V, VI).



V

We have ellaborated the methodology of the quantum-chemical calculation of the inversion barrier of the bond C^3(coumarinic cycle) – C(phenyl cycle) in the compounds (I-VI). In the ground state the angle between the plains of two cycles is equal to ~35-37°. In transition state this angle is equal to 0º. The difference of energies between the ground and transition states characterizes the rotation energy of coumarinic and phenylic cycles. The calculations have been made by semiempiric method of AM1 (Table. 1).



VI

Table 1: The energies of ground and transition states and rotation energies of coumarinic and phenyl cycles

Compound	Ground state energy, kJ/mol	Transition state energy, kJ/mol	Rotation energy, kJ/mol
I	-167,94	-160,78	7,16
II	-136,87	-130,24	6,63
III	655,62	663,08	7,46
IV	612,10	619,60	7,50
V	1030,67	1038,90	8,23
VI	868,18	876,61	8,43

The data of the table 1 show that by the growth of the molecules (I-VI) the coumarinic cycle rotation energy value increases insignificantly.

The modeling of the geometrical data for the given compounds has shown that the aromatic fragments are disposed in different plains, the angles between which are given in the table 2.

Table 2: The angles between aromatic fragments (V, VI) relatively to the bonds >C=CH and the bond coumarin cycle – phenyl cycle in the compounds (I-VI)

Compound	>C=CH-$C_6H_4N(CH_3)_2$-4 **(1)**	Pyridine-C=CH- **(2)**	-C=CH-C(O)-Ph **(3)**	Coumarin-Ph **(4)**
I	-	-	-	35,5°
II	-	-	-	34,8°
III	-	-	-	35,6°
IV	-	-	-	35,8°
V	38,0°	58,7°	37,0°	37,2°
VI	35,0°	58,2°	34,4°	37,4°

As it may be seen from the table 2, the angles between aromatic moieties differ insignificantly.

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P-48. THE SINTERING KINETICS OF CERAMIC TILE BODY OF REDUCED THICKNESS

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In the conditions of market economy a perspective direction of modern development of the industry of building materials and its major scientific and technical problem is working out and introducing resource saving technologies of producing of ceramic tiles for internal facing of walls, which in the given research consist in reduction of products’ thickness at saving of a complexity of demanded physical and chemical properties [1].

The study of chemical, phase composition and structure of ceramic tiles produced by some foreign firms (Italy) carried out by scanning electron microscopy and X-ray diffraction make possible to determine that these tiles are characterized by a relatively low content of SiO_2 and its overall chemical composition is of a great similarity with natural alkaline earth formations such as gabbro, and the mineralogical composition is folded predominantly by alkaline feldspar (labradorite, anorthite), pyroxene and olivine.

On this basis, the basalt was added partially and fully in an amount of 2.5 wt. % to 22.5 wt. % in replacement of granitic screenings in the raw composition for ceramic tiles of interior wall facing. Basalt is like to gabbro and refers to igneous rock. Mineralogical composition of basalt is represented mainly by plagioclase, pyroxene and olivine. Chemical composition is in the table.

Table. Chemical composition of basalt

Raw material	Oxide content, wt. %								
	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	(Fe_2O_3 + FeO)	Loss on ignition
Basalt	52.9	17.4	6.3	3.1	5.8	0.9	0.7	7.3	5.6

Test samples of ceramic tiles have been prepared by semi-dry pressing and firing at 1110±5 °C. It is found that the optimum content of basalt in the ceramic masses is 15 wt. %. The rational combination of basalt with other components of the feedstock composition (fusible clay, refractory clay, dolomite, granitic screenings and silica sand) ensures the presence of crystalline phases (α-quartz, anorthite, hematite and augite) defining the high mechanical strength of the samples (37.0–38.5 MPa) and a liquid phase in an amount required for the better cementation of crystalline phases and to form a dense homogeneous structure of the tiles.

The clinopyroxene crystalline phase – augite (Ca (Mg, Fe, Al) $[(Si, Al)_2O_6]$) is diagnosed in the fired samples of tiles with optimum content of basalt. Augite is a chain silicate which has high hardness and density. However, with introducing the basalt in the composition of masses, it promotes the formation of structure with a high degree of crystallinity.

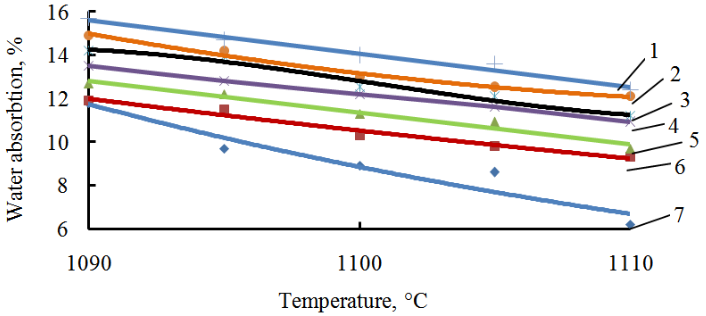
The results of the macrostructure studies show that samples, obtained of raw compositions with 15 wt. % of basalt, are characterized by quantitative reduction of plagioclase and quartz, with simultaneous increase in the content of clinopyroxene compared with samples without basalt. The pore space of tile structure is about 7–14 vol. %, which is associated with the filling of the glassy phase to the pores. The tiles were sintered following a fast firing process at enterprise "Berezastroymaterialy". The results show the possibility of using basaltic rocks as a component of raw material compositions of the ceramic materials for the manufacture of tiles for interior wall facing of reduced thickness (from 7.5 to 5.5–5.0 mm.)

Due to the fact that the developed raw compositions allow obtaining ceramic tiles of reduced thickness, was study the effect of maximum firing temperature on the sintering process of the products of reduced thickness.

