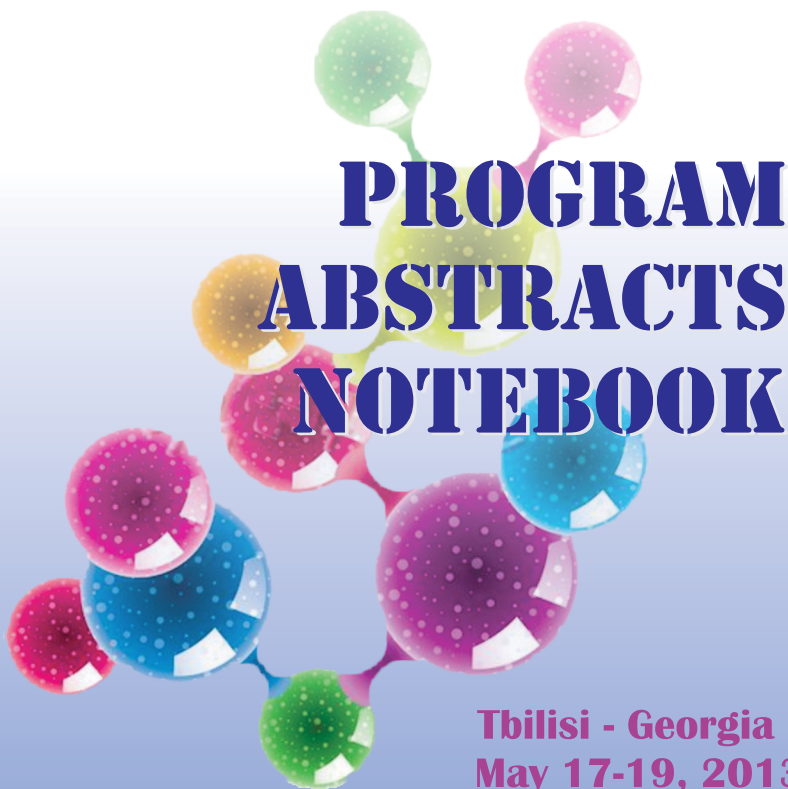


3-rd International Conference of Young Scientists



Georgian Technical University

Association of Professional Chemists
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**International Conference of Young
Scientists
“Chemistry Today – 2013”**

May 17-19, 2013

Georgian Technical University

Tbilisi, Georgia



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Schedule of Events

International Conference of Young Scientists
Chemistry Today – 2013
May 17-19, 2013
Georgian Technical University

May 17, 2013

9.00-10.00	Registration
10.00-10.30	Opening Ceremony
10.30-12.30	Invited Lectures
12.30-13.30	Coffee Break
13.30-15.30	Oral Session
15.30-16.00	Coffee Break
16.00-18.00	Oral Session
18.00-	Free Time

May 18, 2013

9.30-11.30	Oral Session
11.30-12.30	Coffee Break
12.30-14.30	Poster Session
14.30-15.30	Closing Ceremony
15.30-17.30	Lunch
17.30-20.00	City Tour

May 19, 2013

9.00-18.00	Excursion
18.00-	Departure

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Abstracts Book

Oral Presentations

International Conference of Young Scientists
Chemistry Today – 2013
May 17-19, 2013
Georgian Technical University

O1. ARYLGLYOXALS AND THEIR DERIVATIVES AS A VERSATILE REAGENT FOR SYNTHESIS OF FIVE-MEMBERED *N*-HETEROCYCLES*

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Five membered *N*-heterocycles are an important class of heterocycles found in numerous natural products [1], pharmaceuticals [2] and bioactive molecules [3] with antibacterial, antifungal and cytotoxic activities. They also serve as antibiotics [4] and glycosidase inhibitors [5]. They have a wide range of applications as organocatalysts [6], building blocks in organic synthesis [7], chiral auxiliaries and ligands for asymmetric synthesis. Many syntheses of five membered *N*-heterocycles have been reported [8].

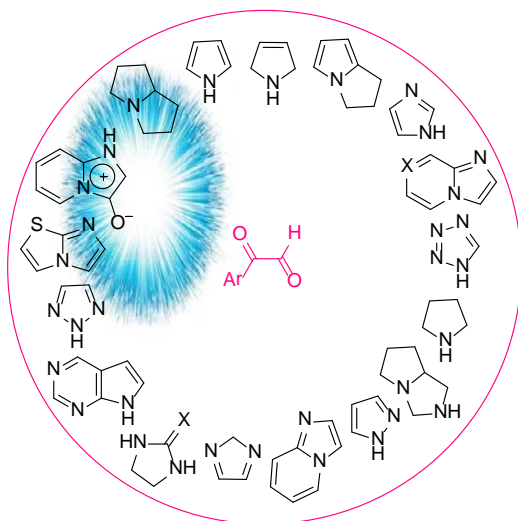
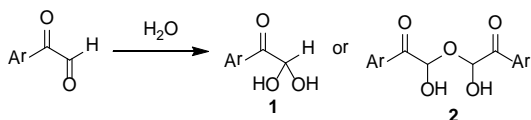


Fig. 1. The Synthesized Five-Membered *N*-Heterocycles Using Arylgyoxals

Phenylglyoxal [9], the simplest arylglyoxal, is a yellow liquid that polymerizes upon standing. By heating, the polymeric material cracks to give back the yellow aldehyde. Phenylglyoxal is recrystallized in hot water to form a colorless crystalline hydrate. Aryl glyoxal-hydrate appear to contain either one or one-half molecule of water and presumably have the structures **1** or **2** (Scheme 1) which upon heating, lose a molecule of water and regenerates the anhydrous arylglyoxal.



Scheme 1. Hydrate Forms of Aryl glyoxals

Aryl glyoxals (ArCOCHO) aromatic α -keto aldehydes, containing both aldehyde and ketone functional groups with different reactivity, are among the most attractive precursors, which are used to synthesize of heterocyclic compounds [10]. However, aryl glyoxals were used for synthesis of broad range of three-, four-, five-, six- and seven-membered heterocycles, herein, we described the uses of aryl glyoxals for construction of five-membered heterocycles such as pyrrolidines, pyrrolines, pyrroles, pyrrolizidines, pyrrolizines, indolizidines, pyrazolines, pyrazoles, imidazolidin-2, 4-diones, imidazolin-2-ones, imidazoles, 1, 2, 3-triazoles, tetrazoles, and fused imidazo-pyridines, pyrimidines, and pyrazines [10].

The aim of this review is covering the literature up to the end of year of 2011, showing the distribution of publications involving use of aryl glyoxals for preparing of five-membered *N*-heterocycles, which was elaborated using the Web of Science, ACS Publications, Wiley Online Library, Science Direct, RSC Publishing, Thieme Chemistry and other sites with the keywords *phenylglyoxal*, *aryl glyoxal*, *glyoxal*, *α -ketoaldehyde* and *1, 2- or α -dicarbonyl compounds* and from a selection of papers related to the synthesis of five-membered *N*-heterocyclic compounds starting with aryl glyoxals and their derivatives.

Figure 1 is illustrated the types of the five-membered heterocycles which were synthesized using aryl glyoxals *via* various type of reactions such as carbonyl-ene, 1, 3-dipolar cycloaddition, four component Ugi, cyclocondensation, Ugi-HWE, aldol-Paal-Knorr, Wittig-dehydrative cyclization and various multi component reactions.

In the current paper, I have presented an overview of the use of aryl glyoxals and their derivatives in synthesis of five-membered *N*-heterocyclic compounds.

Reactions of arylglyoxals were performed in two different ways: (a) reactions took place in more reactive aldehyde group and arylglyoxals have provided one atom in the ring of heterocycles to produce benzoyl substituent or (b) both aldehyde and ketone groups of arylglyoxals were contributed in reaction to provide two atoms of heterocycles rings. As broad spectrum of synthesized heterocycles using arylglyoxals and their derivatives, the reported methods could be interested in material science and medicinal and natural products synthesis.

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- * This abstract is part of our review article entitled: "Arylglyoxals in Synthesis of Heterocyclic Compounds" Chem. Rev.(2013); "Reprinted with permission from. Copyright (2013) American Chemical Society."
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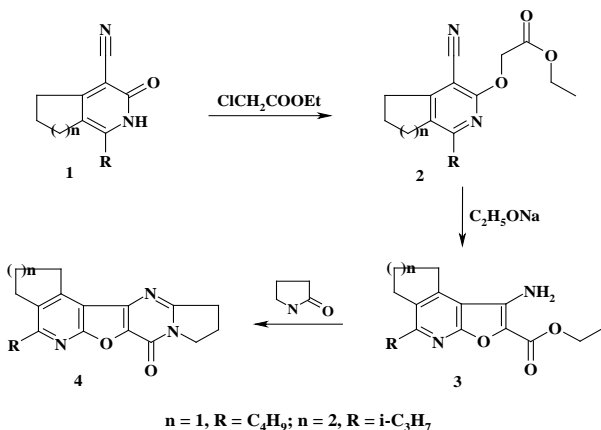
O2. NEW HETEROCYCLIC SYSTEMS BASED ON CONDENSED FURO[2, 3-b]PYRIDINES

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Furo[2, 3-*b*]pyridines are rarely found in naturally occurring alkaloids. However, there is growing interest in the synthesis of these compounds due to the discovery of several biologically active condensed derivatives [1-3].

We previously reported a method of preparing condensed furo[2, 3-*b*]pyridines from appropriate acyclic esters [4, 5]. The aim of this work is to extend this study for the synthesis of novel condensed furo[2, 3-*b*]pyridines. As starting compounds 1-butyl-3-oxo-3, 5, 6, 7-tetrahydro-2*H*-cyclopenta[*c*]pyridine-4-carbonitrile **1** and 1-isopropyl-3-oxo-2, 3, 5, 6, 7, 8-hexahydro-4-isoquinolinecarbonitrile **1** were used, which on interaction with chloroacetic ester were converted into the corresponding ethyl 2-(1-butyl-4-cyano-6, 7-dihydro-5*H*-cyclopenta[*c*]pyridin-3-yloxy)acetate **2** and ethyl 2-(4-cyano-1-isopropyl-5, 6, 7, 8-tetrahydro-3-isoquinolinylloxy)acetate **2**.



Cyclization of O-alkylated derivatives **2** in the presence of sodium ethoxide gave 1-amino-2-carbethoxyfuro[2, 3-*b*]pyridines **3**, which further were used for the

synthesis of new condensed heterocyclic systems. Thus, compounds **3** were cyclized in 4-butyl-2, 3, 7, 9, 10, 11-hexahydro-1*H*-cyclopenta[4', 5']pyrido[3', 2':4, 5]furo[3, 2-*d*]pyrrolo[1, 2-*a*]pyrimidin-7-one **4** and 5-isopropyl-1, 2, 3, 4, 8, 10, 11, 12-octahydropyrrolo[1'', 2'':1', 2']pyrimido[4', 5':4, 5]furo[2, 3-*c*]isoquinolin-8-one **4** by reacting with 2-pyrrolidinone in dichloroethane and in the presence of phosphorus oxychloride.

In the course of these investigations, potentially biologically active derivatives of condensed furo[2, 3-*b*]pyridines have been obtained, which show the promise of investigations in this area of heterocyclic chemistry. The synthesis of two new heterocyclic systems opens new possibilities for its development.

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03. SYNTHESIS OF NEW DERIVATIVES OF THREE NITROGEN ATOM CONTAINING TRICYCLIC SYSTEMS

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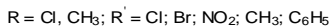
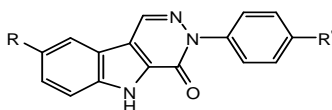
Among the compounds which participate in such natural processes that are important for life, nitrogen-containing heterocyclic compounds occupy considerable place, and especially indole-ring containing derivatives. It is conditioned by their special and various biological activities, which stipulate the vital processes. More than 1000 indolic alkaloids exist in nature.

There are many natural, synthetic and semi-synthetic compounds used in the medical practice. Among them are some well-known preparations like Mexamine, Rezerpine, Vinkristine, Cavintone, Indometacine, Inkazane, Pirazidole, and etc. The plant “*Streptomyces zebensis*” garners a lot of attentions, as it is the source of an active antibiotic CC-1065, which has high anti-cancer activity. This antibiotic contains three pyroloindolic fragments.

Unifying two or more heterocyclic fragments is quite interesting both from scientific and practical standpoint, as it gives the possibility to create new substances with a wide spectrum of physiological activity.

New indolic systems that contain different structural fragments were synthesized by the faculty of organic chemistry. Among them are tricyclic derivatives of pyridazino[4, 5-b]indole, bis-tricyclic isomeric bis-4-oxo-3H, 5H-pyridazino[4, 5-b]indoles and condensed pentacyclic pyridazinopyrrolopyridazinoindole. These compounds carry high potential not only as intermediate products, but also as a substance with a high pharmacological activity. It is known that the derivatives of pyridazino[4, 5-b]indole carry activities against Daun’s syndrome, Alzheimer’s and Parkinson's diseases.

Some of 2-Ethoxycarbonylindole-3-yl-aldehydes and their arylhydrazones are synthesized to discover new biologically active compounds. By intramolecular cyclocondensation of these arylhydrazones 3-aryl derivatives of 8-chlor- 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]indole are obtained by us. General preparative method for obtaining such type of compounds is developed, and Spectral data of obtained products is analyzed.

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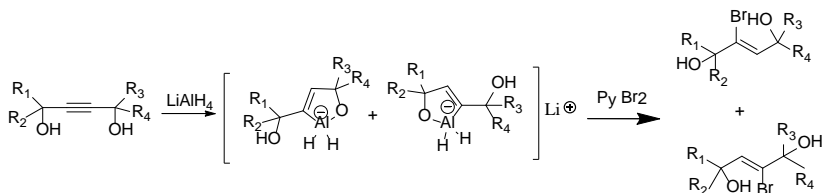
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O4. HYDROALUMINATION – BROMINATION OF ACETYLENIC γ -GLYCOLS

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The reaction of hydroalumination-bromination of substituted acetylenic γ -glycols has been studied. It has been found that the reaction of γ -acetylenic glycols with lithium aluminum hydride and further bromination of the intermediate aluminates with pyridinium dibromide leads to a mixture of regioisomeric bromoalkene diols with Z-configuration of the double bond.



The obtained results allowed to derive the following rule of thumb: the more substituents are at the hydroxyl group in the starting diol, the more is the product in which the bromine atom is at the β -carbon atom relative to the mentioned hydroxyl group. In contrast to the above, in the case of symmetrical secondary 1, 4-diols the reaction leads to a mixture of stereoisomeric bromoalkene diols with a ratio of 1:1; and in the case of phenyl substituents the reaction is not only regio-, but also stereoselective, and forms the bromoalkene diol where bromine atom is attached to the closest to the phenyl group carbon atom of the triple bond, i.e. bromine atom is attached to the sp -hybridized carbon atom adjacent to phenyl group. The same result was observed by us in the hydroalumination-halogenation of phenyl acetylenic α -alcohols [1, 2].

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O5. INDUSTRIAL SEWAGE-THE SOURCE OF ECOLOGICAL AIDS

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Galvanic and metallurgical industries annually release into the sea great quantities of valuable and scarce substances which could be recovered from this sewage for their industrial recycling. Heavy metal salts, acids, alkalis, oils, detergents from galvanic/metallurgical industry and ammonium chloride from cellulose industry aggravate the ecological situation becoming a menace to human health and marine life.

The aim of this study is the removal of metal ions, in particular, the ions of copper, zinc, chromium, iron, manganese and nickel from industrial sewage with the simultaneous metal concentration by electrodialysis method for turning out eco-pure water. The research was done on industrial electrodialysis plants (EDU) where the major component was ion-exchange membrane made by ion-exchange resins. The operation pack of the electrodialysis plant (EDU) is assembled from anionic (MA-40), cationic (MK-40) and bipolar membranes. To determine the most efficient electrodialysis scheme, the total of 12 schemes was put on trial with the seven of the tested schemes. By the utilization of reagent-free, environmentally friendly electrodialysis method to the salt solutions artesian and sea water we show the feasibility of the composite technology development for the manufacture of a number of products and the sea water rectification from galvanic industry sewage. Technological modes for these procedures on 12 electrodialysis schemes with the use of ion-exchange and bipolar membranes have been researched and developed. The most effective seven schemes have been chosen.

These schemes allow to simultaneously achieve several objectives within a single production cycle we: (a)clarified sea water contaminated with galvanic sewage from heavy metals; (b)we produced concentrated solutions of their salts for recycling into galvanic industry; (c) desalinated artesian and sea water, simultaneously produced fresh water, salt concentrate and a high quality acid and alkali in electrode chambers. Each of the developed technologies for each of the above objectives can have a particular industrial implementation where there are the same objectives to be achieved. It is feasible, cost-saving, and moreover it does not create any new ecologic problems but it solves the existing ones. The major feature is that all the set objectives are achieved in a single technologic cycle without an input of any chemical reagents.

O6. PERSPECTIVES OF USING CAP ROCKS OF BARITE-POLYMETALLIC DEPOSIT OF DAVID-GAREDJI IN GLASS AND CEMENT PRODUCTION

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In Georgia there is a deficit of high-conditioned raw materials intended for silicate production that hinders the development of manufacturing fields of glass containers and cement. Hence the usage of local cheap non-traditional raw materials and industrial waste is acquiring an especially actual character.

From this viewpoint very attractive by their mineralogical, petrographical and chemical composition are fieldspartic - quartz formations found in the south-east of Georgia, namely cap rocks of barite-polymetallic deposit of David-Garedji.

The interest to the detailed study of these rocks is due to several reasons:

First - searching for local cheap non-traditional raw materials for the purpose of rehabilitation of glass manufacturing in the country. Rocks having the above mentioned attractive mineralogical-chemical composition, namely quartz-adular metasomatites (hereinafter QAM) conform to operating standards made for fieldspartic-quartz raw materials. After the study it was stated that they are complex materials and contain all basic glass-forming oxides: SO_2 - 65-85%, Al_2O_3 - 6-14%, $\text{N}_2\text{O}+\text{K}_2\text{O}$ - 6-10%, Fe_2O_3 - O, 5-4%. They can completely or partly substitute expensive imported components such as alum earth, quartz sand and soda.

Second – it is actual the use of QAM in cement production as a partial substitute of clay components in the mixture of the clinker raw material. The content of BaSO_4 in QAM is considerably improving the clinker structure and is acting as a mineralizer, a modifier and an alloy at the same time.

Third – from the economic point of view it is very profitable to study cap rocks with subsequent processing because together with barite ore they produce complex deposit that increases the profitability of its processing.

Barite-polymetallic deposit of David Garedji is located in South Georgia – in Bolnisi region, on the right bank of the Mashavera River.