Under the sintering kinetics usually understand the dependence of shrinkage and water absorption from time in isothermal conditions. Shrinkage shows the kinetics of the compaction of the material at the initial and intermediate stages and the kinetics of removal of closed pores at the final stage. Thus, the shrinkage and water absorption curves reflect the processes taking place during sintering. That is why the sintering behavior of the fired samples was evaluated by linear shrinkage, water absorption and porosity measurements [2].

The samples of ceramic tiles with thickness of 7.5 to 4.5 mm were fired in an electric furnace with heating range 10 °C/min at 1090, 1095, 1100, 1105 and 1110 °C.

Analysis of the results of the study the indicators of water absorption of tiles samples shows that with the same parameters of the firing there is a marked difference in the water absorption samples of different thickness (Fig. 1).



Tile thickness, mm: 1 – 7,5; 2– 7,0; 3 – 6,5; 4 – 6,0; 5 – 5,5; 6 – 5,0; 7 – 4,5.

Fig. 12 – Evolution of water absorbtion vs temperature in ceramic tiles of different thickness

It should be noted that with decreasing the thickness of products is intensified the sintering process of masses, which leads to reduction of the time required to achieve the desired degree of sintering. Densification of samples increases with increasing sintering temperature. In addition, for the tiles of thickness of 4.5–5.0 mm in almost at all firing temperatures is observed a significant deformation, which suggests the possibility of obtaining defect-free and vitrified samples of tiles with a minimum thickness of 5.5 mm. The deformation is also observed for samples of tiles of all thicknesses, fired at a temperature of 1100 ^{o}C. Furthermore, shrinkage of the samples of tiles fired at temperatures 1090–1105 °C, is in the range 0.5–1.9%, and rises sharply to 6.2% at 1110 °C. Thus, it can be concluded that the optimum firing temperature of the product is 1090 °C, which allows getting tiles of reduced thickness with the necessary degree of sintering without deformation and any visible defects.

Analysis of the results of determining the mechanical strength of fired tiles indicates that the increase in firing temperature leads to an increase in strength of the samples of different thickness, due to an increase of the glassy phase formed during heat treatment of tiles on the basis of basalt containing raw compositions. However, a sintering temperature of 1090 °C did not have any significant effect on mechanical strength of tiles, because the samples of tiles fired at 1090 °C are characterized by values of strength which below the requirements by the specifications and technical documentation.

It is established that the developed compositions of ceramic masses with basalt can be used for obtaining tiles of reduced thickness (to 5.5 mm) at firing temperature of 1100 °C, that 10 °C below than applied at "Berezastroymaterialy". Ceramic tiles characterize by a reduced thickness, required complex of physical and chemical properties and can reduce the consumption of raw materials during manufacturing by semi-dry pressing on the flow-conveyor lines by single-firing, to ensure the reduction of material capacity of products.

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P-49. SYNTHESIS OF DINITROPYRIDYLACETYLENES VIA SONOGASHIRA REACTION

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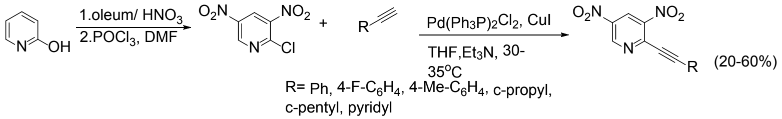
It is well-known that aromatic nitro compounds containing alkynyl substituent in the ortho position to the nitro group are suitable precursors of different heterocycles [1,2]. Currently it is one of the most interesting and developing strategy for heterocyclic ring construction. In this regard the synthesis of new hetarylacetylens is a problem of interest.

As a part of our research on polycyclic heterosystems we have proposed a method for the synthesis of new dinitropyridylacetylenes from 2-chloro-3,5-dinitropyridine in accordance with the following scheme:



It should be noted that Sonogashira reactions of polynitropyridines have not been previously described.

Thus, a number of new dinitropyridylacetylenes were synthesized on the basis of palladium catalyzed cross-coupling reactions.

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This work was supported by the Russian Foundation for Basic Research, Project No. 14-03-31508 mol_a and Grant of the President of the Russian Federation for State Support to young Russian scientists, Grant MK-3599.2013.3.

P-50. I_2BODIPY AS OPTICAL OXYGEN SENSOR

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Creation and development of oxygen sensors have attracted much attention of chemists worldwide because of their broad application in biology, food industry, aircrafting, ecology and life science. Optical detecting method based on luminescence quenching of organic dye has some advantages over analogs; optical oxygen sensors are unexpensive, easily miniaturized and simple to use, and have extraordinary sensitivity and reversibility [1]. Probes available as oxygen sensors are organic dyes and metal-complexes of organic dyes, including the transition metals complexes with organic compounds and metalloporphyrins, which have intensive phosphorescence. Sensitivity of sensors based on transition metal complexes is relatively low [1]. Oxygen sensors based on metal-porphyrin complexes, especially Pt and Pd porphyrin complexes, have a great potential due to the high extinction coefficients, quantum yields, long lifetime and excellent photostability [1]. They possess extraordinary sensitivity at low oxygen concentrations, but characterized by high cost. The disadvantages of optical oxygen sensors based on organic dyes are low photostability, small Stokes shift, short-wave excitation (300-400 nm) and poor sensitivity [4]. These disadvantages can be overcome by using BODIPY dye (Fig. 1), whitch stand out as stable molecules with appropriate luminescent characteristics.

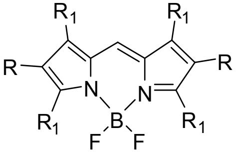

Fig. 1. Structure of BODIPY dye: $R=R_1=H$ – BODIPY; $R=I$, $R_1=CH_3$ – I_2BODIPY.

For synthesis and experimental details see [2].

BODIPY dyes are highly coloured and display narrow absorption band with high extinction coefficient in the visible range. Although BODIPY dyes are well-known for their intense fluorescence, substitution by heavy atoms changes the photophysics of the molecule to a great extent. Although BODIPY dyes are well-known for their intense fluorescence, substitution by heavy atoms changes the photophysics of the molecule to a great extent.