Cap rocks of the deposit are represented in multiple alternations of white, grayish, yellow-pinkish thin and medium-bedded rhyolitic tuffs, tuff silstones, volcanomictous sandstones. In an ascending section they are followed by rhyolitic lava layers, ignimbrites (pseudoringimbrites and welded tuffs) and coarse tuffs. The lower part of the described set of rocks following directly the ore-bearing barite layers with the secondary substitutions (hydrothermal metamorphism) corresponds to the facies of the secondary quartz rocks and in geological literature it is known as quartz-adular metasomatites. The upper part represented by chlorite-carbonate-zeolite facies answers a relatively low-temperatural process of propylitization.

By petrographic and petrochemical researches it was stated that the system of quartz-adular metasomatites is built of solid, metasomatically changed various lump biotite tuff and seldom hornblende biotite rhyolitic tuffs.

Cap rocks cover Barium ore tightly, as a result of which the baritization process in QAM rocks is spread with more or less intensity, though in the ascending section its downward trend is observed.

In laboratory conditions as a result of boiling at high temperatures light green glasses are obtained, the study of their technological properties stated the opportunity of using QAM in the production of colored glass containers. By introducing the above mentioned rocks into the glass mixture there will be completely excluded raw material containing alum earth from the latter and quartz and soda contents will be decreased by 50-60 % and 20-25 % accordingly.

07. PREDICTING SUPERCONDUCTING TEMPERATURE OF ELEMENTS FROM THEIR NEUTRON MASS

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Superconducting temperature of elements as a function of neutron mass in their nucleus is explored and modeled. Empirical observation shows that the more balanced the mass of neutrons is to that of protons in the nucleus, the higher is the superconducting temperature. A mathematical model for predicting superconducting temperature of elements is proposed using Coulomb's Force between incremental charge in nucleus and the outermost electron. The nuclear charge in the model is modulated for incremental neutron mass over protons' and the permittivity of neutron assumed to mask that of vacuum between the nucleus and the outermost electron. Coulomb force is shown to correlate linearly with superconducting temperature of elements for which temperature data was already available. A different linear equation explains the behavior when neutron mass is greater than protons' in the nucleus vs not. Model R^2 is 0.97 when neutron mass is greater and .65 when it is less than protons'. Using known mass of protons and neutrons, and distance to the outermost electron, superconducting temperature is predicted for all elements in the periodic table using the model even though actual data for superconducting temperature for most elements is not yet experimentally known. Seeming anomalies are highlighted. Trends are explained. Key areas for further investigation are outlined.

As for cement production the addition of QAM to the clinker mixture will cause the decrease of clinker burning temperature by 50-70 °C and the increase of the strength as of the earlier (3 days) as well as of the brand (28 days) cement compared with the clinker prepared on the traditional raw material

It should be noted that in glass production it is reasonable to use those parts of QAM of the cap rocks, where the content of BaO is relatively low – 2 mass %, but for producing straight cement the content of BaO can be ranged between 3-15 mass %.

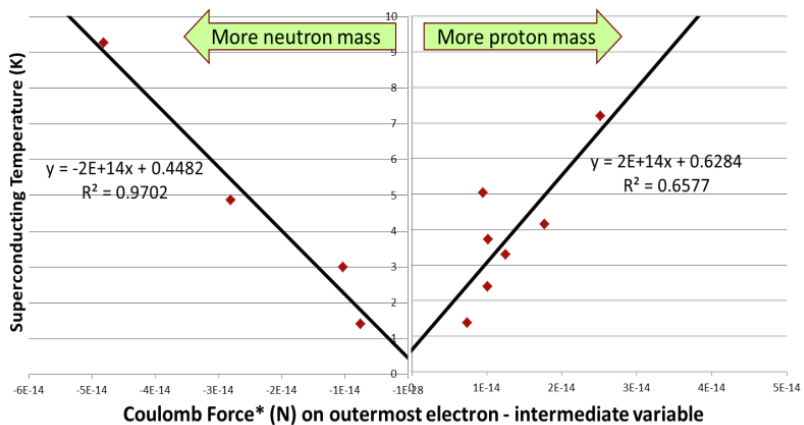


Fig. Coulomb Force, scaled for relative number of protons over neutrons, predicts superconducting temperature of elements.

08. REDUCTION OF PATULIN CONTENT IN APPLE JUICE USING ACTIVATED CARBON

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Patulin (4-hydroxy-4H-furo(3, 2c)pyran-2(6H)-one) ($C_7H_6O_4$) is a mycotoxin produced by several species of *Penicillium* and *Aspergillus* fungi, of which *P. expansum* is the most important common contaminant of damaged fruits such as apples. It is stable to heat processing at pH < 6. Patulin is gradually destroyed during storage in the presence of sulfites, sulfhydryl groups, and ascorbic acid [1].

Fermentation of apple juice to produce alcoholic beverages destroys patulin. Removal of the decayed portions from raw fruit prior to further processing has reduced patulin concentrations in the final fruit juice significantly [2].

Patulin contamination within apple products poses a serious health risk to consumers. Studies done on laboratory animals have demonstrated that patulin has a broad spectrum of toxicity, including mutagenicity and carcinogenicity. Patulin level has been regarded as a quality indicator for fruit used in the processing of apple juice.

Regulations for apple juice in several European countries recommended a maximum permitted level of 50 $\mu\text{g/l}$ as suggested by World Health Organization (WHO). Several countries have set even lower limits for patulin at 25 to 35 $\mu\text{g/L}$ [3].

We are unable to get the toxin-free products by means of industrial processing for apple products. Past researches have shown that patulin levels in apple juice can be reduced during pasteurization, addition of ascorbic acid, irradiation treatment and use of activated carbon [4].

In this study we used selectively acting activated carbon powder – Ercarbon SH (Erbsloh, Germany) for reduction of patulin in clear apple juice. The experiment was performed in Ltd “ Hipp Georgia”s quality assurance laboratory.

Industrial apple raw material with damaged parts was pressed and juice was pasteurized at 95°C during 2 min. After cooling on 55°C, enzymatic treated and clarified juice was filtered by 0.45 μm sizes filter. Apple clear juice sample was divided for 5

parts. The samples of apple juice were diluted to 11.5° Brix and contacted with concentrations of 2, 2.5, 3 and 3.5 g/l activated carbon for 30 minutes. Apple juice and activated carbon samples were agitated by using a magnetic stirrer at the same mixing rate. The samples were filtrated by Whatman filter paper.

In the experimental samples patulin content was determined by liquid chromatographic method (AOAC official method 2000.02). Apple juice samples were extracted with ethyl acetate and then cleaned up by extraction with sodium carbonate solution. The ethyl acetate extract was dried with anhydrous sodium sulphate. After evaporation of the solvent, patulin was quantitatively determined by HPLC with UV-detector at 276 nm and the results are shown in table.

Table. The content of patulin in apple juice samples

Sample No.	Time min	Peak Name	Area mAU*min	Height mAU	Amount ppb
1 (without AC)	8.43	PATULIN	19.693	129.758	200.2573
2 (2 g/l AC)	8.44	PATULIN	4.289	30.729	43.6364
3(2.5 g/l AC)	8.44	PATULIN	2.751	15.714	27.8927
4(3 g/l AC)	8.44	PATULIN	1.248	7.273	12.6776
5(3.5 g/l AC)	8.44	PATULIN	0.593	3.248	5.9808

By the received results were determined that, the content of patulin (ppb) in clear apple juice was decreased: 78, 86, 93 and 97%.

Our results show that the use of powdered activated carbon is very effective in declining the patulin content in the apple juice.

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09. ADVANCED METHOD FOR WASTE WATER TREATMENT BY FENTON REAGENT

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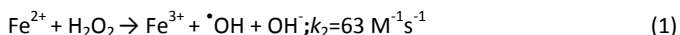
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Fenton reaction involves interaction between iron (II) ions and hydrogen peroxide yielding hydroxide radical able to destroy POPs.

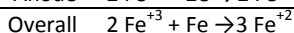


This process is widely used for the waste water treatment. Continuous supply of Fe (II) ions to waste water reactor is a critical factor in treatment technology. Present paper focuses on the novel autocatalytic method of regeneration of Fe (II) ions. Technology has advantages in comparison to the widely used photo- and electro-fenton technologies. In the previous method Fe (III) ions are reduced under absorption of the irradiation energy:



The method fails to provide stable decomposition of contaminants in case of coloured waste waters and consumes energy to feed electric lamps. The other method – electro-fenton also requires energy necessary for reduction of Fe (III) to Fe (II) at the cathode covered by expensive catalyst (IrO-Ti alloy).

In the present study we proposed novel *in situ* technology for regeneration of Fe (II) ions free from above described disadvantages. Method utilizes process of autocatalytic corrosion of iron; in presence of Fe (III) ions iron metal corrodes via autocatalytic heterogeneous electrochemical disproportionation reaction which involves steps of anodic dissolution of iron and cathode reduction of Fe (III) ions:



Overall reaction proceeds spontaneously without consumption of external energy. As follows from figure, autocatalytic method leads to considerable decrease of time during which mineralization of persistent organic pollutant take place.

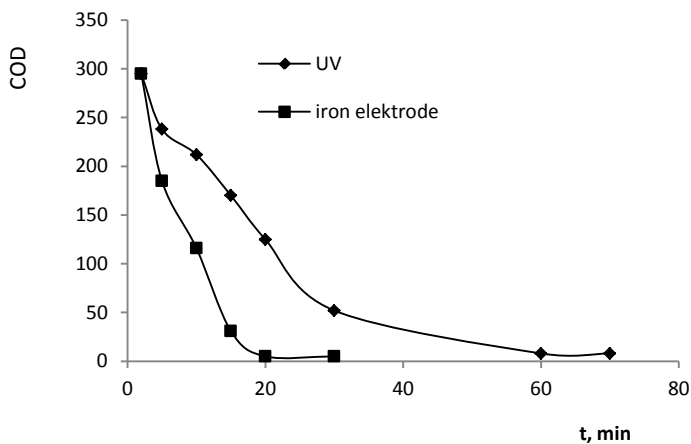


Fig. Variation of chemical oxygen demand with treatment time under UV irradiation and iron autocatalytic corrosion action. Water is contaminated by 70ppm phenol

O10. NEW APPROACH TO THE DESIGN OF ARGININE CONTAINING CATIONIC POLYMERS

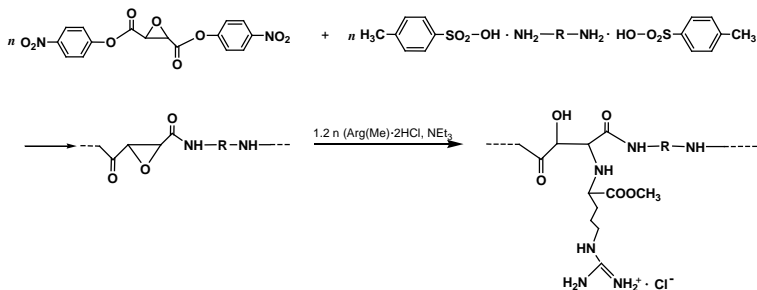
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Polycationic polymers have shown significant promise as non-viral gene delivery vector. However, these gene carriers are not fully satisfactory yet. The basic limitations in the use of synthetic vectors for gene therapy are connected with their poor transfection efficiency and high cytotoxicity; many of them are not biodegradable and cannot be cleared from the body. Thus, the creation of new synthetic carriers is topical. Among synthetic transfection agents those composed of α -amino acid arginine (Arg) are of special interest due to a high transfection activity of the guanidine group [1].

We have elaborated a new two stage/one pot strategy to the synthesis of biodegradable cationic polyamides containing arginine covalently attached to the macromolecules, depicted in scheme below:



Scheme. One-pot synthesis of Arg-containing polymers

In this presentation we are reporting on the synthesis and cytotoxicity study of poly(ethylene malamide) (R= CH₂-CH₂) containing L-arginine methyl ester covalently attached to the macrochains in β -position of malic acid residue *via* α -amino group.

The new Arg-containing cationic polymer showed excellent water solubility, formed nano-complexes with pDNA at much lower Polymer/DNA weight ratios (WR=5-10) compared to the Arg-based polymers (WR=300-1000) obtained previously [2, 3], and demonstrated a high *in vitro* cytocompatibility with Chinese Hamster Ovary (CHO) and insect Schneider 2 (S2) cells within the concentration range 0.02-500 mg/mL for 24 h (Fig.).

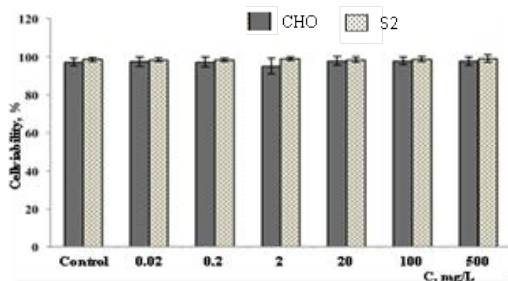


Fig. CHO & S2 cells viability

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O11. NEW BIODEGRADABLE ABA TRIBLOCK AMPHIPHILIC COPOLYMERS AS MICELLAR NANOCARRIERS FOR SPARINGLY SOLUBLE PHARMACEUTICALS

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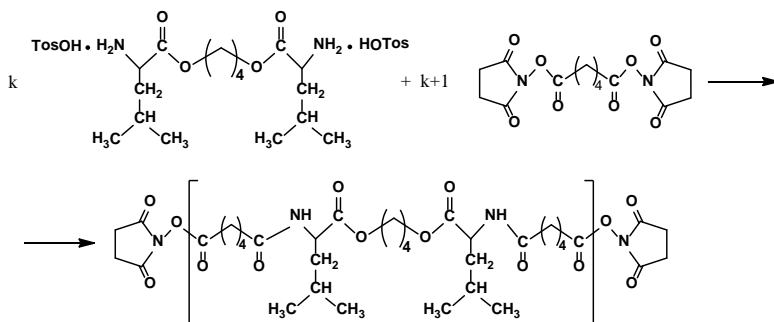
Over the past several decades self-assembled systems at the nanometer scale with unique morphologies and functions have attracted much attention especially in biomedical fields as water-miscible carriers [1], contaminants removers [2] etc. Among these systems polymeric micelles (micelles formed by amphiphilic block-copolymers) are gaining an increasing popularity as pharmaceutical carriers for poorly soluble drugs [3] due to the series of attractive properties as drug carriers, such as reasonable stability both *in vitro* and *in vivo*, and ability of solubilization of various sparingly soluble pharmaceuticals. These micelles can also be used for targeted drug delivery. It is also desirable to have nanocarriers that can be cleared from the body after their function is fulfilled, i.e. to be biodegradable. Only a few amphiphilic block-copolymers were reported capable to form stable micelles with good solubilizing properties. Therefore, the search for new micelle-forming polymers is still topical. While the poly(ethylene glycol) (PEG) still represents the most popular biocompatible hydrophilic block, various hydrophobic blocks can be attached to it. Among these hydrophobic blocks the most promising look nontoxic and biodegradable ones.

In the present paper we are reporting on preliminary data of the successful synthesis of a new class of biodegradable micelle-forming block-copolymers composed of PEG, amino acids and other nontoxic building blocks like fatty diols and dicarboxylic acids. For constructing this new class of biodegradable block-copolymers, we decided to use amino acid-based biodegradable poly(ester amide)s (PEAs) as hydrophobic blocks since these polymers showed reasonable biodegradation rates and excellent biocompatibility [4, 5]. In the present study, the hydrophobic PEA block

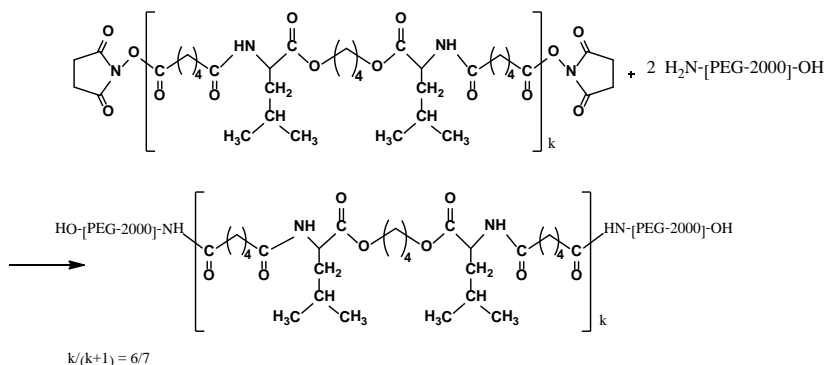
composed of adipic acid, L-leucine and 1, 4-butanediol was exploited.

Among various schemes, we have examined for the synthesis of micelle-forming block-copolymers, the best was found to be the two-step method comprising the synthesis of intermediate oligomeric PEA with two activated N-oxysuccinimidyl ester terminal groups (Step 1 in Scheme 1 below) with subsequent interaction with 2 moles of amino-PEG-2000 (Step 2 in Scheme 1) that results in ABA triblock-copolymer. The intermediate oligomeric PEA was prepared by solution polycondensation of di-p-toluenesulfonic acid salt of bis-(L-leucine)-1, 4-butylene diester, Leu-4, with the excess of di-N-oxysuccinimide adipate, SIA. The mole ratio Leu-4/SIA = 6/7 was selected to obtain oligomeric PEA with an average MW of 4245.8 Da close to the molecular weight of 2 moles of amino-PEG-2000.

Step 1



Step 2



This ABA triblock-copolymer was tested for the micelle-forming property. For this, 20 mg of the polymer was dissolved in 10 mL of distilled water and analyzed using DLS. According to this preliminary study the micelles size at the given concentration was 5 nm. The critical micelle concentration (CMC) of obtained micelles was 0.25mM. We assume that the micelles are formed by the folded molecules.

A systematic study (that includes the measurements of CMCs and zeta-potentials) of the micelle-forming properties of the new block-copolymer depending on the size of the hydrophobic PEA block is in progress now.

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O12. SYNTHESIS OF THE NOVEL CATIONIC CHARGED OCTAHEDRIC Co(III) COMPLEXES

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In the fast growing field of asymmetric organic catalysis, designing of chiral organic anions used as stereoinductors in reactions proceeding via cationic transition states is a recent up-to-date trend [1]. At the same time asymmetric catalysis with chiral metalcomplex cations as stereoinductors still remains relatively unexplored [2].

Our work is devoted to synthesis of new bis-salicylidene octahedral cation Co^{III} complexes which can be used as catalysts for the asymmetric formation of C-C bonds in future.

For creating a new type of compounds we used ligands composed of cyclohexane-diamine and various derivatives of salicyl aldehyde (3-OMe, 3-allyl, etc.).

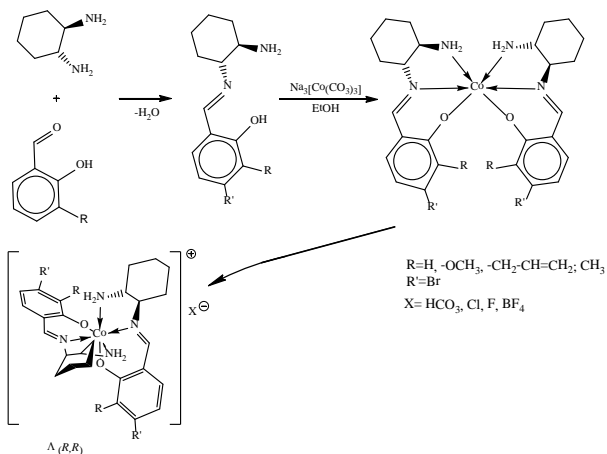


Fig.1. Synthesis of new chiral cationic complexes

It should be noted that we were able to get X-chiral complexes of Co^{III} cations and

studied their structure by physicochemical analysis methods.

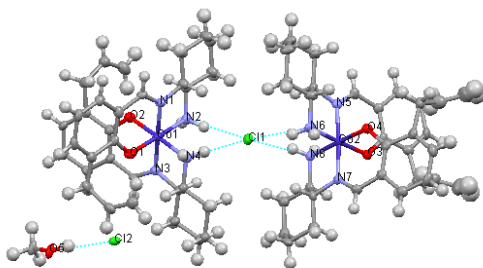


Fig.2.The X-ray structure of the chiral cationic Co^{III} complex

NMR spectra of the complexes with various achiral anions have different values of chemical shift of the amino group NH. (e.g. modified bis-salicylidene octahedral cation Co^{III} complexes with cyclohexanediamine and salicyl aldehyde in the chiral ligand as well as Cl⁻ or F⁻ achiral anions) Fig.3.

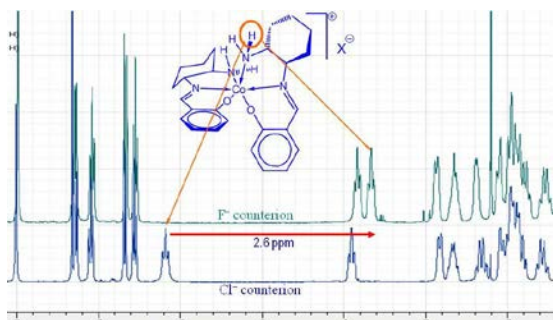


Fig.3 NMR spectra of the chiral cationic Co(III) complex with different counterions

This phenomenon can be explained by the presence of strong hydrogen bonds between counterions and protons of the amino group.

We can conclude that they possess Brønsted acids properties and these cationic complexes are organic Brønsted acids, which are activated by metal. Hence, we can use them as catalysts in the asymmetric catalytic reactions.

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O13. RISK OF CHAKVISTSKALI AND KHOROGLISTSKALI RIVERS BY PESTICIDES

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Among the most important land pollutants are widely met carcinogenic substances, to which belong such stable organic pollutants, as chloroorganic pesticides and polychlorinated biphenyls.

Pesticides represent the large group of artificially created substances, which are used for reducing the amount of rodents (insecticides) mushrooms (fungicides) weed plants (herbicides) in order to increase in productivity of agriculture etc. Though, their use is profitable from the economic standpoint, since they increase the productivity, exterminate the pests and rodents but on the other hand they cause the reduction of value of food products.

At present more than 5 mln tons of pesticides are available at the world market. According to the Custom department of Georgia, in 2005 705, 5 tons of plant-protecting agents of various name, 27, 5 tons of insecticides of various name, 657 tons of fungicides, and 21, 0 tons of herbicides have been imported in the country.

In 2006, 2800 hectares of arable lands and 8800 hectares of perennial plantings have been processed by pesticides. Amount of out of date pesticides found out in former storage facilities reached 15 tons.

Stable organic pollutants are transformed in the soil under the influence of microorganisms. Depending on conditions, their decomposition occurs both via oxidation, and via reduction mechanisms. Under aerobic conditions takes place the decomposition by oxidation, while under anaerobic – by reduction. For instance, DDT is transformed in DDD. As one can see, not only pesticides are hazardous, but their metabolites, too. That's why when selecting pesticides should be taken into account their degradability, rate of decomposition, influence on useful organisms, soil type and so on. These characteristics are different for various pesticides.

O14. THE PROSPECTIVE ADDITIVE IN CEMENT PRODUCTION

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There should be occupied an important place by a thermal energetic in Georgian energetic potential. This will be an essential step to solid fuel mining. TKbibuli activated coal quarry production have given us opportunity to replace totally or partly an expensive and scarce gas fuel. Currently the local cement industry is using the Tkibuli coal as a fuel of clinker production. Accordingly, the equipment of the plants has been upgraded. Also in the plants has been installed a new coal mill and its facilities. Besides, a thermal electric station has been activated in Tkibuli and it had been decided to open the same station in Gardabani. Mentioned thermal electric stations use Tkibuli coal.

There is created an ash after coal burning (especially Tkibuli coal) which utilization is necessary from economic, ecologic and other points of view. The ash is an active hydraulic additive which might be used in cement production, particularly in cement grinding. Herewith, the ash fits the standard of active hydraulic additive and gives opportunity to replace other nonstandard additives.

The presentation describes quantity of the ash as an additive, raw coal portion in the burnt ash and other factors which influence final product quality.

It is determined that the raw coal portion in the burnt ash must up to 2%. And it is possible to add 10-30% of the ash in cement without any negative influence on cement characteristics.

O15. THE ANALYSIS OF A CHEMICAL COMPOUND OF FRUITS AND CORNELL STONES (A CORNELL ORDINARY OR MAN'S - (CÓRNUS MAS L.) FAMILY DOGWOOD) EXTENDED IN THE FORM OF NATURAL THICKETS IN EAST GEORGIA

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Cornelian cherry is widespread in Central Asia, on Caucasus, in Moldova, to Crimea. Natural thickets of a Cornelian cherry dogwood widespread in Georgia. Grows highly in mountains and on edges of woods, coast of the rivers, places forms small thickets. Fruits are edible, juicy, sweet-sour, knitting, pleasant on taste, and after frosts their taste considerably improves.

Fruits Cornelian cherry dogwood are considered valuable in the biological relation. In their pulp contains: from 10 to 17 % of sugar (glucose and fructose); to 3.5 % of organic acids (apple, lemon, amber); tannin content, pectinaceous and nitrogenous substances, flavonoids (1-5 %); vitamins C (50-160 mg of %) and P, provitamin A; essence. Among the minerals which are to this tasty berry, it is necessary to allocate iron, калий, phosphorus, sodium, calcium and magnesium.

The cornel sometimes surpasses a black currant in the maintenance of vitamin C - in 100 g its berries 50 mg of ascorbic acid contain.

Cornel stones contains up to 34 % fat oils. A bark contains Glycoside Corinne, tannins, apple and other organic acids and leaves - vitamin E.

From stones pressing also received fat oil, cornel Berries (extended in the form of Natural thickets in east Georgia) contain to 150mr vitamin C %, vitamin P and carotine, fruit acids (to 5 %): apple, amber and lemon, about 17 % of glucose and fructose, nitrogenous and pectinaceous substances (to 0.9 %) essence, flavonoids (to 4 %) painting and tannins.

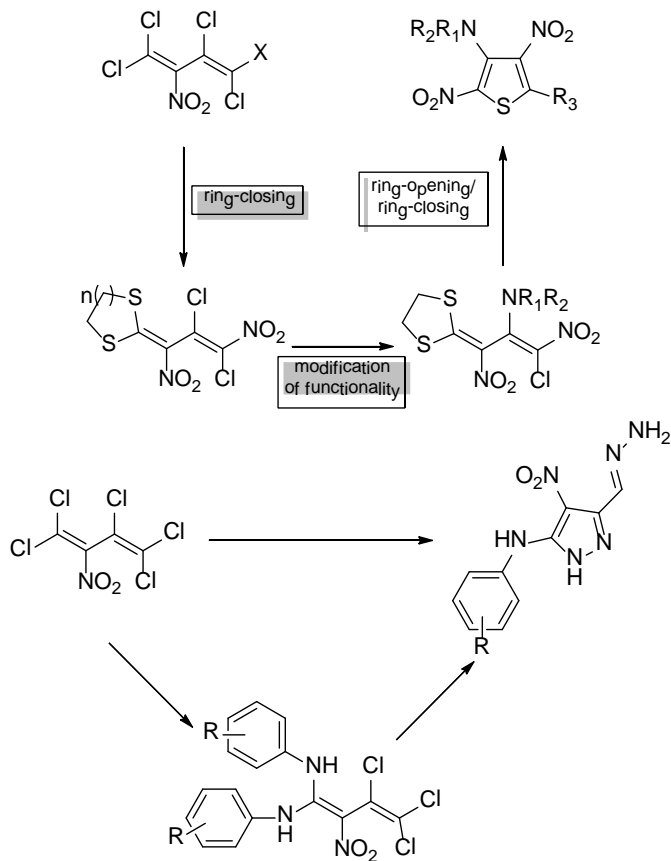
O16. HIGHLY EFFICIENT SYNTHESIS OF 5-MEMBERED HETEROCYCLIC COMPOUNDS

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Design and utilization of novel multi-functionalized synthons constitutes a powerful strategy to build useful molecules, especially 5-membered, 6-membered, and even 8-membered cyclic structures [1]. Polyhalogenated nitrobuta-1, 3-dienes are a unique class of alkene derivatives that have been recognized as a versatile synthon in organic synthesis [2]. Significant substitution effects have been observed and published [3] on the reactivity of these synthons containing two electron-withdrawing groups (EWGs). The vinylic S_N reaction of a unique class of alkene is one of the most fundamental approaches for the formation of new carbon-carbon and carbon-hetero atom bonds [4] enables a new bond selectively at the β position of the electrophilic alkenes in which the EWGs act in concert for maintenance of the regioselectivity of the molecule.

As part of our research to develop dithiolanes and 1, 1-diamino substituted polyhalogenated nitrobuta-1, 3-dienes for the construction of diverse carbo- and heterocyclic structures, we have reported the synthesis of highly substituted perfunctionalized thiophenes, pyrazoles. The results herein enlighten an original and attractive access to the 2, 4-dinitrothiophenes and 5-amino-4-nitropyrazole, which originates from the functionalized dinitrobutadienic building block whose key point is represented by nitro groups serving activating functionality of chloro atoms on C-1 to facilitate the synthesis of dinitrothiophenes, easily. Due to their high functionality, these 5-sulfanyl substituted 3-amino-2, 4-dinitrothiophenes and 5-amino-4-nitropyrazole are valuable building block for the predictable synthesis of bioactive heterocycles with high synthetical potential.



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**O17. COMPARATIVE HIGH-PERFORMANCE LIQUID
CHROMATOGRAPHY ENANTIOSEPARATIONS ON
POLYSACCHARIDE BASED CHIRAL STATIONARY PHASES
PREPARED BY COATING TOTALLY POROUS AND CORE-SHELL
SILICA PARTICLES**

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This work reports comparative high-performance liquid chromatographic separations of enantiomers with chiral stationary phases (CSPs) prepared by coating cellulose tris(4-chloro-3-methylphenylcarbamate) (Fig. 1) on totally porous and on core-shell type silica of comparable particle diameter. Benzoin (a) trans-stilbene oxide (b) and 2,2-dihydroxy-6,6-dimethylbiphenyl (c) (Fig. 2). Several interesting observations were made: (1) the selectivity of separation was higher on core-shell type CSP compared to totally porous CSP at comparable content of chiral selector (polysaccharide derivative); (2) Much flatter dependence of plate height on the mobile phase flow rate was observed for columns packet with CSP prepared with core-shell silica compared to the ones packed with CSPs prepared with totally porous particles; (3) at low mobile phase flow rates core-shell CSP provided lower resolving ability compared to a commercially available CSP having four times higher content of chiral selector along with higher retention of chiral analytes. However, at high flow rates core-shell type CSP performed similarly or better than the commercial column in regards of plate count (N) and peak resolution (Rs) per column length and within a given total analysis time. The advantage of CSP prepared with core-shell silica is obvious from the viewpoint of plate numbers and resolution calculated per unit time (i.e. speed of analysis).

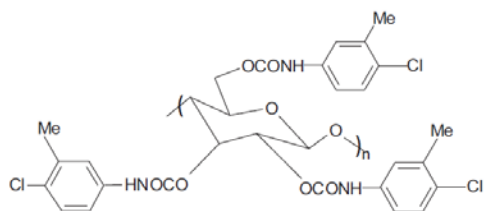


Fig.1 Cellulose tris(4-chloro-3-methylphenylcarbamate)

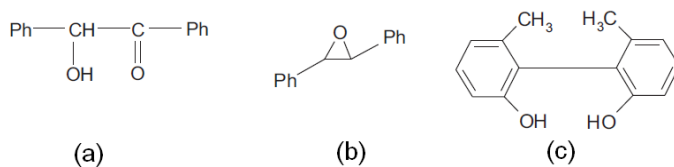


Fig.2 Benzoin (a) trans-stilbene oxide (b) and 2,2'-dihydroxy-6,6'-dimethylbiphenyl (c)

Abstracts

Poster Presentations

*International Conference of Young Scientists
Chemistry Today – 2013
May 17-19, 2013
Georgian Technical University*

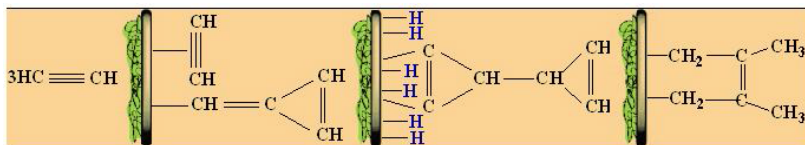
P1. HYDROOLIGOMERIZATION OF ACETYLENE FROM ELECTROCRACKING GAS OVER Ni/CNFS CATALYST

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Carbon nanofibers (CNFs) supported nickel catalysts (Ni/CNFs) for hydrogenation of hydrocarbons were prepared by a slurry type impregnation procedure method for the reaction of electrocracking gas in the presence of acetylene and hydrogen in a flow system are investigated. Samples containing 5.0 wt% Ni are capable of complete acetylene conversion over a period of 5 h at 170 °C when using a 27-29% C₂H₂ and 61-64% H₂ from the percentage of composition of electrocracking gas diesel fraction feed stocks. The amount of ethane and ethylene equivalent to approximately half of acetylene converted with propane, propylene and methane formation low, As well as the remaining percentages of acetylene converted into higher hydrocarbons through hydrooligomerization.

Predominant product distributions are linear alkenes (C₄₊-C₅₊) followed by branched alkenes (isobutene and isopentene) traces of dienes. Other products, that appear are liquid hydrocarbons or (green oils). Catalytic experiments were performed in a fixed bed reactor at atmospheric pressure, using gas hourly space velocity (GHSV) in 5920 h⁻¹ (30 ml/min) of feedstock gas.



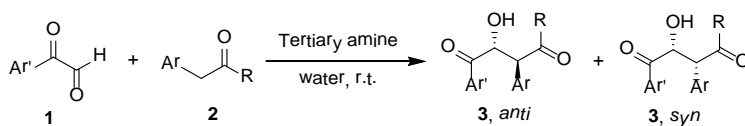
P2. STEREOSELECTIVE SYNTHESIS OF β -HYDROXY KETONES VIA TERTIARY AMINE CATALYZED ALDOL REACTION IN WATER

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β -Hydroxycarbonyl compounds are found in several natural and un-natural compounds, which exhibit wide range of biological activities, such as antibiotic and anti-cancer activities [1], and also are important building blocks in the synthesis of polyfunctional compounds and natural products [2]. Therefore, the syntheses of β -hydroxycarbonyl compounds gain considerable attention in organic synthesis. The aldol reaction is one of the most versatile synthetic tools for construction of C—C bonds in organic synthesis [3], which led to formation of β -hydroxycarbonyl structural units. Not only reactions in water exhibit interesting reactivity and selectivity, which are different from conventional organic solvents, but also water is one of the most abundant and cheap solvents, and makes the reactions environmentally amenable, much safer and easier to handle [4]. Therefore, the organic reactions in aqueous media have attracted much attention in synthetic organic chemistry [5].

In continuation of our works on arylglyoxals chemistry [6], herein we wish to report the syntheses of β -hydroxycarbonyl compounds *via* direct aldol reaction of ketones with arylglyoxals hydrate in water in the presence of catalytic amount of a tertiary amine (scheme).



Scheme. Tertiary Amine Catalyzed Aldol Reaction of Arylgyoxals

We first studied the aldol reaction in water in the presence of different tertiary amines such as Et₃N, DMAP and DABCO, and also NaOH at room temperature. When DABCO was used, corresponding β -hydroxycarbonyl compounds **3** were obtained in excellent yields with good to excellent stereoselectivity. The reactions were carried out by addition of DABCO to a mixture of **1** (0.5 mmol) and **2** (0.5 mmol) in water and stirred at room temperature for appropriate time.

Electron-withdrawing substituted phenylglyoxals such as 4-Cl and 4-Br worked as well as electron-donating substituted phenylglyoxals such as 3-MeO, 4-MeO and 3, 4-(MeO)₂ in DABCO-catalyzed aldol reaction in water. Phenyl-, 4-Cl-phenyl- and 4-Br-phenylglyoxals underwent aldol reaction with excellent *syn*-selectivity, while electron-donating substituted phenylglyoxals afforded corresponding β -hydroxycarbonyl compounds **3** as a mixture of two stereoisomers (*syn* and *anti*).

As shown in figure, the *syn/anti* ratio was determined by ¹H NMR, using the intensity of the H_a for two isomers. The coupling constant (³J_{H_a, H_b) for signal of the *anti*-isomer is higher than that of the *syn*-isomer. According to the ¹H NMR spectrum, the H_a signal for the *syn*-isomer has a higher δ value than that for the *anti*-isomer. For instance, in the ¹H NMR spectra of 2-hydroxy-1, 3-bis(4-methoxyphenyl)pentane-1, 4-dione, the signal at $\delta = 5.78$ ppm (³J_{H_a, H_b = 4.4 Hz) is contributed by the *syn*-isomer, while the one at 5.28 ppm (³J_{H_a, H_b = 5.6 Hz) is contributed by the *anti*-isomer.}}}

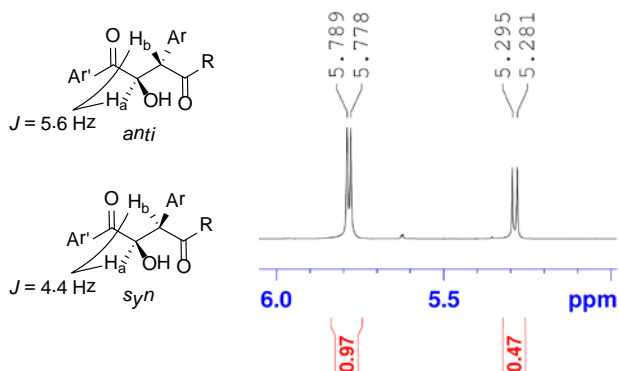


Fig. Identification of *Anti* and *Syn* Isomers by ¹H NMR

Another characteristic feature of the present protocol is the high chemoselectivity of the aldol reaction toward phenylglyoxal, in preference to benzaldehyde. When aldol reaction of phenylglyoxal with **2** in the presence of 1 equiv. of benzaldehyde was carried out under same conditions, only **3** was isolated and benzaldehyde was recovered without changes.