Absorption spectrum of I_2BODIPY in ethanol (Fig. 2a) is presented by narrow bands at 534 nm. Fluorescence (Fig. 2a) maximizes at 553 nm and characterizes by quantum yield 0.04 at room temperature. Phosphorescence at 77K (Fig. 2a) is presented by band with maximum at 790 nm and described by quantum yield of 0.60 and life time of 0.58 ms.

Samples of methylcellulose impregnated by I_2BODIPY solution under the argon atmosphere show phosphorescence (Fig. 2b) which disappeared when oxygen is introduced to the flow cell. Typical changes of the phosphorescence intensity under switching between pure argon and pure oxygen are shown at Fig. 3a.

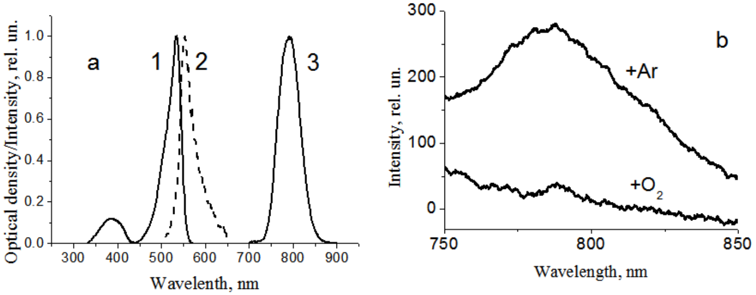

Fig. 2. a) Absorption – 1 (293K), fluorescence (λ_{exc}=500 nm, 293K) – 2 and phosphorescence (λ_{exc}=520 nm, 77K) – 3 spectra of 10^{-5}M I_2BODIPY in ethanol, normalized to 1; b) luminescence spectra of I_2BODIPY in methylcellulose matrix in the argon and oxygen atmospheres at λ_{exc}=500-520 nm for the sample with 10^{-4}M of I_2BODIPY.

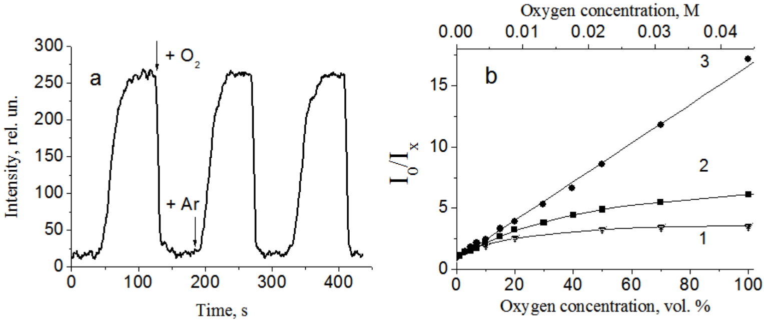

Fig. 3. a) Typical change in phosphorescence intensity (790 nm) under excitation 500-520 nm for the sample with 10^{-3}M of I_2BODIPY; b) Stern-Volmer plots for I_2BODIPY sequestered in methylcellulose with different concentrations of impregnating dye solution: 1 – 10^{-5} M, 2 – 10^{-4} M, 3 – 10^{-3} M. Lines are the best fits to the experimental data.

The sensitivity of the prepared samples determined as I_0/I_{100} ratio, where I_0 – phosphorescence intensity under 100% argon and I_{100} – under 100% oxygen, was 3.6, 6.2 and 17.6 for I_2BODIPY concentration in impregnating solution of 10^{-5}, 10^{-4} and 10^{-3} M respectively.

A sensor material based on organic dye I_2BODIPY in methylcellulose matrix for O_2 determination in the gas phase has been reported for the first time. A fully reversible material with 17-fold sensitivity and fast response was developed. The sensitivity and oxygen detection limit dependence of the active substance concentration in matrix is shown.

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P-51. APPLICATION OF LIQUID-PHASE MICROEXTRACTION PRECONCENTRATION OF IMPURITIES FOR HIGH-SENSITIVITY DETERMINATION OF TOXICANTS IN WATER AND AIR SAMPLES

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Determination of toxicants is performed using high-sensitivity methods, such as gas-chromatography-mass-spectrometry. But even in this case it is necessary using of preconcentration of impurities.

In the last few years, unconventional methods of preconcentration is more interest, in particular, the methods of microextraction preconcentration. Classic liquid-liquid microextraction has significant disadvantages: the use of large volumes of expensive and toxic solvents; formation of emulsions; difficulties of automation. A serious problem is the disposal of toxic extractants, it’s volumes can reach tens to hundreds of milliliters. Efficiency of concentration using conventional liquid-liquid extraction is often insufficient. Microextraction preconcentration, particularly with ultrasonic dispersion of an extractant, is economically and environmentally advantageous method. It allows to get a high concentration using micro volumes of extractant in the time interval - the order of several minutes. This allows to increase the sensitivity of the analysis at least about 2-3 orders.

We have developed a technique of highly high-effective concentration of primary toxicants from water using ultrasonic nanodispersion of extractant. Microamounts of extractant are distributed in the form of an emulsion over the entire volume of analyzing water. Due to this mass transfer surface increased with 10^4-10^5 times. It leads to the establishment of equilibrium in the system. Further aggregation of the extract phase was performed by centrifugation.

As the solvents we used extractants with dencity higher than that of water (carbon tetrachloride) and the low-density solvents (hexane, octane). In the latter case, for collecting the extract we used the capillary.

Analysis of the extracts was performed by gas chromatography-mass spectrometry and gas chromatography with electron capture and flame ionization detection.