In conclusion, a new green and simple methodology for construction of β -hydroxycarbonyl along with γ -diketonestructural motifs was developed. Reactions were carried out in water at room temperature using DABCO as catalyst. Electron-withdrawing substituted phenylglyoxals afforded the β -hydroxycarbonyls with excellent

syn selectivity, while arylglyoxals with electron-donating substituents gave corresponding β -hydroxycarbonyls as a two diastereoisomers with ratio of about 2/1 of *syn/anti*.

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P3. SYNTHESIS OF *N*-PHENYL SUBSTITUTED DIHYDROPYRIDINES POSSESSING (2-PYRON-3-YL)VINYL MOIETY VIA $ZrOCl_2 \cdot 8H_2O$ -CATALYZED HANTZSCH REACTION

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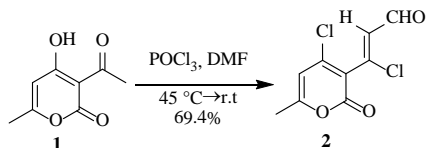
The 4-aryl-substituted 1, 4-dihydropyridines (1, 4-DHPs) are among the most studied heterocyclic compounds that present interesting pharmacological and biological properties [1]. They have been used as organic calcium channel modulators [2], antidiabetic [3], antiviral [4], antitumor [5], antioxidant [6], and anti-inflammatory agents [7]. Therefore, the development of new synthetic methods leading to 1, 4-DHPs with different substituents [8] or heterocycles [9] has attracted much attention in organic synthesis. The Hantzsch synthesis is a classical method for the preparation of 1, 4-DHPs [10] and has been one of the most important basic reactions in organic chemistry for its use in pharmaceutical synthesis. However, due to the drastic reaction conditions, long reaction times, and low yields, the classical Hantzsch reaction was modified by several methods [11].

Due to their easy availability and low toxicity, Zr(IV) salts have recently attracted much attention as a catalyst for organic transformations [12]. To our knowledge, there have been only a few reports on the metal oxysalt-based organic reactions.

As part of our research on synthesis of pyrone derivatives [13], herein we wish report the synthesis of β -chloroacrolein with 2*H*-pyran-2-one moiety **2**, and its uses in a simple and environmentally benign synthesis of new *N*-phenyl dihydropyridines possessing 2-pyrone moiety *via* Hantzsch reaction between β -chloro acrolein **2**, aniline and β -keto esters at room temperature using $ZrOCl_2 \cdot 8H_2O$ as catalyst.

β -Chloroacrolein **2** was synthesized from commercially available dehydroacetic acid **1** in 69.4% yield *via* Vilsmeier–Haack reaction as outlined in Scheme 1. The structure of compound **2** was established from FT-IR, 1H NMR, ^{13}C NMR, 2D-NMRs (HMQC and HMBC) and mass spectral data and elemental analyses. The values of coupling constant 3J of the proton signals of $=\underline{C}H-CO-\underline{H}$ in the 1H NMR spectra equal to 6.8 Hz indicate that these atoms are located in the *S*-cis position [14]. It was shown by the study of isomer composition of β -aryl- β -chloroacroleins, arising from aryl ketones [15] in the reaction with Vilsmeier-Haack reagent, α -unsubstituted acroleins are

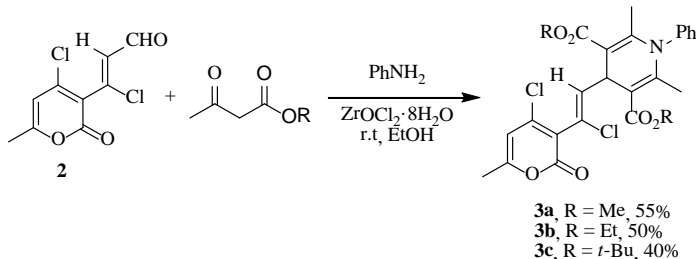
obtained exclusively as a Z isomer. Therefore **2** has S-cis-Z-configuration at the side chain.



Scheme 1. Synthesis of β -chloroacrolein **2**

Methyl, Ethyl and *t*-butyl acetoacetate were treated in the Hantzsch reaction with **2** and aniline, catalyzed with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in ethanol at room temperature in 25 min, and corresponding dihydropyridines **3a-c** were obtained in 40-55% yields (Scheme 2). The reactions were carried out by addition of 1 mmol of **2** in a solution of 2 equiv. of β -keto ester and 1 equiv. of aniline in EtOH and stirring at room temperature for appropriate time.

The structure of products **3a-c** was established from FT-IR, ^1H NMR, ^{13}C NMR and elemental analyses.



Scheme 2. Synthesis of *N*-phenyl substituted dihydropyridines possessing β -chloroacrolein at C4-position

In summary, a β -chloroacrolein possessing 2-pyrone moiety **2** was synthesized and treated with β -keto esters and aniline under Hantzsch reaction conditions to afford corresponding dihydropyridines in moderate to good yields.

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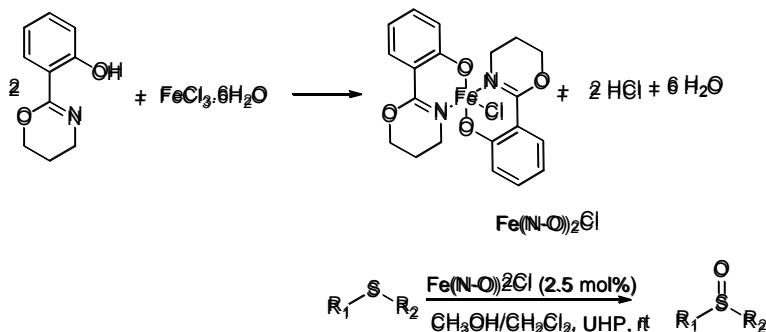
**P4. A NOVEL IRON(III) COMPLEX CONTAINING AN N, O- TYPE
BIDENTATE OXAZINE LIGAND AS CATALYST FOR THE SULFIDE
OXIDATION**

M. Amini

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The selective oxidation of sulfide to sulfoxides remains a challenge and is of interest because of the importance of sulfoxides and sulfone as synthetic intermediates towards the synthesis of various agrochemical and pharmaceutical products and biologically active molecules [1]. Although a variety of catalytic systems have been used to achieve this conversion [2], most are associated with drawbacks such as long reaction time, harsh reaction condition, expensive and toxic catalyst, and low selectivity.

We recently reported highly efficient method for the oxidation of sulfides by using of a Fe(III) complex with salicylidene benzoyl hydrazine as ligand [3]. In order to study the effect of the ligand and complex structure on catalytic reactivity, herein we describe the synthesis of a new Fe(III) complex [Fe(N-O)₂Cl] ((N-O)=2-(2'-hydroxyphenyl)-5, 6-dihydro-1, 3-oxazine) and the use of this complex as a catalyst in the oxidation of sulfides in the presence of urea hydrogen peroxide (UHP) as an oxidant under air at room temperature (scheme). This is the first report on the catalytic activity of anoxazine- Fe(III) complex in oxidation reactions.



Scheme. Synthesis and catalytic activity of [Fe(N-O)₂Cl] complex.

The reactions of FeCl₃·3H₂O and 2-(2'-hydroxyphenyl)-5, 6-dihydro-1, 3-oxazine (N-

O) as a bidentate O, N donor ligand afford a five-coordinated iron(III) complex $[\text{Fe}(\text{N}-\text{O})_2\text{Cl}]$ with the distorted trigonal-bipyramidal configuration. Complex $[\text{Fe}(\text{N}-\text{O})_2\text{Cl}]$ were isolated as air-stable crystalline solids and fully characterized, including by single-crystal X-ray structure analysis (fig.). The complex crystallizes in the monoclinic crystal system and space group $P 1 21/c 1$. The structure shows that the two ligands are coordinated to iron in the expected bidentate fashion through O and N. The coordination geometry of iron may thus be described as trigonal bipyramidal with near C_2 symmetry. The oxygen donor and chloride ions occupy three equatorial sites and the nitrogen donors occupy the two axial positions.

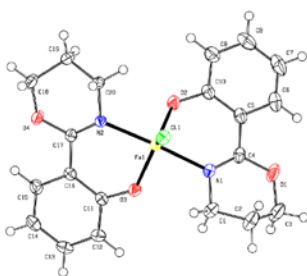


Fig. ORTEP diagram of the complex $[\text{Fe}(\text{N}-\text{O})_2\text{Cl}]$ with thermal ellipsoids are drawn

Complex $[\text{Fe}(\text{N}-\text{O})_2\text{Cl}]$ shows very efficient reactivity in the oxidation of sulfides to their corresponding sulfoxides using urea hydrogen peroxide (UHP) as the oxidant at room temperature under air. Arylalkyl, arylbenzyl, dibenzyl, diaryl and dialkyl sulfides underwent clean and selective oxidation to the corresponding sulfoxide under air, in impressive selectivity (86-99%). Significantly, the very good conversions of substrates depending on the nature of the sulfide, in the range of 63-91% (TON=11.4-18.2) were obtained for all cases.

In conclusion, the novel five-coordinated Fe(III) complex $[\text{Fe}(\text{N}-\text{O})_2\text{Cl}]$ has been synthesized and characterized by physico-chemical methods. In this study we have demonstrated the effectiveness of this complex as a catalyst for the oxidation of sulfides to their corresponding sulfoxides. Easy preparation, mild reaction conditions, high yields of the products, short reaction time, high selectivity and low cost make this catalytic system a useful method for oxidation reactions.

Reference

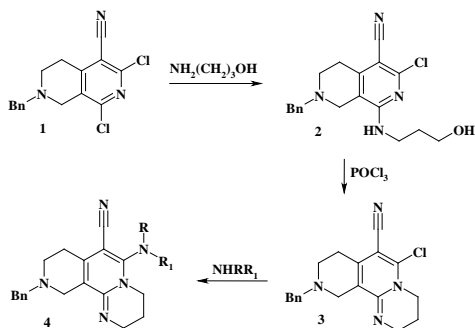
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P5. SYNTHESIS 6-AMINO DERIVATIVES OF NEW HETEROCYCLIC SYSTEM: 10-BENZYL-7-CYANO-3, 4, 8, 9, 10, 11-HEXAHYDRO-2H-PYRIMIDO[2, 1-a][2, 7]NAPHTHYRIDINES

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The combination of the 2,7-naphthyridines and pyrimido[2,1-a]pyrimidines heterocyclic which brings to the organization of the new heterocyclic system is very interesting both from the side of biology and chemistry, because the derivatives of the 2,7-naphthyridine and pyrimido[2,1-a]pyrimidine have various biological activities such as cardiotonic, antiarrhythmic, bronchodilator and antibacterial [1-3]. Using different reactivity of the chlorine atom in the dichloro derivatives **1** we got 6-propanolamine derivative **2**, which under the action of phosphorus oxychloride turned into 6-chloropyrimido[2,1-a][2,7]naphthyridine **3**. The further reaction with different amines brings to the desired 6-amino derivatives **4**.



$R+R_1 = -(CH_2)_{4-7}, -(CH_2)_5-, -(CH_2)_2CHCH_3(CH_2)_2-$.

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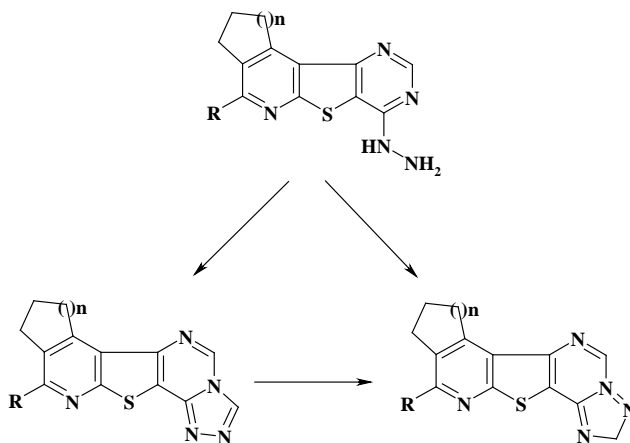
P6. SYNTHESIS OF CONDENSED PYRIDOTHIENOPYRIMIDINES WITH A FUSED TRIAZOLE RING AT THE PYRIMIDINE RING

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The broad spectrum of biological activity of condensed thienopyrimidines and the possibility of further modification of their cyclic structure makes these compounds extremely attractive for the synthesis of new biologically active molecules. So, triazolopyrimidine are interesting not only as heterocyclic systems, but also as compounds with high biological activity.

In this study we have developed methods for obtaining of derivatives of new pentacyclic heterocyclic systems – cyclopenta[4', 5']pyrido[3',2':4,5]thieno[2,3-c][1,2,4]triazolo[4, 3-c](1, 5-c)pyrimidines and [1, 2, 4]triazolo[3'', 4'':6', 1'](5'', 1'':6', 1')pyrido[4', 5':4, 5]thieno[2, 3-c] isoquinolines.



$n=0, 1$; R=morpholino, pyrrolidino.

These compounds were synthesized starting with condensed hydrazine derivatives, cyclization of which with triethyl orthoformate acid resulted triazolo[4, 3-c]pyrimidi-

nes and by their interaction with formic acid were obtained thermodynamically more steady triazolo[1,5-c]pyrimidines. It is assumed then in both cyclization the initially formed triazolo[4,3-c]pyrimidines, which are further undergo to Dimroth rearrangement with formation of triazolo[1,5-c]pyrimidines.

To prove the rearrangement fact triazolo[4,3-c]pyrimidines undergo to boiling in formic acid with allocation triazolo[1, 5-c]pyrimidine. Rearrangement of Dimroth also carried at boiling triazolo[4,3-c]pyrimidines in ethanol presence of sodium ethylate. All synthesized triazolo[4,3-c]pyrimidines have higher melting points then the triazolo[1,5-c]pyrimidines, as well as distinguished by the position of the proton signal of triazoles ring in the NMR ^1H spectra.

Thus, derivatives of new pentacyclic heterocyclic systems, namely, triazolo[4,3-c]pyrimidines and triazolo[1,5-c]pyrimidines, were synthesized in this study. As well the rearrangement of condensed triazolo[4, 3-c]pyrimidines to triazolo[1,5-c]pyrimidines was carried out.

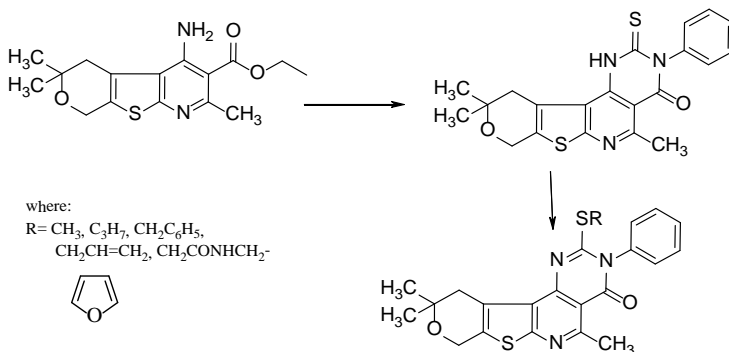
P7. SYNTHESIS OF DERIVATIVES OF NEW HETEROCYCLIC SYSTEM – PYRANO[4', 3':4, 5]THIENO[2, 3-b]PYRIDO[4, 3-d] PYRIMIDINES

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Pyrimidopyrimidines display diverse pharmacological activities. Thus, pyrido[2,3-d] pyrimidines render antitumor activity [1]. Pyrido[3,2-d] and pyrido[4,3-d] pyrimidines are known as tyrazin kinase inhibitors [2, 3].

The aim of this study is to develop methods for obtaining of the new condensed tetracyclic system - pyrano[4',3':4,5]thieno[2,3-b]pyrido[4,3-d] pyrimidines. The synthesis comprises reacting ethyl ester 4-amino-2,6,6-trimethyl-5,8-dihydro-6H-pyrano[4',3':4,5]thieno[2,3-b] pyridine-3-carboxylic acid with phenyl isothiocyanate. The result is a obtaining 5,5,10-trimethyl-3-phenyl-2-thioxy-1,3,4,8,10,11-hexahydro-2H-pyrano[4'',3'':4',5']thieno[3',2':5,6]pyrido[4,3-d]pyrimidin-4-one, with its future alkylated with various alkyl halides, leading to the formation of corresponding thioalkyl derivatives.



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**P8. EFFICIENT SYNTHESIS OF HIGHLY FUNCTIONALIZED PIPERIDINES
BY ONE-POT FIVE COMPONENT REACTION USING BiCl₃ AS
ANTIMALARIALS**

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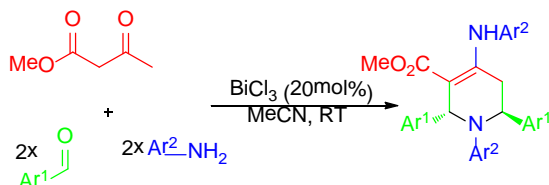
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The piperidine ring is common in a number of biologically important natural products [1]. Of these, 1,4-disubstituted piperidine scaffolds are of particular importance, some as established drugs [2]. And some bearing tetrahydropyridine (THP) frameworks (also convertible to the corresponding piperidines) are important in antiparasitic, antiviral, anticancer, antimicrobial, and antimalarial [3]. For these important reasons, there are several recent reports on the synthesis of piperidine scaffolds [4].

Recently, due to its commercial availability and recyclability, BiCl₃ mediated organic reactions have gained much attention in organic synthesis. In continuation of our studies involving heterocyclic chemistry [5-8], we have developed a BiCl₃-catalyzed versatile and efficient, one pot highly diastereoselective synthesis of diverse functionalized piperidines from the reaction of aromatic aldehydes, acetoacetic esters, and amines in MeCN at room temperature (scheme).



Scheme.

In summary, we have developed a five-component condensation reaction for the formation of highly substituted piperidines, which are pot, atom and step economic. In general the yields are good and the piperidines product precipitates from the reaction allowing for easy isolation.

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P9. THE IMPACT OF CALCIUM ION ON THE BIOCHEMICAL PARAMETERS OF BERRIES DURING PRESERVATION

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Berries are an important natural source of biological active substances, antioxidants, essential amino acids, and micro and macro elements. However a short period of fruit bearing, low levels of storability and transportability does not allow us to take full advantage of the harvest and ensure long-term supply of the population.

There are a lot of ways to slow down metabolism in the cells, extend the storage period of berries and reduce the losses. One of the ways to do this is to use calcium ion to treat fruits.

In addition to cellulose and hemicellulose the cells walls of berries contain pectin substances. Protopectin is the substance in which the pectin molecules are combined by free carboxyl groups through a calcium ion. A calcium ion in the molecule accounts for the strength and insolubility of protopectin.

In order to extend the marketing period of berries we studied the impact of a calcium ion on the storage period and changes in the biochemistry. The research was conducted on strawberries and raspberries. The samples were treated with 1% and 2% calcium chloride solutions. The exposition time was 1 minute, the solution temperature – 20-22 °C. The samples were kept in the normal atmosphere at 0-1°C temperature and 85–90% humidity.

The research showed the advantage of 2% calcium chloride solution over 1% solution. The research results confirm that a calcium ion slows down consumption of storage substances as compared to a control sample. After 12 days of storage the content of soluble dry substances was reduced by 4.5% in the solution treated berries and by 8.3% - in the control samples.

The research also revealed that content of organic acids in the treated samples was higher than in the control samples during the whole storage period. At the first stage sugar contents increased in both treated and untreated berries. This was more noticeable in the solution treated berries. Evidently, a calcium ion does not

slow down starch hydrolysis. Activation of alfa-amylase accounts for a higher content of sugar in the solution treated berries. However, at the same time the consumption of sugars was more intensive in the control samples. In the solution treated samples final content of sugars was only slightly different from the original one. The results of this research supplement the other data and can be considered a common regularity.

The research showed the impact of calcium chloride concentration on mass reduction and losses caused by microbiological diseases. The results showed the reduction of losses in the samples treated with 2% solution of calcium chloride. This was revealed in both strawberries and raspberries. In strawberries treated with 2% calcium chloride the mass reduction was 1.6% lower than in control samples, in raspberries – 1.8% lower. In case of microbiological diseases these were 2% and 1.5% respectively.

In view of the above we can conclude that a calcium ion has a positive impact on the extension of the berries storage period. The consumption of storage substances slows down and berries preserve nutritional value and palatability.

P10. WOUND HEALING AGENT POLY[OXY-1-CARBOXY-2-(3, 4-DIHYDROXYPHENYL)-ETHYLENE] FROM SYMPHYTUM ASPERUM AND S. CAUCASICUM

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Through the ages Comfrey (*Symphytum*) extracts have been used in folk medicine in treatment of different kinds of disorders and wounds due to analgesic, antimicrobial and anti-inflammatory effects. However, the presence of hepatotoxic pyrrolizidine alkaloids in these plants limits the chronic consumption products made from it.

The aim of present investigation was the obtaining and characterization of pyrrolizidine alkaloids-free preparations of *Symphytum asperum* and *S. caucasicum*, as well as the determination of active compounds responsible for their curative properties.

Water-soluble high-molecular preparations from the crude polysaccharides of *S. asperum* and *S. caucasicum* were isolated by ultrafiltration on membrane filters with cut-off values of 1000 kDa and the elucidation of their principal structural units was carried out. The main structural element of these preparations was found to be a regularly substituted polyoxyethylene, namely poly[oxy-1-carboxy-2-(3,4-dihydroxyphenyl)ethylene] (POCDPE) with 3-(3,4-dihydroxyphenyl)glyceric acid residue as the repeating unit (Fig.1)[1].

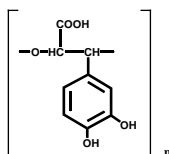


Fig.1. Poly[oxy-1-carboxy-2-(3, 4-dihydroxyphenyl)ethylene]

The results obtained with both excisional and burn wound models revealed the expressed reparative action of POCDPE ointments. Wound healing activity of ointment containing high-molecular polysaccharide fractions from comfrey roots, free of allantoin and pyrrolizidine alkaloids, revealed that by efficacy it is superior to allantoin ointment. Burn wound area in animals, treated with ointments

containing 2, 5% of POCDPE (B) and allantoin (C) since day 2 of the experiment was, respectively, 40 and 10 % less than in control group (A) ($p < 0.01$). Primary eschars in groups Band C were torn away on day 8-10, while in control - on day 12-14. Full healing in animals treated with ointment (B) was achieved 3 days earlier than in (C) and 5 days earlier than in control group.

The work is supported by Sh. Rustaveli National Science Foundation grant AR/109/8-403/11 (agreement #10/21 02.04.2012).

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P11. ASYMMETRIC SYNTHESIS OF ENANTIOMERICALLY ENRICHED FURAN CONTAINING HETEROCYCLE SUBSTITUTED α -ALANINE

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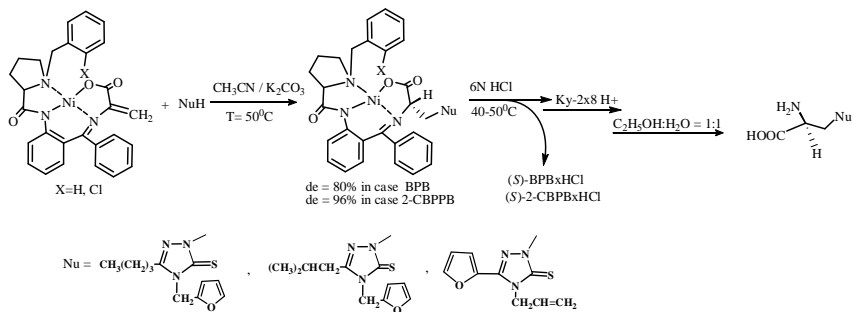
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Furan derivative are an important class of heterocyclic compound that possess important biological properties, such as antihyperglycemic [1], analgesic [1], anti-inflammatory [1], antibacterial [1], antifungal [1], antitumor [1], antiviral [2] and psychotropic [2]. From last few decades a considerable amount of attention has been focused on synthesis of Furan derivatives and screening them for different pharmacological activities.

Certainly, the synthesis and study of amino acids with furan rings in the side chain radical and peptides based thereon is considered today one of the most important problems in modern pharmacological chemistry, bioorganic chemistry and biotechnology.

The goal of our research work is elaboration of efficient high-selectivity method for asymmetric synthesis of new heterocyclic substituted amino acids (*S*)- β -[4-(furan-2-ylmethyl)-3-isobutyl-5-thioxo-1,2,4-triazole-1-yl]- α -alanine, (*S*)- β -[4-(furan-2-ylmethyl)-3-butyl-5-thioxo-1,2,4-triazole-1-yl]- α -alanine, (*S*)- β -[4-allyl-3-(furan-2-yl)-5-thioxo-1,2,4-triazole-1-yl]- α -alanine. The asymmetric addition of furan containing heterocyclic nucleophiles to the C=C bond of dehydroalanine moiety in Ni^{II} complexes of Schiff's base with chiral auxiliaries (*S*)-2-N-(*N'*-benzylpropyl)aminobenzophenone and (*S*)-2-N-(*N'*-2-chlorobenzylpropyl)aminobenzophenone proceeded in CH₃CN in the presence of K₂CO₃ at 40-50°C (see scheme).



The results show, that the stereoselectivity of the reaction of nucleophilic addition in case of the complex containing Cl-atom at the 2th position of Ph-group of N-benzyl prolyl moiety is increased (up to 96%).

After decomposition of the mixture of the diastereomeric complexes and ion-exchange purification the heterocyclic substituted derivatives of (S)- α -alanine were isolated with high optical purity (>99%).

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Acknowledgement

The work has been carried out in the frame of Volkswagenstiftung Project-ID Az 86 223

P12. PROTEIN LABELING VIA 24-MEMBER MACROCYCLIC POLYAZOMETHINES CONTAINING THE ACTIVE DICHLOROTRIAZINE GROUPS

Kh.Tophuria, N. Obolashvili, Z. Geliashvili

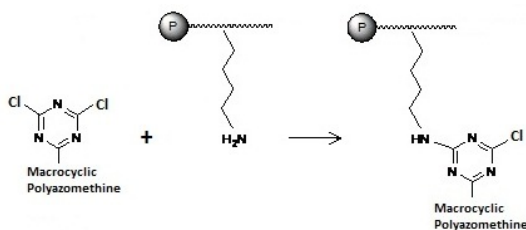
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Our recent publication has been dedicated to the application of 24-member macrocyclic polyazomethines as the fluorescent probes for the labeling aldehyde and ketone groups containing bio-molecules such as thiosine, serine, threonine containing proteins [1, 2].

To increase the stability of colored samples and sensitivity of staining methods of biological materials on the base of 24-member macrocyclic polyazomethines have been synthesized the new fluorescent probes containing active dichlorotriazine groups.

The active groups of dyes are mainly fixed on the protein molecules through the amino groups, more precisely through the ϵ -amino group of lysine. As it is known, in certain conditions dichlorotriazine group is able to specifically react with lysine amino groups to form covalent bonds. The protein's identification method using mentioned groups containing markers is more sensitive, and hence, is essential for the solution of histochemical issues.

In the presented research paper we have investigated the capacity of application of the 24-member macrocyclic polyazomethines containing active dichlorotriazine groups as fluorescent probes [3].



Scheme. Protein labeling by 24-member macrocyclic polyazomethines containing dichlorotriazine groups

The staining process of protein has been carried out at the room temperature in neutral media by applying solutions of synthesized dyes in ethanol with two different concentrations 1-1.5% and 10-12%, which has been added to proteins in ratio 10/1. For the fully denaturation of protein the stained samples have been heated on the water bath up to 60°C. The labeled conjugates are characterized by a visible yellow luminescence.

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P13. RADIOACTIVITY RESEARCH OF SUPERFICIAL WATERS IN EAST PART OF GEORGIA

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Radioactivity and its following ionize sized radiation had existed, before human subsistence on earth, likewise as in space. The negative effect of radiation towards vital organisms was confirmed at the times of A. Beckel (1896-1897). After Chernobyl Tragedy in 1986, Georgia had been admitted at the fourth place of danger areas after Russia, Ukraine, and Belorussia.

We can see the following picture in consisting part of 0-40 centimeter of Strontium within the earth width in West Part of Georgia.: Racha – Lechkhumi, Kvemo Svaneti 0-174, Imereti - 25-1050, Guria -83-171, Adjara -101-1205, Samegrelo -90-827, Apkhazia – 89-1392, Zemo Svaneti -0, BK/KG.

In East Part of Georgia: Mtskheta-Mtianeti-11-416, Tbilisi -71-411, Shida Kartli-0-397, Kvemo Kartli-95-696, Kakheti-25-566, in South Part of Georgia 86-393.

The consisting part of 0-40 centimeter of Cesium within the earth width in West Part of Georgia is following: Racha-Lechkhumi , Kvemo Svaneti0-177, Imereti –15-965, Guria 0–640, Adjara 10-1098, Samegrelo 166-1279, Apkhazia 0-637, Zemo Svaneti 0 BK/KG.

In East Part of Georgia Mtskheta-Mtianeti 0-385, Tbilisi 0-168, Shida Kartli 0-173, Kvemo kartli 0-343, Kakheti 20-469, in South part of Georgia 39-319.

So That, to sum up, The territory of Georgia, especially West part of Georgia (excluding Svaneti) is polluted by radio nuclides. This pollution exceeds (30 or 40 times) the average, limited, accepted radiation level. .Unfortunately, according this view, the superficial waters of Georgia isn't investigated properly.

The similar types of researches were conducted by Robert Kuptsis, N. K. Ignatovich and A. Konshin in 20-s of 20-th century. They had studied the radio activity of water supply from natural streams in different Georgian regions: the superficial waters in Svaneti, Pshavi, Samegrelo, Abastumani and Nakalakevi.

Their research methods confirmed their contemporary measuring skill methods of radiation. The researchers hadn't conducted the identification of radio nuclides producing radiation. Their works can be characterized as fragmenting, and there is an evident difference between their data/information acquisition. In 60-s of 20th

century Science Academy correspondent member of Georgia, Dimitri Eristavi pursued the investigation successfully, studying radioactivity of mineral water in Bordjomi.

According to Vernatsky and Persman theories the chemical elements in rivers and other types of superficial waters are always represented by ions. These scientists explain origin of ions according existing mineral salts within earth and their electrical dissociation. Supposedly all this process is concerned to Chernobyl Tragedy.

So far, the existence of radioactive elements in superficial waters is mainly concerned to the fact—how are these elements extended (spread) within earth. We also paid attention to mineral fertilizers in Kakheti, especially to use a phosphatase as a catalyzer. The highest concentration of Uranus is represented in all phosphatase mines. What is the main source of earth pollution?

The main goal of our research was to investigate the radio activity of water supply in different regions of Georgia. Our researches had been conducted by contemporary highly equipped apparatus. Research are providing according to ISO and EPA standards.

The goal of our investigation is to identify and define the existence of radio nuclides, likewise their identification and concentration. At the beginning we pursued the following research works: we've studied the existence of radio nuclides in water supply in different regions of Kakheti and the investigations of their genesis are already launched.

P14. SPRAYING OF NATURAL CLAY-GYPSUM PRODUCTION HAZARDOUS SUBSTANCES

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Contamination of free air with hazardous substances represents spraying of any substance in free air in the result of human activity which negatively affect or possibly will affect human health and natural objects.

For studying environmental influence and evaluation of possible effects it is necessary to make ecological analysis of manufacture disposal area, determine the ecological condition caused by manufacture activity influence on environmental objects. That is why it is very important to determine spraying of contaminants for learning natural clay-gypsum production influence on free air.

In the result of natural clay-gypsum manufacturing dust, nitrogen oxides and carbon (II) oxide are excreted in the free air.

To receive one tone of natural clay-gypsum expenditure of natural gas is 50m³ and production of natural clay producing facility is 3.0t/h.

Table. Spraying of natural clay manufacture hazardous substances

Hazardous substances	Maximal emission	Maximum permissible concentration Mg/m ³		Type of danger
		Maximum single MPC	Average circadian MPC	
Inorganic dust	6.98	0.5	0.15	3
Nitrogen dioxide, NO ₂	0.178	0.085	0.040	2
Carbon oxide	0.415	5.0	3.0	4

Inorganic dust causes allergy, conjunctivitis, pulmonary fibrosis, chronic atrophic inflammation of upper airways, irritation.

Nitrogen oxides cause irritation of skin, airways and eye mucosa membrane, allergic disorders, asthma, bronchopneumonia, convulsions.

Carbon oxide represents blood poison, causes headache, dizziness, vomiting, suffocation, convulsions and death.

It is obvious that spraying hazardous substances by natural clay-gypsum manufacture is quite dangerous either for people or environment. Thus, for reduction of emissions of hazardous substances cleaning facilities, providing reduction of emissions, must be installed in manufacture and respectively putting concentrations of hazardous substances in the limits of MPC concentrations.

P15. SYNTHESIS OF NEW SULFUR-CONTAINING HETERO POLYCYCLIC COMPOUNDS RANGE OF QUINOLINE

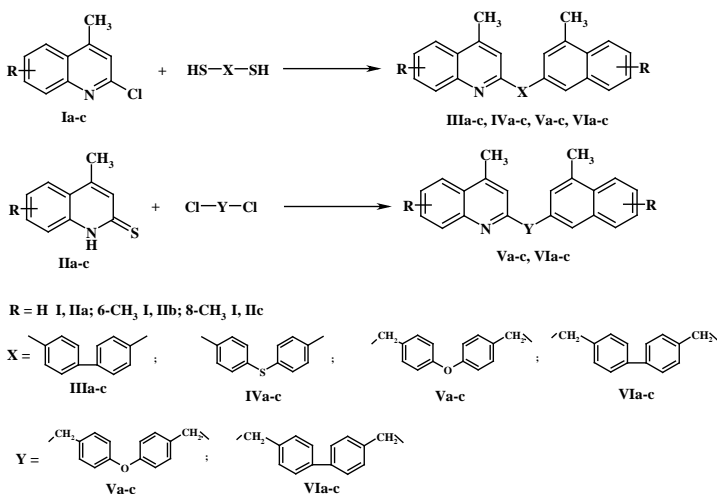
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The quantity of people with severe genetic diseases is increasing all over the world. Currently, over 6, 000 species of such diseases are known [1, 2]. Abnormalities in chromosomes are one of the common chromosomal disorders. According to statistical data six out of six hundred children is born with any type of chromosomal abnormality [1, 2]. Only devices of a single gene can cause serious diseases (cancer, diabet). Some genetic disorders are passed down from the parents' genes, but others are always or almost always caused by new mutations or changes to the DNA [1, 2]. Currently, some low-molecular synthetic compounds become increasingly common, which may bind specific sequences of in the DNA nucleotides at genome [3-5]. Such compounds may be used as radioprotectors, antimicrobial, anticancer drugs [3-5]. These synthetic compounds (Luotonon A, Batracyclin, PD153035, Comtotecine, Mappicine ketone, Lurtotecan) show a good affinity for the substrate and the high specificity of DNA-binding. However, to screen disorders in genes or chromosomes such drugs must change their physical and/or chemical properties (e.g. intensity of their luminescence) upon reacting with polynucleotides [6, 7]. In particular such compounds may be used to detect and diagnoses various diseases and harmful effects in human body based on an analysis of pathology in terms of the content and the structure of nucleic acids at different physiological states. It is known that fused aromatic system with two or more (preferably 5 - or 6-membered) cycles containing at least one heteroatom are widely used as DNA fluorophores [3-7]. In search for such compounds quinoline derivatives are very promising compounds. However, the search for new more sensitive and specific compounds still actually, as currently used compounds have some importunate disadvantages [3-7]. They have poor solubility in water at 37°C, which requires application of addition compounds. Moreover, even low concentrations of those compounds have undesirable side effects and may show some toxic effects on the human body [8-10].

Taking into account the above and in order to synthesize new hetero polycyclic compounds range of quinolines we studied the behavior of benz-substituted 4-methyl-2-chloroquinolines with some nucleophiles. As nucleophiles, we used biphenyl-

4,4'-dithiol, 4,4'-thiodibenzenethiol, 4,4'-oxybis(4,1-phenylene)dimethylenethiol and biphenyl-4,4'-diyldimethylenethiol. Interaction is carried out by boiling a mixture of 2:1 ratio of the starting compounds in ethanol. Resulting in high yields were obtained corresponding substituted 4,4'-bis(4-methylquinolin-2-ylthio)biphenyles, bis(4-(4-methylquinolin-2-ylthio)phenyl)sulfanes, 4,4'-bis((4-methylquinolin-2-ylthio)methylene)oxybis(4,1-phenylenes) and 4,4'-bis((4-methylquinolin-2-ylthio)methylene)biphenyls. The latter compounds (Va-c and VIa-c) were also obtained by counter synthesis, by the reaction of benz substituted 4-methyl-2-thioxo-1,2-dihydroquinolines with the corresponding dichloro derivatives (4, 4'-oxybis((chloromethylene)benzene) and 4, 4'-bis(chloromethylene)bipheyl) in the basic alcohol.