High efficiency of the method was showed performing concentration of volatile halogenated organic compounds, polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCBs), esters of *o*-phthalic acid. Achieved enrichment factors were at the level 310-1030 (PAH), 30-230 (for volatile organohalogen derivatives) 62-350 (*o*-esters of phthalic acid). The detection limits were $3\cdot10^{-5}$–$5\cdot10^{-7}$ $mg\cdot L^{-1}$ (PAH), $1\cdot10^{-4}$–$5\cdot10^{-6}$ $mg\cdot L^{-1}$ (for volatile organohalogen derivatives) $1\cdot10^{-5}$–$1\cdot10^{-6}$ $mg\cdot L^{-1}$ (for *o*-esters of phthalic acid) $1\cdot10^{-5}$–$1\cdot10^{-6}$ $mg\cdot L^{-1}$ (PCB). Achieved detection limits at least ten times less than the maximum permissible concentrations of these toxicants. Thus, the reached detection limits allows to control of environmental conditions long before a critical situation.

Developed methods successfully tested by analyzes of different water samples: tap, river, artesian and bottled.

Liquid-phase microextraction method also used to analyze the air. In this case, the pre- cryogenic air concentration of impurities into atmospheric moisture was used. For this purpose, air was pumped through the tube, cooled by liquid nitrogen. Frozen atmospheric moisture containing impurity components of air formed in a tube. After pumping air, ice was thawed and melted water was removed from the hub. Then the microextraction concentration of impurities from the melt water was conducted. And then, the gas chromatography-mass spectrometric analysis of the extract was performed. Achieved enrichment factors of impurities from the air was from $2\cdot10^{4}$ (benzene) to $1\cdot10^{5}$ (for benzo(a)pyrene), and the limits of detection of toxicants in the air was $(1\text{-}5)\cdot10^{-5}$ $g\cdot m^{-3}$. This approach allowed us to solve the problem of background of sorbent as in solid-phase extraction. Reduced volumes of expensive extracts to three - four orders of magnitude, completely solved the problem of disposal of highly toxic extractants.

P-52. SEARCH FOR NOVEL IMMUNOSTIMULATORS IN THE NUMBER OF 3,7-DIAZABICYCLO[3.3.1]NONANE DERIVATIVES

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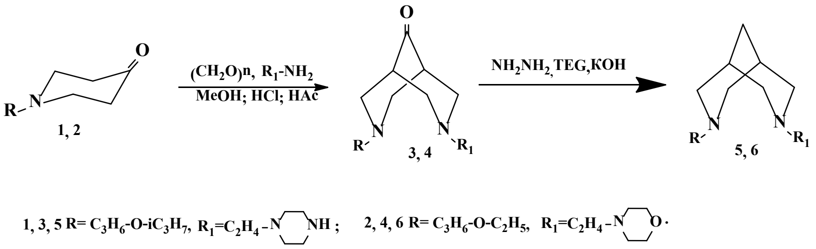
Immune system diseases remains a major health problem in the world, because of immune system disorders cause abnormally low activity or overactivity of the immune system. The immune system defends the body from developing potentially harmful diseases and conditions caused by bacterial, parasitic, fungal and viral infections. The immune system also restricts tumors and cancerous growths inside the body. However, problems with the immune system can lead to illnesses and infections. Immune responses can be weakened by various external influences. Immunomodulators weaken or modulate the activity of the immune system.

Various 3,7-diazabicyclo[3.3.1]nonane derivatives have received the attention of medicinal chemist due to their wide range of biological activities, which include analgesic-anti inflammatory, opiate antagonist, antibacterial, antiarrhythmic and antispasmolytic [1-8]. In the present study it was envisaged that a molecule entity possessing such bicyclic systems could possess immunomodulatory activity. The objective of the study was to develop potent immunomodulators incorporating 3-ethoxypropyl or 3-(propan-2-yl-oxy)propyl and (2-piperazin-1-yl)ethyl or (4-morpholin-1-yl)ethyl groups linked to bispidine system to enhance the hydrophilicity and lipophilicity of the synthesized compound.

Due to structural similarity of novel alkoxyalkyl substituted 3,7-diazabicyclo[3.3.1]nonanes with bispidine derivatives, which have been earlier synthesized in the Lab of the Chemistry of Synthetic and Natural Drugs of JCS "Chemical Sciences Institute named after A.B. Bekturov" pharmacological properties of the target compounds were predicted using the PASS program [9, 10]. The resultsof the prediction of biological activity showed that the synthesized compounds **5** and **6** should possess high immunomodulatory, immune-stimulating and analgesic activity.

The starting 3,7-diazabicyclo[3.3.1]nonanes **3**, **4**, containing various azacyclic systems attached at 7-position of bispidine ring were synthesized via a route involving double Mannich reaction of N-alkoxyalkylpiperidin-4-ones **1, 2** with paraformaldehyde and primary amines: 1-(2-aminoethyl)piperazine or 4-(2-aminoethyl)morpholine, in the methanol in the presence of glacial acetic acid.



1, 2 3, 4 5, 6

1, 3, 5 R= C_3H_6-O-iC_3H_7, R_1=C_2H_4-N NH ; 2, 4, 6 R= C_3H_6-O-C_2H_5, R_1=C_2H_4-N O.

Characterization of these 3,7-diazabicyclo[3.3.1]nonan-9-ones **3**, **4** via IRand NMR analysis was completed. Infrared analysis of bispidone **3, 4** revealed the bands at 1736 cm^{-l} for the C=0 group**.**

From the ^1H and ^{13}C spectra compounds **3**, **4** the following general features for the bicyclic system was deduced that this compounds in deuteriochloroform solution adopt a chair-chair conformation. In the ^1H NMR spectra the range of values for $W_{1/2}$ of H1,5 is in the range ≈10 Hz which is in a good agreement with values for flattened chair-chair conformations in related bicyclic systems.

The vicinal constants $^3JH(2,4,6,8)_{ax}$ – H1(5) ≈ 5 Hz confirm that those compounds should adopt the same preffered comformations in solution, a flattened chair-chair form.