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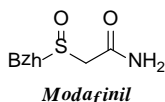
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P16. SYNTHESIS OF ANALOGUES OF “MODAFINIL” DRUG

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Modafinil is an eugeroic drug. It is approved by the United States' Food and Drug Administration (FDA) for the treatment of narcolepsy, shift work sleep disorder [1, 2] and excessive daytime sleepiness associated with obstructive sleep apnea.



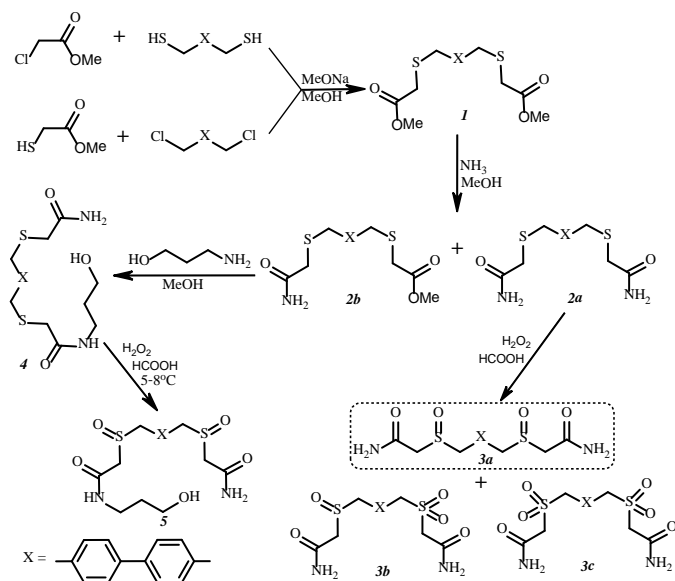
Despite extensive research into the interaction of modafinil with a large number of neurotransmitter systems, its precise mechanisms of action remain unclear [3, 4]. It was shown that Modafinil elevates hypothalamic histamine levels [5], leading some researchers to consider modafinil a "wakefulness promoting agent" rather than a classic amphetamine-like stimulant [6]. Modafinil seems to inhibit the actions of the dopamine transporter, thus leading to an increase in extracellular and thus synaptic concentrations of dopamine [7].

Although Modafinil has proven to be effective drug, it has many side effects like life-threatening skin reactions, and different other types of hypersensitivity effects [8]. To overcome such undesirable effects we suggested to synthesis of analogues "modafinil" which contain amount dual pharmacophore of fragments in there molecules.

The synthesis of dimethyl 2,2'-[biphenyl-4,4'-diylbis (methanediylsulfanediyl)] diacetate (**1**) has be conducted by two different ways. It is shown that ether **1** with high yields may be obtained independently from the synthesis pathway. The latter is subjected to ammonolysis at different temperatures. The temperatur eof reaction geatly influencing the produt composition. Particulrly, a mixture of amide-ester **2b** and diamide **2a** is forming at room temperature, while diamide **2a** is main product of reaction at 55-60 °C.

To mimic the sulfoxide group in the structure of modafinil, syntsize diamide **2a** oxidized by hydrogen peroxide in formic acid medium. The results of the NMR analysis show that at room temperature sinthesis condiitions in addition to main

product (disulfoxide **3a**) a mixture of sulfoxide-sulfone **3b** and disulfone **3c** are forming. It is shown that low temperature (0-5 °C) synthesis increases the yield of desired disulfoxide **3a** product. However, disulfoxide **3a** has poor solubility. To improve its solubility some structural modifications are preferred. Particularly, aminolysis reaction of amido-ester **2b** is studied using 3-aminopropanol-1. This reaction results in formation of corresponding modified amide **4**. Oxidation of the latter compound with hydrogen peroxide at formic acid medium (0-5°C) allows us to synthesize corresponding structurally modified disulfoxide **5**.



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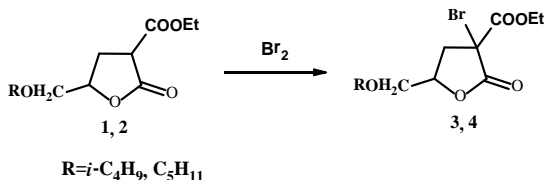
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P17. SYNTHESIS OF NEW SPIROHETERYL-DERIVATIVES OF BUTANOLIDES

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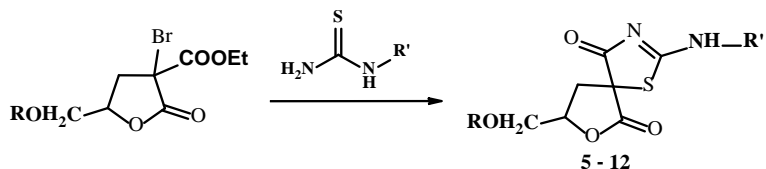
Some halogen-substituted butanolides[1-3] are known to be a good source of raw materials for synthesis of various classes of compounds that present definite biological interest[4-6]. With the purpose of expanding the assortment of heterocyclic lacton-containing compounds as well as studying chemical behavior of 2-ethoxycarbonyl-4-alkoxymethyl butanolides **1, 2** we have investigated the bromination reaction of the latter. It has been shown that **1, 2** are readily brominated in the inert solvents with equimolar quantity of bromine at room temperature.



The best results were achieved when the reaction proceeded in dry carbon tetrachloride to afford 2-ethoxycarbonyl-2-bromo-4-alkoxymethyl butanolides **3, 4**. The availability of two electro-acceptor groups in position 2 of butanolide cycle increased mobility of bromine atom that enabled to assume that they could be used as initial substances for synthesis of heterocyclic compounds containing a butanolide fragment. Among the above-mentioned compounds, heterocyclic compounds spiro-joint with a butanolide ring, particular representatives of which are used in medicine in the treatment of ascites, edemate, nephritic syndrome, are of special interest [7, 8].

Proceeding from aforesaid, the investigations in this field are urgent. Aimed at studying chemical properties of the obtained 2-ethoxycarbonyl-2-bromo-4-alkoxymethyl butanolides their behavior with thiourea and arylsubstituted thioureas under condition of Hunch's reaction has been studied. It has been established that as result of such interactions were obtained in good yields spiroheteryl-joint butanolides

of a new structure, namely, 2-aza-3-amino- or substituted arylamino-4-thia-7oxa-8-alkoxymethyl spiro[4,4]-2-nonen-1, 6-diones **5-12**.



R= *i*-C₄H₉, R' = H (5); R' = *o*-CH₃-C₆H₄ (6); R' = *o*-CH₃O-C₆H₄ (7); R' = *p*-Br-C₆H₄ (8);
R = C₅H₁₁, R' = H (9); R' = *o*-CH₃-C₆H₄ (10); R' = *o*-CH₃O-C₆H₄ (11); R' = *p*-Br-C₆H₄ (12):

Biological researches showed that they have membrane- stabilizing activity.

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**P18. SYNTHESIS OF SOME NEW COMPLEX COMPOUNDS ON THE
BASE OF (BENZO[d]THIAZOL-2-YL)THIOACETIC ACID**

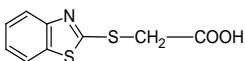
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In modern organic chemistry one of the important tasks is the synthesis of new biologically active compounds. Currently world-wide scientists' attention focus on Epiphysis and its fundamental hormone – melatonin (N-acetyl-5-methoxytryptamine). It is established that the melatonin effects on the multiplication of cancer cell in vitro and in vivo conditions [1, 2].

Therefore we have synthesized new structure analogous of melatonin. In our work as a starting material we used 2-mercaptobenzothiazol. By interaction of last one with monochloroacetic acid we have synthesized 2-(benzo[d]thiazol-2-yl)thioacetic acid:



It's very important furthermore complex compounds on the base of which is possible the synthesis of some new biologically active substances. We have synthesized new complex compounds on the base cobalt and nickel chlorides where the ligand is 2-(benzo[d]thiazol-2-yl)thioacetic acid.

The structure of these compounds has been established on the base of elemental analysis and spectroscopic investigations.

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P19. CYCLOTRIMERIZATION OF BENZODIOXINE: SYNTHESIS OF A NOVEL 36 π AROMATIC COMPOUND

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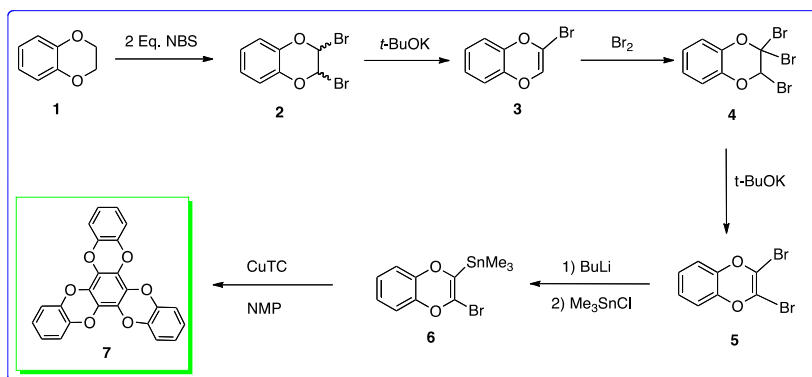
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Various 1, 4-benzodioxin derivatives have been shown to display very important pharmacological properties including anti-inflammatory, diuretic, anti-hyperglycemic, and calcium antagonistic activities. Some of them are also antagonists of R-adrenergic receptors at the origin of anti-hypertensive properties, while others have affinities with serotonin receptors, which are involved in nervous breakdown and schizophrenia [1].

In addition to this, for the several years, considerable interest has been aroused on synthesis and chemistry of aromatic compounds. As a result of extended research in this field numerous types of aromatic compounds including hetero atoms have become available.



In this work we interested in functionalization reactions of benzodioxine. In addition to several novel benzodioxine derivatives, a new hetero aromatic hydrocarbon **7** was obtained [2].

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P20. SEPARATION OF ENANTIOMERS OF SELECTED CHIRAL BETA-BLOCKER DRUGS BY USING NOVEL POLYSACCHARIDE-BASED CHIRAL STATIONARY PHASES IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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The goal of the present study was systematic screening of novel polysaccharide-based chiral column for separation of enantiomers of chiral beta-blocker drugs by using various mobile phase conditions. In our studies the emphasis was placed on the elution order of enantiomers and the mechanisms of enantioselective recognition by these new materials. These studies require spiking the racemic samples with enantiomerically pure forms of chiral drugs. Since many beta-blocker drugs are not available commercially in enantiomerically pure forms, some of them must be resolved in advance by us in the micropreparative way. Up to now 16 representative drugs of this series were analyzed on 6 different chiral columns of Lux series: Lux Cellulose-1, Lux Cellulose-2, Lux Cellulose-3, Lux Cellulose-4, Lux Amylose-2 and SP-6. The instrumentation used was high performance liquid chromatograph (Agilent 1200 HPLC) equipped with the autosampler, binary pump, column thermostat, variable wavelength detector and Chemstation chromatographic software for the instrument management and data accumulation/treatment. With the necessity of the preparative separation in mind the screening was started with pure methanol and acetonitrile as mobile phases. In contrast to older generation of polysaccharide-based chiral columns the Lux series of chiral columns can be used in all 3 principal modes of chromatography (polar organic-, normal- and reversed-phase conditions). Polar organic mobile phases offer certain advantages for preparative separation of samples. The major advantages are higher solubility of analytes in these mobile phases, sharp chromatographic peaks and shorter analysis time. These advantages translate in high productivity of separation. In this presentation the results of our preliminary studies on the separation of 16 chiral analytes on 5 above mentioned columns with methanol and acetonitrile as mobile phases are presented. Several interesting examples of the reversal of enantiomer elution order based on the composition of stationary and mobile phases were observed.

P21. ENANTIOSEPARATION OF CHIRAL ANTIMYCOTIC DRUGS BY HPLC WITH POLYSACCHARIDE-BASED CHIRAL COLUMNS AND POLAR ORGANIC MOBILE PHASES WITH EMPHASIS ON ENANTIOMER ELUTION ORDER

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The separation of enantiomers of 10 chiral antimycotic drugs was studied on polysaccharide-based chiral columns with polar organic mobile phases. The emphasis was placed on some interesting examples of enantiomer elution order reversal observed depending on the chemistry of the chiral selector, separation temperature, major component, as well as the minor additive in the mobile phase. In particular, it was found that the elution order of enantiomers of chiral drug terconazole was opposite on cellulose- and amylose-based columns with the same pendant group. The affinity pattern of enantiomers of another chiral drug bifonazole was opposite towards to two amylose-based chiral selectors with different pendant groups. The affinity pattern of terconazole enantiomers also changed on some columns when the alcohol-based mobile phase was replaced with acetonitrile. An interesting effect of the minor acidic (formic acid) additives to the mobile phase on the affinity pattern of terconazole enantiomers was observed on Cellulose-2 and Cellulose-4 columns. In addition, a reversal of elution order of bifonazole enantiomers was observed on Amylose-2 column by variation of a separation temperature.

**P22. ENANTIOSEPARATION OF SELECTED CHIRAL SULPHOXIDES IN
HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WITH
POLYSACCHARIDE-BASED CHIRAL COLUMNS AND POLAR
ORGANIC MOBILE PHASES**

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Study of physical and chemical mechanisms of separation of enantiomers is very important issue in separation science. High-performance liquid chromatography (HPLC) represents the major method for separation of enantiomers. For better understanding of chiral recognition mechanisms a determination of enantiomer elution order is very important.

In the present work the enantiomer elution order of chiral sulphoxides has been studied in HPLC by using polar-organic mobile phases and novel type of chiral columns such as Lux Cellulose-1, Lux Cellulose-2, Lux Cellulose-3, Lux Cellulose-4, Lux Amylose-2 and SP-6. The interesting examples of the enantiomer elution order reversal were found based on the composition of the stationary as well the mobile phase.

**P23. THE ENANTIOMERIC ANALYSIS OF CHIRAL DERIVATIVES OF
PHENOXYPROPIONIC ACID BY HPLC USING POLYSACCHARIDE
CHIRAL STATIONARY PHASES**

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The derivatives of phenoxypropionic acid are widely used as agrochemicals (mostly herbicides). Most of the above mentioned derivatives are chiral substances and nowadays the aspects of their action, accumulation in agricultural plants and their degradation is mostly unknown.

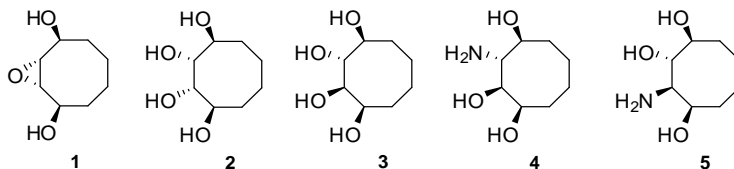
The aim of this work is the development of new methods of analysis by HPLC using new types of polysaccharide chiral stationary phases and polar-, organic-, normal- and reversed phase eluents. Especial attention in the present project will be paid to the enantioseparation mechanisms. The effect of the composition of the stationary and mobile phase, as well as separation conditions on the enantiomer elution order will be studied. At the present stage the screening of enantiomer separations only with polar-organic mobile phases are performed. The results of these studies are highlighted in the presentation.

P24. SYNTHESIS OF NOVEL C8-CARBASUGARS AS GLYCOSIDASE INHIBITORS

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C8-carbasugars and related aminocyclitols are a class of polyhydroxylated cyclo-octanoics (**1-3**). The syntheses of 3-aminocyclooctanetriols (**4** and **5**) which are analogues of cyclooctanetetriols (**2** and **3**) are unknown yet. More recently, attention has been increasingly accorded to these aminocyclitols and derivatives since aminocyclooctanepentaols are glycosidase inhibitors [1].



Cyclooctene endoperoxide obtained by photooxygenation of *cis, cis*-1, 3-cyclooctadiene was the key compound in the synthesis. Reduction of the endoperoxide with zinc or thiourea followed by acetylation of the hydroxyl group and OsO₄/NMO oxidation of the double bond gave cyclooctane-1, 2, 3, 4-tetraol (**2**) [2] stereospecific. Interestingly, epoxidation of cyclooctene-1, 4-diol with *m*-CPBA also afforded *trans*-epoxy-diol **1**. Cyclooctane-1, 2, 3, 4-tetraol (**3**) was easily obtained by hydrolysis of epoxy-diol **1** [2]. Epoxidation of *cis, cis*-1, 3-cyclooctadiene with *m*-CPBA followed by various chemical transformation of the cyclooctene epoxide afforded 3-aminocyclooctanetriol (**4**) [3] as sole product. In the second part of this study, various chemical transformation of the cyclooctene-1,4-diol gave 3-aminocyclooctanetriol (**5**) stereospecific.

Finally, we have synthesized some cyclitols and its derivatives containing eight-membered-rings: **1-5** starting from the easily available *cis, cis*-1, 3-cyclooctadiene,

with a concise and efficiency. All of the synthesized cyclitols (**1-5**) exhibited strong enzyme-specific inhibition against α -glycosidase.

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P25. REGARDING THE EFFECT OF BASIC AND ACIDIC ADDITIVES ON SEPARATION OF ENANTIOMERS OF SOME CHIRAL BETA-BLOCKERS WITH POLYSACCHARIDE-BASED CHIRAL COLUMNS AND POLAR ORGANIC MOBILE PHASES

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This article reports the systematic study of the effect of basic and acidic additives on HPLC separation of enantiomers of some β -blocker drugs on polysaccharide-based chiral columns under polar organic mobile-phase conditions. In contrary to generally accepted opinion that the basic additives improve the separation of enantiomers of basic compounds, the multiple scenarios was observed including the increase, decrease, disappearance and appearance of separation, as well as the reversal of the enantiomer elution order of studied basic compounds induced by the acidic additives. These effects were observed on most of the studied 6 chiral columns in 2-propanol and acetonitrile as mobile phases and diethylamine as a basic additive. From acidic additives formic acid was used systematically and acetic acid and trifluoroacetic acid were applied for comparative purposes. This study illustrates that the minor acidic additives to the mobile phase can be used as for the adjustment of separation selectivity and the enantiomer elution order of basic compounds, as well as for study of chiral recognition mechanisms with polysaccharide-based chiral stationary phases.