To prepare the potencial immunomodulators the Wolff-Kishner reduction of obtained bispidinones **3**, **4** with hydrazine hydrate in the presence of KOH in triethylene glycol at 160–170°C for 5 hours was carried out.

The structures 3,7-diazabicyclo[3.3.1]nonanes **5**, **6** were determined by IR and NMR spectroscopies. The absence of absorption band of carbonyl group in IR spectra both compounds is an evidence of target products forming.

^1H NMR spectrum analysis revealed that 3,7-diazabicyclo[3.3.1]nonane derivatives have a bicyclic unit in a chair-chair conformation.

Using of cyclodextrin complexes can lead to advantageous changes in the chemical and physical properties of pharmacologically active molecules, such as modification of liquid substances to powders, increasing the solubility and bioavailability of such compounds, stabilisation of light- or oxygen-sensitive substances, fixation of very volatile substances, improvement of solubility of substances,p rotection against degradation of substances by microorganisms, masking of ill smell and taste. Because of all synthesized compounds are oils to prepare solid forms the interaction of bispidines with β-cyclodextrin was carried out.

The synthesized compounds were screened for their immunomodulatory effect and toxicity. The effect of the synthesized compounds was evaluated and compaired to the drug levamizol. Administration of cyclophophamide has significantly lowered the levels of hemoglobin, leukocytes, lymphocytes and monocytes. The using of nontoxic bispidines **5**, **6** has significantly ameliorated the above blood counts and has exceeded the effect of levamisole.

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P-53. BIOACTIVE NATURAL COMPOUNDS FROM HELLEBORUS CAUCASICUS A.BR.

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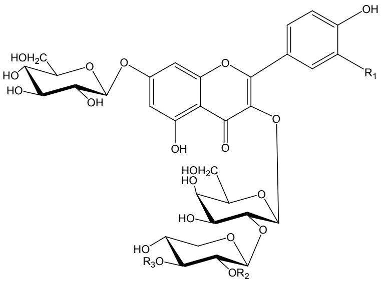
Helleborus genus (fam. Ranunculaceae) combines about 20 species, distributed in Europe and Asia. Mainly subterranean organs of plant species are used and studied. Various compounds of steroid class, including bufadienolids, furo- and spirostanol glycosides, ecdysteroids are reported to date and interesting biological activities of plant extracts are described [1].

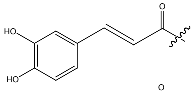
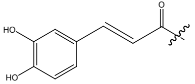
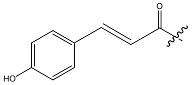
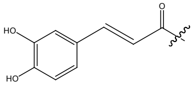
Flavonoids are considered as taxonomic markers of the Ranunculaceae family [2]. In recent years from the aerial parts of *Helleborus viridis*, *H. foetidus* and *H. niger* acylated flavonol glycosides and phenolic glucoside derivatives have been isolated [3-5]. The polar extracts of three *Helleborus* taxa (*Helleborus odorus* Waldst. Et Kit, *H. multifidus* and *H. hercegovinus* Martinis) significant antiproliferative and strong antioxidant activities have exhibited; Since the active principles responsible for these bioactive properties remain unclear, further studies are suggested to be performed towards the isolation and characterization of single compounds [6].

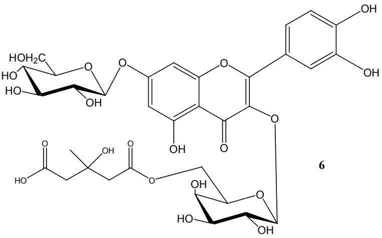
TABLE 1. *In vitro* trolox equivalent antioxidant capacity (TEAC) of flavonoids of*Helleborus caucasicus* A.Br

compound	TEAC value (mM ± SD)
1	1.485 ± 0.045
2	0.679 ± 0.051
3	1.195 ± 0.038
4	0.668 ± 0.025
5	1.204 ± 0.034
6	1.240 ± 0.027
7	0.410 ± 0.031
quercetin 3-*O*-glucoside	1.650 ± 0.004

Chemical structures:



	R1	R2	R3
1	OH	H	H
2	OH		H
3	H		H
4	OH		H
5	OH	H	



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Helleborus caucasicus, a Caucasian endemic specieswidespread in Georgia, so far only for its steroid content has been researched. From the underground and aerial parts of plant polyhydroxylated and polyunsaturated furostanol glycosides, namely Caucasicosides A-M, have been isolated along with, bufadienolides, ecdysteroid, furospirostanol and bisdesmosidic spirostanol saponins [7-8]. As a part of our ongoing research for the first time the phenolic composition of *Helleborus caucasicus* leaves and the antioxidant potential of isolated single compounds have been investigated. This study led to the isolation of six flavonoids (compounds 1-6) never reported before, together with flavonoide glycoside, sterol and γ-pyron derivative, described here for the first time in *Helleborus* genus. The structures of single compounds were established by spectrometric (ESI-MS) and spectroscopic (UV, NMR) means. Compounds **1**, **3**, **5** and **6** exhibited high antioxidant activity.

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P-54. SYNTHESIS OF SOME NEW INDOLE-3-YL HYDRAZONES FOR OBTAINING PYRIDAZINOINDOLES

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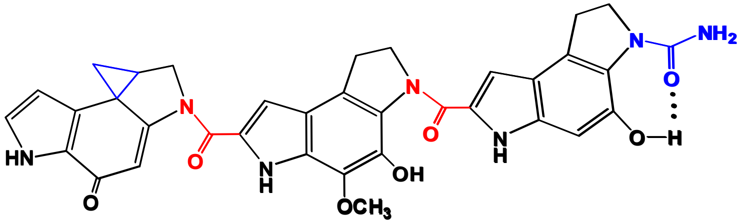
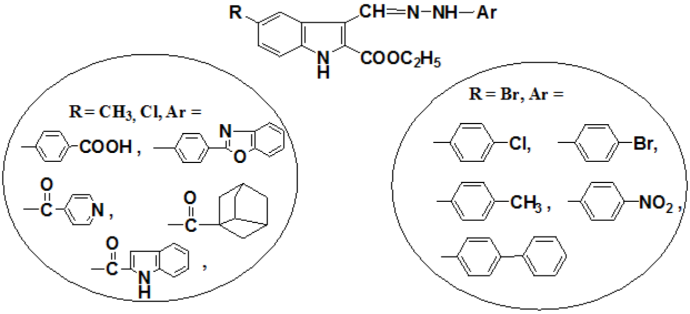
In 1987-88, a group (Duocarmicine group) of highly biologically active, anticancer antibiotics were extracted from the plant "Streptomyces zebensis" and from the bacteria "Streptomyces". One of these antibiotics is CC-1065. It consists of three Pyrroloindolic fragments. The biological activity of this compound noticeably exceeds activity of other known compounds, including Adriamicine, Distamicine A, Netrophsine, Nogalamicine etc. What distinguishes CC-1065 from other compounds is that it binds DNA basic pairs with hydrogen bonds, which helps it to firmly establish its position. One molecule usually binds 7 to 11 different basic pairs, which causes to increase the melting point of DNA, which, in turn, distracts its ability to duplicate. The biggest flaw of this group of compounds is that their selectivity is extremely weak. Their high toxicity is the reason none of them is used in practice nowadays.



The discovery and research on Duocamicine group and its properties commenced new wave of studies directed toward synthesis of parts of these compounds and its structural analogues. Variety of new compounds with similar properties have been synthesized ever since, including bisindole and bispyrroloindole analogues.

Some of 2-Ethoxycarbonylindole-3-yl-arylhydrazones are synthesized to discover new biologically active compounds. By intramolecular cyclocondensation of these arylhydrazones 3-arylderivatives of 8-clor- and 8-methyl-4-oxo-3H,5H-pyridazino[4,5-b]indoles are easily formed.

Thus 4',8-disubstituted derivatives of 3-phenyl-4-oxo-3H,5H-pyridazino[4,5-b]indolewere obtainned and general preparative method for obtaining of such type of compounds was developed.



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P-55. KLASON LIGNIN AS PROMISING CATHODE MATERIAL FOR LITHIUM BATTERY

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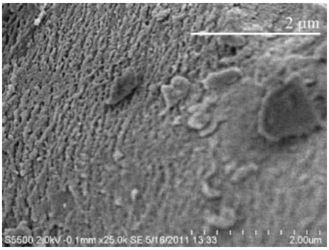
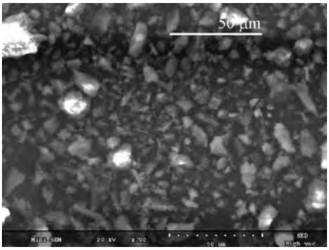
Lithium batteries with inorganic cathode materials are widespread energy sources for high-technology equipment due to the excellent performance. However conventional electrochemical systems are characterized by significant limitations of the component base, because of natural resources exhaustibility and no renewability. In addition mining operations attends significant CO_2 emissions (70–100 kg per 1 kWt·h). The organic compounds are alternative class of the electrode materials. Environmentally friendly synthesis of non-toxic organic compounds is the way to designing of the sustainable energy sources. Electroactive redox properties of organic materials are at the stage of intensive investigation since 1990th years. At present a number of organic compounds were synthesized, the large knowledge base about fundamental processes in the organic lithium batteries was accumulated, and some practical devices were developed, for example organic radical battery invented by NEC Corporation. However state-of-the-art organic lithium batteries suffers from grave disadvantages, such as low practical specific capacity, dissolution of the compounds into the electrolytes, limited discharge voltage, etc. Thus search of promising organic compounds for both anodes and cathodes is required to design high performance sustainable lithium batteries.

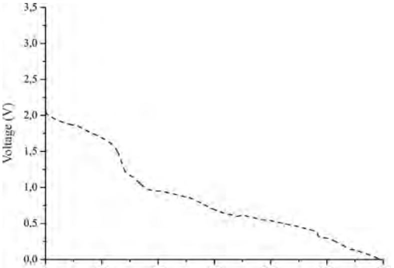
In this work the electrochemical performance (vs. Li/Li^+) of battery cathode based on Klason lignin (KL) extracted from the buckwheat husks was investigated. The possibility of KL usage as energy storage material was found. Electrochemical reactions between Li and KL groups were suggested. The husks of buckwheat (the genus *Fagópyrum Mill.*) were used as precursor (2002, 2010, and 2012 year’s harvest, Dalnerechensk, Russia) in the delignification process.





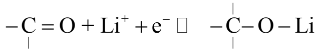
The elemental analysis of Klason lignin by EDX was performed on an EDX-800HS (Shimadzu, Japan) spectrometer. In accordance to the EDX results, the KL contains C – 64 wt. % and O – 35 wt. %. Note that it is impossible to detect hydrogen using the EDX method. Concentration of inorganic components (impurities) is approximately 1 wt. %.

The KL microstructure characterization by SEM was performed on a high-resolution S5500 microscope (Hitachi, Japan). Heterogeneous morphology surface of each KL particle facilitates to the diffusion of Li^+ ions in the cathode bulk during the lithium battery operation. At the sametime the KL particle size changes up to 300 μm significantly decreases the electrolyte/cathode interface area. Thus Klason lignin was ground in KM1 (Janetzki, Poland) ball mill to prepare the cathode material. According to the SEM data the ball mill using is results in finer grinding, due to size of 15 μm for approximately 70 % of particles was achieved.



The galvanostatic discharge of Li/KL was carried out between OCV and 0 V at 75 µA cm^{-2} on an Analytical Celltest System (Solartron, UK). The curve indicates that the OCV value for the system Li/KL is 3.3 V. However within a 3 h of the Li/KL operation the voltage decreases down to the 2 V due to electrolyte reduction and formation of the SEI as well as occurrence of electrochemical reactions caused by the complex composition of lignin.