P26. ENANTIOMER ELUTION ORDER REVERSAL OF FLUORENYL-METHOXYCARBONYL-AMINO ACID IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WHEN USING THE POLYSACCHARIDE-BASED CHIRAL COLUMN AND DIFFERENT MOBILE PHASES

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N-protected amino chiral acids are widely used as starting materials in pharmaceutical chemistry and biochemistry. Therefore, development of new methods not only for determination of enantiomeric purity of amino acid derivatives but also for their large scale production is very important.

FMOC is well now protecting group for α -amino acids and together with suitability for detection by fluorescence spectroscopy provides also enhanced UV-VIS absorbance to amino acid derivatives. Therefore, it is widely used in HPLC.

The goal of the present project is a study of enantiomer elution order of various amino acid (among them also FMOC) derivatives on novel polysaccharide-based chiral stationary phases and polar-, normal-phase and reversed-phase eluents. The effect of various minor additives and separation temperature on the enantiomer elution order will be also studied.

On the present (initial) step of the project the enantiomer elution order of FMOC-amino acids on polysaccharide-based chiral stationary phases with methanol and acetonitril as the mobile phases was studied.

**P27. COMPARATIVE ANALYSIS OF ESSENTIAL OIL COMPOSITION OF
MATRICARIA AUREA GROWING IN SAUDI ARABIA AND JORDON**

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The composition of the essential oils obtained from the aerial parts of *M. aurea* growing in Saudi Arabia and Jordan were analyzed by gas chromatography-based techniques (GC–FID, GC–MS, Co-GC, LRI determination, database and literature search) using polar as well as non-polar columns, which resulted in the identification of a total of 133 components in Saudi oil and 110 compounds in Jordanian oil accounting for 95.03% and 94.04% of the total oil composition, respectively. The main constituents of Saudi Arabian essential oil were α -bisabolol (27.806%) Caryophyllene oxide (21.658 %) (E, E)- α -Farnsene (16.3%) (Z)-spiroether (7.454%) (E)-Nerolidol (1.957 %) (E)- β -Farnsene (1.387%) (Z)- β -Farnsene (1.275%) and Germacrene D (1.009%) whereas the main constituents of Jordanian essential oils were (E, E)- α -Farnsene (50.206%) Caryophyllene oxide (8.54%) (E)- β -Farnsene (8.066%) (Z, E)- α -Farnsene (4.432%) and Germacrene D (1.895%).

**P28. PREPARATION OF INORGANIC–ORGANIC HYBRID
NANOCOMPOSITE WITH CORE-SHELL STRUCTURE**

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A series of polystyrene encapsulated with Zinc oxide (ZnO) has been synthesized in this thesis. The polystyrene were synthesized by Pickering emulsion polymerization technique without using any surfactant. The polymers were thoroughly characterized by Gel permeation chromatography (GPC) Fourier Transform Infra Red (FTIR) Nuclear magnetic resonance (NMR) thermogravimetric (TGA) Differential Scanning calorimetry (DSC) techniques. The emulsions were also characterized by Transmission Electron Microscopy (TEM).

The ZnO distribution in the PS matrix was also characterized by the Scanning electron microscopy (SEM). The PS synthesized by this technique has good molecular weight build up when comparable with commercial PS. The thermal property of the PS-ZnO oxide was found to be improved. The DSC analysis showed difference in T_g and T_m of the synthesized PS-ZnO when compared with Commercial polystyrene CPS.

P29. EFFECTIVE PLANT SORBENT FOR REMOVE METALS

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We developed technology for obtaining plant sorbent – pectate - Na^+ and used it for obtaining metals. It is obtained water soluble complexes of citrus polysaccharides and d-metals Co^{+2} , Cu^{+2} , Fe^{+2} , Mn^{+2} , Ni^{+2} , Zn^{+2} . It is established complex-making conditions and boundary concentrations of metals.

From juice production waste by combined membrane technology based on electromembrane and baromembrane processes obtained new plant sorbent-pectates sodium -pectin- Na^+ sorbent and polymetal complexes with d -metals: Ni^{2+} , Fe^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} .

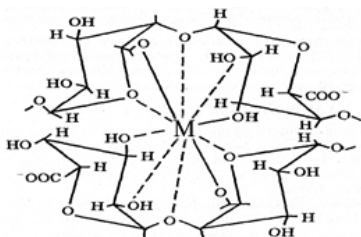


Fig.1 Pectin- Me - complexes

The sorbent we proposed has ability to work in two direction:

- To clarify food products (wine, wine materials and juice) natural and industrial waste waters contaminated with heavy metals;
- For prophylactic purposes, it will have ability to extract toxic biogenic elements from organism;

It is developed technology for obtaining 100% salinity, fully deetherificated pectate- Na^+ sorbent with high ion-exchange and complex-making ability. It is obtained metal-complexes with biogenic d-metals-microelements (Co^{2+} , Cu^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Zn^{2+} .) in water soluble and insoluble form (fig.1).

Set the threshold concentration of heavy metals - 0.009-0.02 N and efficiency of the process of substitution of sodium ions in the sorbent on the investigated metals, accounting for 25% (fig.2).

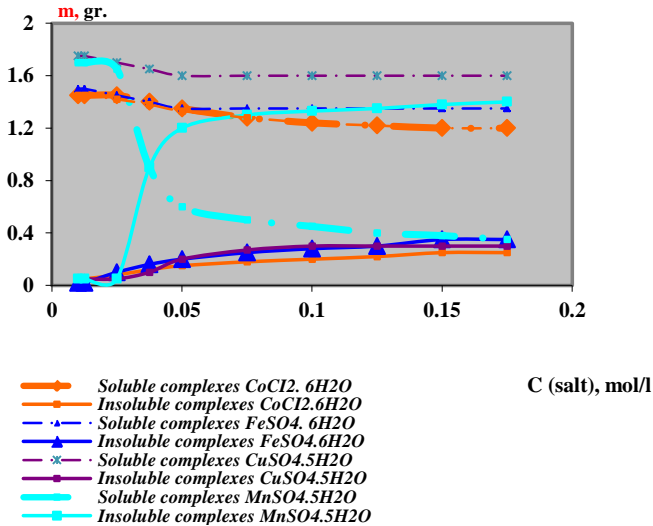


Fig.2 Comparison of data on the allocation of water - soluble and insoluble metal complexes of sodium from the system pectates - metal salt

By IR spectroscopy is defined and proven composition, structure, solubility and complex-making ability of pectin - Na+sorbent with metals including biogenic and heavy metals (Fig.3):

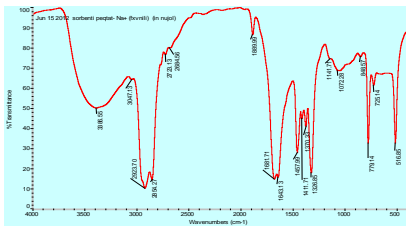


Fig.3 a. Pectin - Na⁺ sorbent (insoluble form)

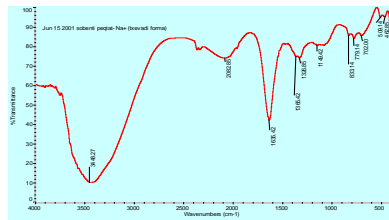


Fig.3 b. Pectin - Na⁺ sorbent (soluble form)

Obtaining pectin and pectin-Na⁺ sorbent by processing wastes and using them for extraction of heavy metals will solved important ecological, economic and social problems:

- Obtained pectin-Na⁺ sorbent and water-soluble and insoluble forms of

polymetal complexes is used for correction of technological processes such as dimetallization-detoxication of water, natural and industrial waste waters to get optimal technological modes for demineralization of wine and winematerials;

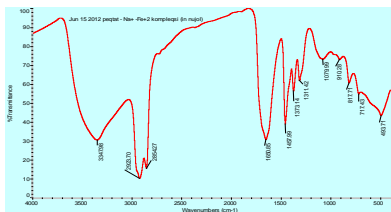


Fig.3c. Pectin - Na⁺ sorbent –Fe²⁺

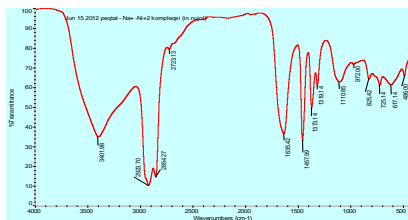


Fig.3 d. Pectin-Na⁺ sorbent - Ni³⁺

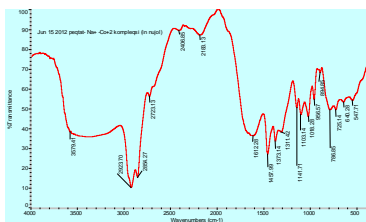


Fig.3 i .Pectin-Na⁺ sorbent - Co²⁺

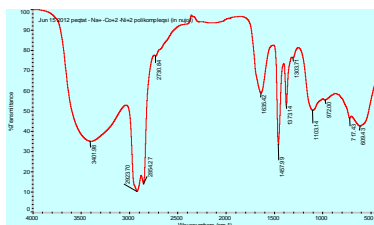


Fig.3g. Pectin-Na⁺ sorbent - Co²⁺ - Ni³⁺

- Extraction of metals from industrial juices, natural and galvanic production waste waters will be possible by sorbent obtained on the basis of pectin;
- Pectin-Na⁺ sorbent can be used as a regulatory of blood mineral composition (K⁺, Na⁺, Zn²⁺, Fe²⁺ etc.) and for anemia patients for increasing erythrocytes and haemoglobin in blood;
- Pectin-Na⁺ sorbent obtained from it can be used in pharmaceutical industry to make medical preparations: against absorption of radionuclides and their decorporation, regulatory of digestive tract, for extraction of heavy metals from organism and other preparations;
- If water-soluble polymetal complexes are used, they will be fastly involved in metabolism processes in organism and will act against anemia, regulate immunity and restore resistance of organism.

P30. THE UNITY OF SYMMETRY AND ASYMETRY – THE BASIS OF LIFE

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The dialectical unity of symmetry and asymmetry is considered as the basic of life. The development of the notion of symmetry from the ancient times to the present day is demonstrated. It is noted that the principles of symmetry play a dominating role in the perception of the world around us and in the existence of limitations in the diversity of structures and the number of possible versions imposed by these principles. Diverse manifestations of symmetry in animate and inanimate nature are analyzed.

The specific features of symmetry in the flora and the fauna, the existence of enantiomorphs, are discussed. There are demonstrated the manifestations of symmetry on the atomic level, the existence of certain symmetry of nuclear forces and permutation symmetry of particles in the Universe. The Pauli Exclusion Principle and the fermion and the boson character of particles are considered.

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P31. SYNTHESIS AND IR ABSORPTION SPECTRA OF MIXED-LIGAND COORDINATION COMPOUNDS OF COPPER (II) MANGANESE (II) COBALT (II) AND NICKEL (II) WITH ORTHO-AMINO-4-METHYLPYRIDINE AND PARADIMETHYLAMINO BENZALDEHYDE ISONICOTINOYLHYDRAZINE

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Mixed-ligand coordination compounds of copper (II) manganese (II) cobalt (II) and nickel (II) with paradimethylaminobenzaldehyde isonicotinoylhydrazine (L) and ortho-amino-4-methylpyridine (oAm4mpy) are synthesized. Copper (II) chloride, cobalt (II) and nickel (II) nitrates and manganese (II) and nickel (II) sulfates have been taken as initial salts. Synthesis has been carried out in ethanol solutions.

Synthesized coordination compounds are separated in solid form. Composition, individuality, solubility of obtained compounds in different solvents is established.

IR absorption spectra of synthesized coordination compounds are studied in order to establish the rule of coordination for paradimethylaminobenzaldehyde isonicotinoylhydrazine, ortho-amino-4-methylpyridine, acidoligands and water molecules. Spectra are located in 400-4000 cm^{-1} range.

As the results of identification of IR spectra show, hydrazone molecule forms coordination bonds with metal-complex former by means of nitrogen atom of azomethine groups and oxygen atom of carbonyl group. Ortho-amino-4-methylpyridine forms coordination bond with metal by means of atoms of nitrogen heterocycle. Water molecules are generally intraspheric in coordination compounds, except of several compounds.

Structure of synthesized compounds is offered on the basis of obtained data.

P32. SWEET TEA

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Georgia is a land-pure country. For the purpose of rehabilitation of the region's agriculture, food industry and decrease of its profitability we need to search and introduce new crops, improve and introduce technology of their processing. Stevia (*Stevia rebaudiana* Bertoni) is one of such crops. Its popularity worldwide is caused with sweet diterpene glycosides (stevioside is 300 times, but rebaudioside – 400 times sweeter than saccharose) containing in its leaves [1]. Nowadays its cultivation and sale is permitted in many countries of the world. Its consumption rate is fixed by 5.5g daily, what equals 15-20g of sugar. Stevia and its products are considered not only prophylactic for diabetics and obese people, but many other kinds of physiological activity are established. Many developed countries of the world attached strategic importance to development of technology and production of medicinal and prophylactic, diabetic products having purpose to provide human's health and duration of life.

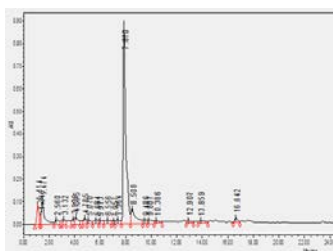


As per technology developed by the group of scientists for the purpose of receipt of stevia leaves extract the raw material is exposed to extraction in hot water for some period of time. Then the extract is filtered and concentrated up to concrete concentration and sedimented. This sediment is used for tea sweetening. As for filtrate and decoction, they are the waste of sweet tea production process. Their use will make production more effective. Dry tea or fermented or green tea are grinded and mixed in concrete proportion. It is noted, that the sediment is absolutely water-soluble and contains both sweet diterpene glycosides and compounds typical for tea

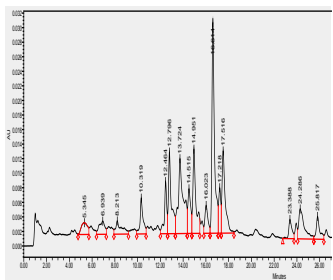
leaves (phenol compounds). The second positive factor, increase of extractiveness of product (ready tea products shall meet concrete requirements, but they often do not comply therewith) what makes tea draw more intensive.

Tea and stevia are mixed in the following proportion: green tea not packed, stevia extracts (in case of use of liquid extract it is calculated on dry mass) 12:1, black tea and not packed stevia extracts 9:1. Mixing process takes 3-5 minutes.

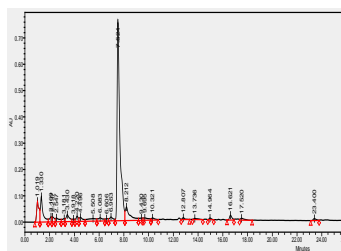
Drying of mixed mass of tea and stevia is performed with any kind of dryer at 90-100°C. Drying is considered completed, when residual moisture in the product achieves 5%.



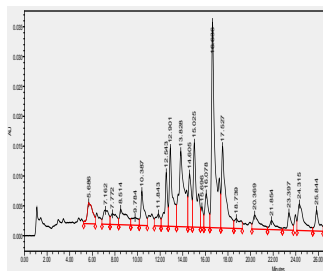
Tea extract HPLC 280nm



Tea extract HPLC 360nm



Sweet Tea extract HPLC 280nm



Tea extract HPLC 360nm

HPLC of produced product permits that chemical structure don't changes much while sweating by stevia.

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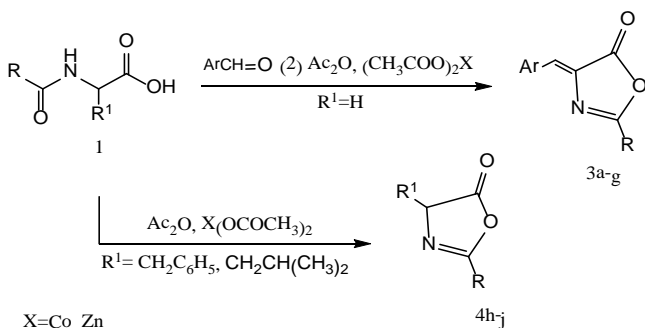
P33. SYNTHESIS OF 5(4H)-OXAZOLONES CATALYZED WITH COBALT AND ZINC ACETATES

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5(4H)-Oxazolones have found a wide application in organic chemistry both for the synthesis of physiologically active compounds and as syntons in synthesis of different classes of compounds. Various methods for the synthesis of 5(4H)-oxazolones are known, sodium, calcium and bismuth acetates being used as catalysts.

This work is devoted to study of the possibility to use cobalt or zinc acetate as catalysts in the synthesis of both unsaturated (3) and saturated 5(4H)-oxazolones (4).



- a) R = C₆H₅, Ar = 3-O₂NC₆H₄; b) R = Ar = C₆H₅; c) R = C₆H₅, Ar = 4-CH₃OC₆H₄;
 d) R = 4-*t*-C₄H₉C₆H₄, Ar = C₆H₅; e) R = 4-*t*-C₄H₉C₆H₄, Ar = 3,4-CH₂O₂C₆H₃;
 f) R = 4-*t*-C₄H₉C₆H₄, Ar = 3-O₂NC₆H₄; g) R = CH₃, Ar = 3-O₂NC₆H₄;
 h) R=4-CH₃OC₆H₄, R¹=CH₂C₆H₅; i) R = C₆H₅, R¹=CH₂C₆H₅;
 j) R = C₆H₅, R¹=CH₂CH(CH₃)₂.

The reaction of N-acylamino acids (1) with aromatic aldehydes (2) in the presence of acetic anhydride resulting in formation of unsaturated 5(4H)-oxazolones was carried in the presence of 0.06-0.6 equivalent of cobalt or zinc salts in ethanol medium at room temperature or in the absence of a solvent under conditions of

microwave irradiation. According to the obtained data, variation of cobalt or zinc acetate amounts within the limits of 0.06-0.6 equivalent insignificantly affected the yield of 4-(3-nitrobenzylidene)-2-phenyloxazol-5(4H)-one (**3a**). Similar effect was also observed when the reaction was carried out both under conditions of room temperature for 1 *h*, and of microwave irradiation for 1.5 *min*. However, comparison of the data of synthesized unsaturated 5(4H)-oxazolones **3b-g** showed that synthesis with microwave irradiation led to higher yields as compared with experiments performed at room temperature.

Comparison of the data of oxazolones **3a-c** synthesis with zinc acetate with those of experiments with cobalt acetate confirmed the excellence of the latter.

We used cobalt and zinc acetate as catalysts in the synthesis of saturated 5(4H)-oxazolones (4h-j). In this case the reaction of N-benzoylamine acids in the presence of acetic anhydride was carried out both at room temperature and by microwave irradiation at 120 °C for 3 *min*. In both cases the target oxazolones **4(h-j)** was obtained in high 90-98% yields.