On the discharge profile of Li/KL battery two voltage plateaus are distinguished because of step-by-step electrochemical reactions between Li^+ ions and oxygen of different functional groups of lignin. The plateau from 2 to 1.5 V is longer in comparison with 1.5–1 V region. The Li/KL specific capacity of 125 mAh·g^{-1} in the OCV–1.5 V region are results from electrochemical interactions of Li^+ ions and carbonyl groups of Klason lignin (Eq. 1). Voltage decrease from 1.5 to 1 V within a further discharge is yielded by 50 mAh·g^{-1} due to the reduction of –OH functions (Eq. 2). The existence of hydrogen in discharged Li/KL battery was confirmed by gas chromatography testing of atmosphere generated during the operation process. In the range of 1–0 V the electrochemical reactions between Li$^+$ ions and C–O–C groups of lignin are possible (Eq. 3). Note that interaction mechanism of Li$^+$ ions and ether functions is investigated in detail for a number of aprotonic dipolarorganic solvents


$$-\underset{|}{\mathrm{C}}=\mathrm{O}+\mathrm{Li}^{+}+\mathrm{e}^{-}\ \square\ -\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{O}-\mathrm{Li} \qquad \text{(Eq. 1)}$$

$$2\mathrm{C}_6-\mathrm{C}_3-\mathrm{OH}+2\mathrm{Li}^{+}+2\,\mathrm{e}^{-}\rightarrow 2\mathrm{C}_6-\mathrm{C}_3-\mathrm{O}-\mathrm{Li}+\mathrm{H}_2 \qquad \text{(Eq. 2)}$$

$$\mathrm{C}_6-\mathrm{C}_3-\mathrm{O}-\mathrm{R}+2\mathrm{Li}^{+}+2\mathrm{e}^{-}\rightarrow \mathrm{C}_6-\mathrm{C}_3-\mathrm{O}-\mathrm{Li}+\mathrm{R}-\mathrm{Li}, \qquad \text{(Eq. 3)}$$

where (C_6–C_3) – phenylpropane structural unit of lignin, R: (C_6–C_3); CH_3.

Thus the specific capacity of Li/KL battery in the voltage range of OCV–0 V at current densities of 75 µA·cm^{-2} achieves the high value of 600 mAh·g^{-1}.

In summary, the availability of Klason lignin extracted from the buckwheat (the genus *Fagópyrum Mill.*) husks as resources-economy cathode material for lithium batteries has been shown for the first time. The maximum specific capacity of the Li/KL battery up to 600 mAh·g^{-1} was achieved practically. The mechanism of electrochemical reactions in the lithium/lignin cell has been discussed. The grinding has a pronounced effect on the particle size, morphology, and electrochemical behavior of the Klason lignin. The results show the perspectivity of the Li/KL batteries usage as long-term low-rate power sources.

P-56. NMR SPECTROSCOPIC STUDY OF SUPRAMOLECULAR INCLUSION COMPLEXES OF 1-(2-ETHOXYETHYL)-4-(HEXYNE-1YL)-4-HYDROXYPIPERIDINE WITH β-CYCLODEXTRIN

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From the perspective of the creation of new domestic medicines are particularly important supramolecularnanocapsulatedcyclodextrins complexes withpiperidine derivatives. They can produce solid dosage forms such as liquids, contribute to the stabilization of active substances to the action of external factors such as light, heat, increase the solubility, improve bioavailability, mask undesirable odors and taste of biologically active compounds. Development of new forms of drugs at the present stage is the most interesting because of the need for less toxic and more effective pharmacological standpoint substances. Encapsulation of biologically active molecule it contributes to the protection from biodegradation and efficient and selective drug delivery to target[1].

Choice as substrates for the supramolecular complexes of piperidine derivatives due to the high pharmacological activity of nitrogen heterocycles. Currently, extensive research on the synthesis flow homologs, analogs and derivatives of various piperidine observed in the field of synthetic chemistry. Evaluation is the ability of the nature of substituents and homologues affect the pharmacological properties of the molecule.

As receptor supramolecular systems have been widely used oligosaccharides cyclic structure consisting of various amounts of D-glucopyranose units - cyclodextrins (CD) (Figure 1). In this paper, for the encapsulation of piperidine derivatives was usedβ-CD. The molecule of β-CD has the shape of a truncated cone, the inner surface of which hydrophobic binding placed protonsH_3andH_5, and on the outer - H_2andH_4[2](Figure 1).

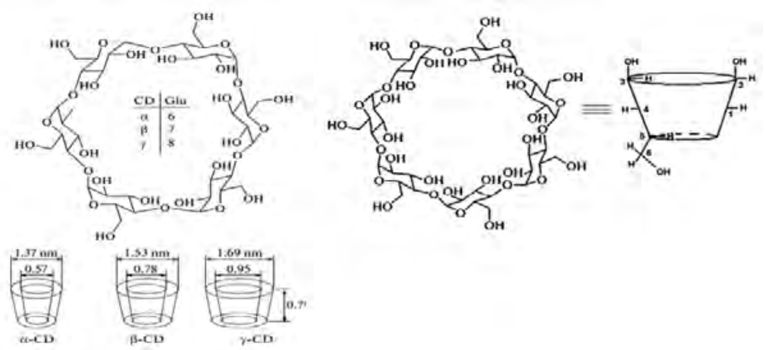

Figure 1: Schematic representation of the molecular structure of cyclodextrins

In this work, as objects of study were selected 1-(2-ethoxyethyl)-4-(hexyne-1-yl)-4-hydroxypiperidine. In order to confirm the formation of the inclusion complex, and the establishment of its structural features has been used a method of NMR spectroscopy [3].Indicator of the formation of supramolecular complexes, as well as the strength of intermolecular interactions between the receptor and the substrate were the values of chemical shifts NMR spectra of^{1}Hand^{13}Cbefore and after complexation. In the case of encapsulation of 1-(2-ethoxyethyl)-4-(hexyne-1-yl)-4-hydroxypiperidine β-CD molecule, there are four possible combinations of complex formation (Figure 3):