P34. INVESTIGATION OF COMPLEX FORMATION PROCESS OF NICKEL WITH FULVIC ACIDS

T. Makharadze

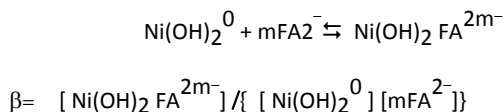
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Fulvic acids actively participate in complex formation processes taking place in natural waters, form stable complexes with heavy metals and stipulate migration forms thereof in natural waters.

In spite of researches, experimental data on stability constants of complex compounds of fulvic acids are heterogeneous. Therefore, it's difficult to investigate complex formation processes taking place in natural waters, identify migration forms of heavy metals and evaluate and assess chemical-ecological condition of natural waters.

We aimed at determining stability constant of nickel fulvic complexes. According to the data found in the literature stability constants of nickel fulvic acids differ in several lines from each other. Value of $\lg \beta$ changes from 3.3 to 7.1.

At pH 8, in diluted solutions, a dominant form of Ni (II) is represented by dihydro-complexes - $\text{Ni}(\text{OH})_2^0$. If considering fulvic acids as two-base acids, the reaction between Ni dihydrocomplex and the anions of fulvic acids may be written in the following way:



The complexing process was studied by the dissolubility method. Previously sedimented Nickel hydroxide was use as solid phase.

At pH=8, the system Ni-FA-H₂O was studied. It was established, that in such conditions dominates the complex with correlation 1:1. Stability constant of nickel fulvic complex was calculated based on experimental data: $\beta[\text{Ni}(\text{OH})_2\text{FA}]^{2-} = 4.7 \times 10^5$ ($M_w = 6340$) $\beta_{\text{Ni}(\text{OH})_2\text{FA}^{2-}} = 5.2 \times 10^5$ ($M_w = 1350$).

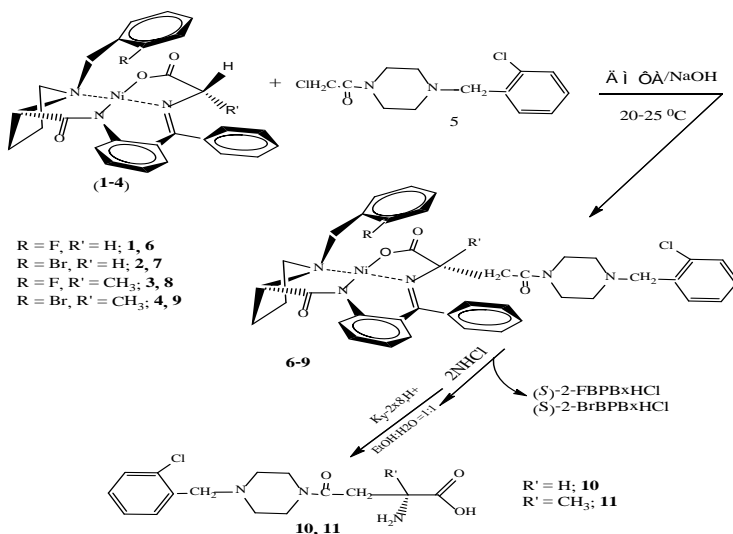
P35. STEREOSELECTIVE SYNTHESIS OF (*S*)-(*N*-CARBOXYL-*N'*-2-CHLOROBENZYLPIPERAZINYL)-ALPHA-ALANINES

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It is established that *N, N'*-disubstituted piperazines reveal anesthetic and analgesic properties [1, 2]. Many derivatives of piperazine possess antihistamine activity and are less toxic in comparison with analogous preparations [3]. However, optically active α -amino acids containing *N, N'*-disubstituted piperazine heterocycles have not been found in literature.

Asymmetric synthesis of a new type of enantiomerically enriched non-protein analogs of α -alanine containing *N*-carbonyl-*N'*-2-chlorobenzyl piperazinyl fragment is reported in this article. The method of synthesis implies C-alkylation of Ni (II) complexes of Schiff's base with glycine and alanine with chiral auxiliaries (1-4). *N*-carbonyl-*N'*-2-chlorobenzylpiperazinyl chloromethane was used as alkylating agent, the reaction was carried out in DMF/NaOH at room temperature (Scheme).



Using complexes based on 2-FBPB (R=F) increase in the de (on average 93%) and sharp decrease in the duration of synthesis (5-25 min) were observed. Optically pure derivatives of (*S*)- α -alanine and (*S*)- α -methyl- α -alanine containing N, N'-substituted piperazine heterocycles (ee >95%) were isolated after decomposition of a mixture of (*S, S*)- and (*S, R*)-diastereoisomeric complexes.

References

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P36. REFINING JET FUEL USING GEORGIAN CLAY SOIL

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The presented work deals with refining jet fuel, with various catalysts. Three compounds chosen for the initial catalytic conversion of hydrocarbons with same carbon-bearing hydrocarbons, particularly C₁₃ and C₁₅ queue solid tridecane and pentadecane, heptylbenzene and nonylbenzene and hydroproduced – cheptylcyclohexane and nonylcyclohexane.

The distilled hydrocarbon analogs are in jet fuel, of the kerosene - gazoil fraction of the composition and the synthesis of analogues allows us to theoretically determine the mechanism of their derivative analogs and study the properties of the transforming process with hydrogenation refining, using different catalysts [1-7].

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P37. THE COMPLEX RESEARCH OF PHOTOISOMERISATION PROCESS OF RHODOPSIN RETINAL

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The human eye contains two types of light-sensitive cells (photoreceptors): highly sensitive rods are responsible for night vision, and less sensitive cones - for color vision. The rods of the eye retina of marine invertebrates, fishes, almost all terrestrial vertebrates and man contain the rhodopsin - a light-sensitive pigment (chromoprotein, approximately 40%). It is responsible for the color of the retina and the perception of electromagnetic radiation in "visible range", underlying in vision process. Rhodopsin consists of two components. The part that absorbs visible light is called a chromophore - retinal (aldehyde of retinol (vitamin A)) and the protein of the visual pigments, which are bound to retinal, called opsin.

The mammalian rhodopsin structure is similar to bacteriorhodopsin - the membrane proteins of Archaea. The halophilic archaea has the ability to carry out extremely non-chlorophyll type of photosynthesis. Bacteriorhodopsin carries proton transfer across the plasma membrane.

As is known, the absorption of a photon by rhodopsin leads to a number of its photochemical transformations - photolysis. The primary act in this process is the isomerization of 11-*cis*-retinal to all-*trans* form, which has the same chemical structure as the *cis*-form, but a different physical structure - a straight, not bent molecule. The absorption of a photon leads to the weakening of bonds in the retinal molecule and subsequent repulsion of the methyl groups located in different planes, according to the retinal structure, causing the rotative moment that causes the molecule to straighten the bend with rotation [1].

After absorption of light energy rhodopsin begins to disintegrate. Since the orientation of the reactive sites of all-*trans*-retinal no longer fits in with the orientation of the protein reactive sites of opsin, this form of retinal begins to separate from opsin. "Strained" conformation of isomerized chromophore transforms its energy into further conformational changes of rhodopsin. In vertebrates photolysis ends with separation chromophore from the protein (opsin) and output

of retinal [2].

The method of computer modeling has been reproduced the photoisomerization process of retinal. For this aim HyperChem program was used. The experiment showed that the absorption of a photon leads the electron density distribution in such way that the charges on the ends of the retinal molecule coincides with the charge of the environment, as a result of the electrostatic interaction leads to the ejection of retinal out. This is accompanied by the release of the channel in the cell membrane. The photolytic decomposition of rhodopsin causes the excitation of the visual nerve due to changes in ion transport in the photoreceptor [3].

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P38. SYNTHESIS OF SOME NEW AZACROWN ETHERS AS NEW RECEPTORS

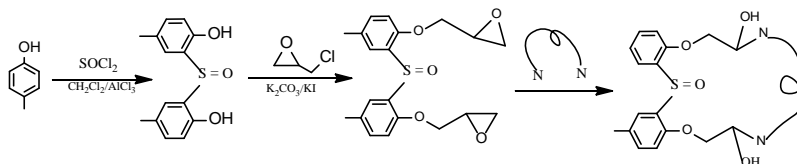
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The research, for aza-crownethers applications has solved many significant problems in different fields of science and technology, such as chemistry, biology, analysis and microanalysis, metal separations and transport, molecular recognition, medical and industrial uses, biophysics, catalysis, agriculture and ecology [1]. The preparation of new aza-crown ethers has attracted many attentions recently, because of they are significant metal ion complexing agents as well as being valuable intermediates for the synthesis of related compounds such as lariat ethers and cryptands [2, 3]. In this research work, we wish to report the synthesis of some new ligands, such as azacrownethers. The OH functional group in these ligands presents variety and important properties, for many applications in different fields. These ligands have biological activity; also OH group can be functionalized with other important groups and form stronger ligands such as lariat ethers.

The dibenzosulfoxide (1) was synthesized by the reaction of thionyl chloride and p-cresol. The reaction of epychlorohydrin with dibenzosulfoxide (1) in refluxing dry acetone, in the presence of KI and K₂CO₃ gives bisepoxide(2). The new ligand (3) was achieved by treatment of bisepoxide(2) with a suitable diamine compounds. The structure of all prepared compounds is proved by spectral data including IR, HNMR and ¹³CNMR.



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P39. CLEAN SEA WATER - A MERIT OF ELECTRODIALYSIS

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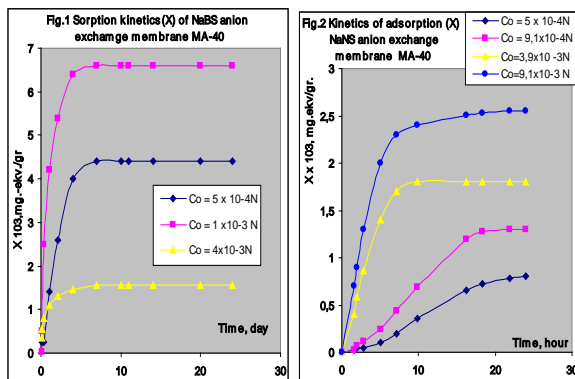
The paper deals with natural and waste waters from organic compounds by electro dialysis. The processes of the sorption kinetics and dynamics of organic electrolytes (sodium benzene sulfonate, naphthalene-2-sulfonate and cetylpyridinium chloride by ion-exchange membranes are studied.

The studies were conducted in solutions of organic electrolytes: sodium benzene-sulfonate $C_6H_5SO_3Na$ (NaBS), naphthalene-2-sulfonate sodium $C_{10}H_7SO_3Na$ (NaNs) and cetylpyridinium chloride $C_{10}H_{33}NC_5H_5Cl \times H_2O$ (CPCI) on classic: cation - MK-40 and anion-exchange-MA-40 membranes. Sorption of organic ions was determined in systems: MK-40-CPCI, MA-40-NaBS and MA-40-NaNs.

Sorption study was conducted under static conditions for loss of concentration of organic ions in solution in contact with the membrane and by potentiometric titration with the MA-40.

The concentration of tested substances was determined by spectrophotometry at the absorption bands of 260 nm. - for CPCI $2.5 \times 10^{-4}M$, 275 nm.- for NaNs $2.5 \times 10^{-4}M$ and 275 nm. for NaBS $2.5 \times 10^{-3}M$.

All measurements were performed at room temperature:



It is established that the sorption of organic ions membranes has ion-exchange character, and the sorption kinetics and specificity is determined by the size of the non-polar part of the ions; the establishment of sorption equilibrium (τ) increases in the ion- $BS^- < NS^- < CP^+$; in the latter case more than one month.

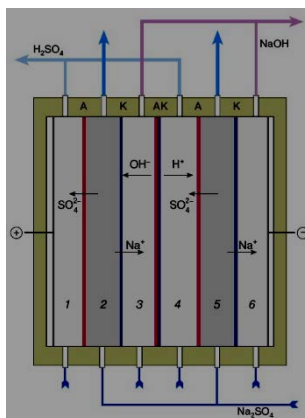
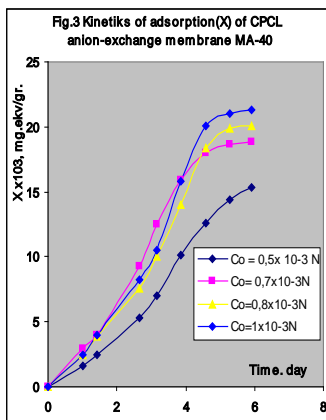


Fig. 4 Scheme of electrodiyalysis process

Results of studies have shown that organic ions such as BS^- and NS^- do not represent danger at water desalination by electrodiyalysis, while the sorption of CP^+ leads to poisoning of membrane.

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P40. THE SYNTHESIS AND STABILITY OF SOME THIOSUBSTITUTED CUMULENE COMPOUNDS

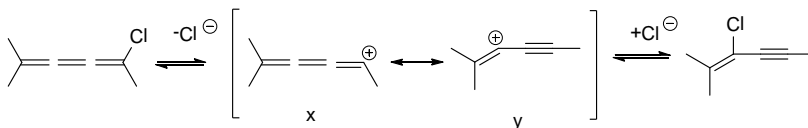
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It is known that thiosubstituted compounds are used as electronic conductors, ferromagnets, electron-accepting supramolecules, and optical materials in material chemistry and as stabilizers in polymer chemistry [1]. Butatrienes are very valuable compounds for their use in polymer chemistry. Unlike alkanes and most alkenes, cumulenes tends to be rigid, which makes them appealing for molecular nanotechnology [2-4].

In this study, thiosubstituted butatriene compounds were obtained from some thio-substituted butadienes. Tris(thio)-substituted butatrienyl halides partly isomerize to the tris(thio)-substituted butenyynes even at room temperature, in a solvent medium. Tetrakis(thio)-substituted butatrienes are more stable than butatrienyl halides. The solvolysis of butatrienyl halides gives the ambident vinyl cation which has positive charge on a disubstituted carbon in both mesomeric structures (x and y). The possible isomerization mechanism has been explained in the previous study by our group [5]. The structures were characterized by microanalysis and spectroscopic methods (FTIR, NMR, MS etc.).



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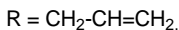
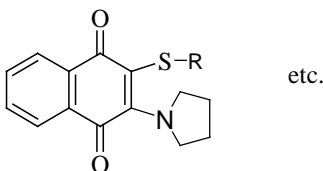
P41. THE INVESTIGATION OF NAPHTHOQUINONES WITH N- AND S-NUCLEOPHILES

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Naphthoquinones are prevalent motifs in various natural products, which are associated with diverse biological activities. Among the naphthoquinones, N, S-1, 4-naphthoquinone derivatives are interesting molecules because of their possible biological activity and they are found in some antitumor, antibacterial, and antifungal agents [1-3]. Especially, 2,3-disubstituted-1,4-naphthoquinone derivatives have antibacterial, and antifungal properties. [4]

In this study, new N, S-substituted naphthoquinone compounds were synthesized from reactions of 2, 3-dichloro-1, 4-naphthoquinone with different nucleophiles such as thiols and heterocyclic amines. The structures of the obtained compounds were confirmed by IR and NMR spectroscopy. Structural characterization is supported by elemental analysis and by mass spectrometry.



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P42. NEW HETEROCYCLIC COMPOUNDS RETAINING AROMATIC THIOLS

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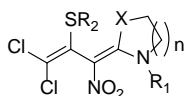
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Since the electron-withdrawing groups (EWGs) such as nitro, carbonyl, or cyano groups activating vinyl group significantly causes a change in the electron density distribution and responsible for the formation of active reaction centers in the electrophilic molecule, the reactivity capability of halogen atoms in the conjugated dienes and regioselectivity of the molecule towards to nucleophiles can be affected if it is possible to additionally introduce a selectively activating EWG in the molecule [1].

It is known that these reactions occur via a double addition-elimination mechanism and further displacement of the chloride. These processes have been used to prepare three-, four-, five-, and six-membered heterocyclic rings. The reactions of polyhalogenated mononitrobutadiene compounds as members of halonitroalkenes have been extensively studied [2, 3].

In this study, the reactions of 5-membered or 6- membered cyclic polyhalogenated nitrodienes with aromatic thiols are examined. In result of these reactions, new heterocyclic compounds containing thio group were synthesized and the structures were characterized with microanalysis and spectroscopic methods (FTIR, NMR, MS etc.).



$R_1 = -\text{Ph}, -\text{CH}_2-\text{Ph}$
 $R_2 = -\text{Ar}$
 $n = 1, 2$
 $X = \text{NH}, \text{S}$

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P43. NEW HETEROCYCLIC COMPOUNDS BASED ON POLYHALOGENATED NITRODIENES

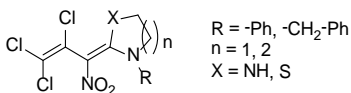
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Nitro-substituted polyhalogenatedbuta-1,3-dienes are useful and valuable precursors for versatile synthetic applications which became the subject in the last decade of investigations due to their rich chemistry as well as biological properties of the molecules [1]. A number of publications dealing with the reactions of versatile soft and hard nucleophilic reagents such as thiols, dithiols, piperazine, and piperidine derivatives with perhalo-2-nitrobuta-1, 3-diene, and perhalobuta-1, 3-diene to obtain S-, N-, S, S-, S, S-, and N, S-substituted diene compounds are available in the literature [2].

The reactions of nucleophiles with polyhalogenated nitrodiene compounds have been performed in our previous studies [3]. New polyhalogenated heterocyclic nitrodiene compounds obtained from these reactions are known to have biological activities [4, 5].

In this study, the reactions of polyhalogenated nitrodienes with various nucleophiles are examined as the continuation of our previous studies. In result of these reactions, new heterocyclic compounds were synthesized and the structures of obtained compounds were explained with microanalysis and spectroscopic methods (FTIR, NMR, MS etc.).



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**P44. QUANTUM-CHEMICAL MODELING OF THE THALIDOMIDE
DRUGSYNTHESIS REACTION**

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The thalidomide is an immunomodulatory agent with the chemical name: N-(2, 6-dioxopi-peridin-3-yl) phthalimide. Thalidomide usually is subscribed as a sedative, tranquilizer drug against nausea and vomiting. One of the cases of thalidomidesynthesis represents the interaction between Phthalimide and glutarimidewith secretion of hydrogen (the dehydration reaction) [1-2].

In present study we calculated the geometrical and electronic characters of the intermediate products of the synthesis reaction of the Thalidomide, such as the heat of formation (ΔH_f) the ionization potential (I) the dipole moment (μ) the net atomic charges (qi) and the bond orders (Pij) using quantum-chemical semi-empirical AM1 method [3].

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Notebook

Invited Lectures



Prof. Ramaz Katsarava, Georgia

"Amino Acid Based Biodegradable Polymers - Versatile Materials for Numerous Biomedical Applications"



Prof. George Kvesitadze, Georgia
Academician,
National Academy of Georgia

"Ecological Potential Of Plants "

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