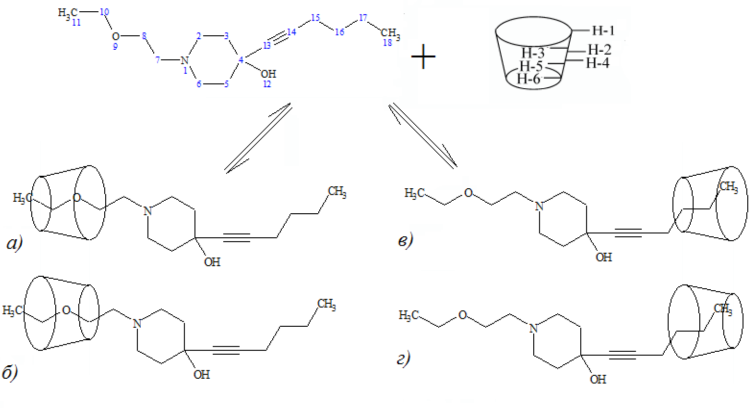

Figure 2 - The alleged structure of supramolecular complexes incorporating 1 - (2-ethoxyethyl) -4 - (hexyne-1-yl)-4-hydroxypiperidine with β-CD

In the analysis of the NMR spectra, it was found that the maximum value is observed internally Δδ H-3 and H-5 protons β-CD, indicating the formation of supramolecular complex internal inclusions. In case the maximum value of the piperidine substrate Δδ obtained for H-16, H-17 and H-18, whereby it can be assumed that the self-assembling supramolecular complex realized alkynyl substituent introduction into the hydrophobic portion of the molecule β-cyclodextrin from a wider ring of its molecule [4, 5] (Figure2, *г*).

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P-57. ION ASSOCIATION AND SOLVATION OF LITHIUM BIS-(OXALATO) BORATE IN ETHYL ACETATE

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The investigation of ion-molecule (solvation) and ion-ion (association) interactions, as well as the dynamics of ions in electrolyte solutions with a low dielectric constant is of great interest primarily for the development of contemporary electrochemical devices. The main feature of these solutions is the formation not only of ion pairs, but also ionic triples and higher order aggregates.

In this work the results of the experimental investigation of electric conductivity and ion association of lithium bis-(oxalato)borate, LiBOB, in ethyl acetate in temperature range 278-328 К are presented.

The values of limiting ionic conductance of simple ions and triple ions and association constants for ion pairs (I) and ion triples (IIa, IIb) formation were obtained from experimental data on the concentration dependence on conductivity of LiBOB solutions in ethyl acetate using Lee-Wheaton equation [1] and data processing algorithm, published previously [2, 3]. The following equilibria were taken into account

$$(Li^+)_s+(BOB^-)_s \Leftrightarrow (LiBOB)_s,\ K_A \qquad (I)$$

$$(LiBOB)_s + (Li^+)_s \Leftrightarrow ((Li_2BOB)^+{}_s),\ K_{T+} \qquad (IIa)$$

$$(LiBOB)_s + (BOB^-)_s \Leftrightarrow ((Li(BOB)_2)^-{}_s),\ K_{T-} \qquad (IIb)$$

The association constants of positively and negatively charged triple ions were assumed to be equal ($K_T=K_{T+}=K_{T-}$). Association constants for ionic pairs (lgK_A) have sufficiently higher values and slightly changes within investigated temperature interval. Association constants for triple ions (lgK_T) have lower values than association constants for ion pairs (lgK_A) and both decrease as the temperature rises.

To elucidate the role played by the dielectric properties of the solvent and solvation effects in interionic association, we have analysed the pair interionic potential in terms of Coulomb, $U_{\pm}^{\mathrm{Coul}}(r)$, and short-range non-Coulomb, $d_{\pm}=const$, interionic potentials [4]

$$U_{\pm}(r)=\begin{cases}\infty, & r<a\\ U_{\pm}^{\text{Coul}}(r)+d_{\pm}, & a<r<R^{*}\\ U_{\pm}^{\text{Coul}}(r), & r<R^{*}\end{cases},$$

where a and R^{*} are the interionic distances in the contact (CIP) and solvent shared (SSIP) ion pairs, respectively. We used the experimental $\lg K_A$ and the Ebeling model for the Coulomb ionic association constant K_A^{Coul} [5] to determine $d_{\pm}$ by the equation [6]

$$K_A=\frac{4\pi N_A}{1000}\left\{\exp\left(-\frac{d_{\pm}}{k_BT}\right)\left[K_A^{\text{Coul}}(a)-K_A^{\text{Coul}}(R^{*})\right]+K_A^{\text{Coul}}(R^{*})\right\}.$$

In the studied systems the negative values of the non-Coulomb potential $d_{\pm}$ are observed indicating the reinforcement of ion association due to difference in solvation of free ion and ion pairs.

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Invited Lectures

·Prof. Elizbar Elizbarashvili, Georgia
"Macrocyclic azomethines for optical imaging"

Prof. Valentine Nenajdenko, Russia
"Sulflower and other chemical flowers”

Prof. Igor Trushkov, Russia
"Donor-acceptor cyclopropanes in synthesis of carbo- and heterocycles"

Dr. Mikayel Aznauryan, Switzerland
"Probing the structure and dimensions of unfolded proteins with single molecule fret spectroscopy”

Dr. Artur Mardyukov, Germany
"Brushes exhibiting versatile supramolecular interaction structured via microcontact chemistry"

Organizers

APC Georgia

Partners

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