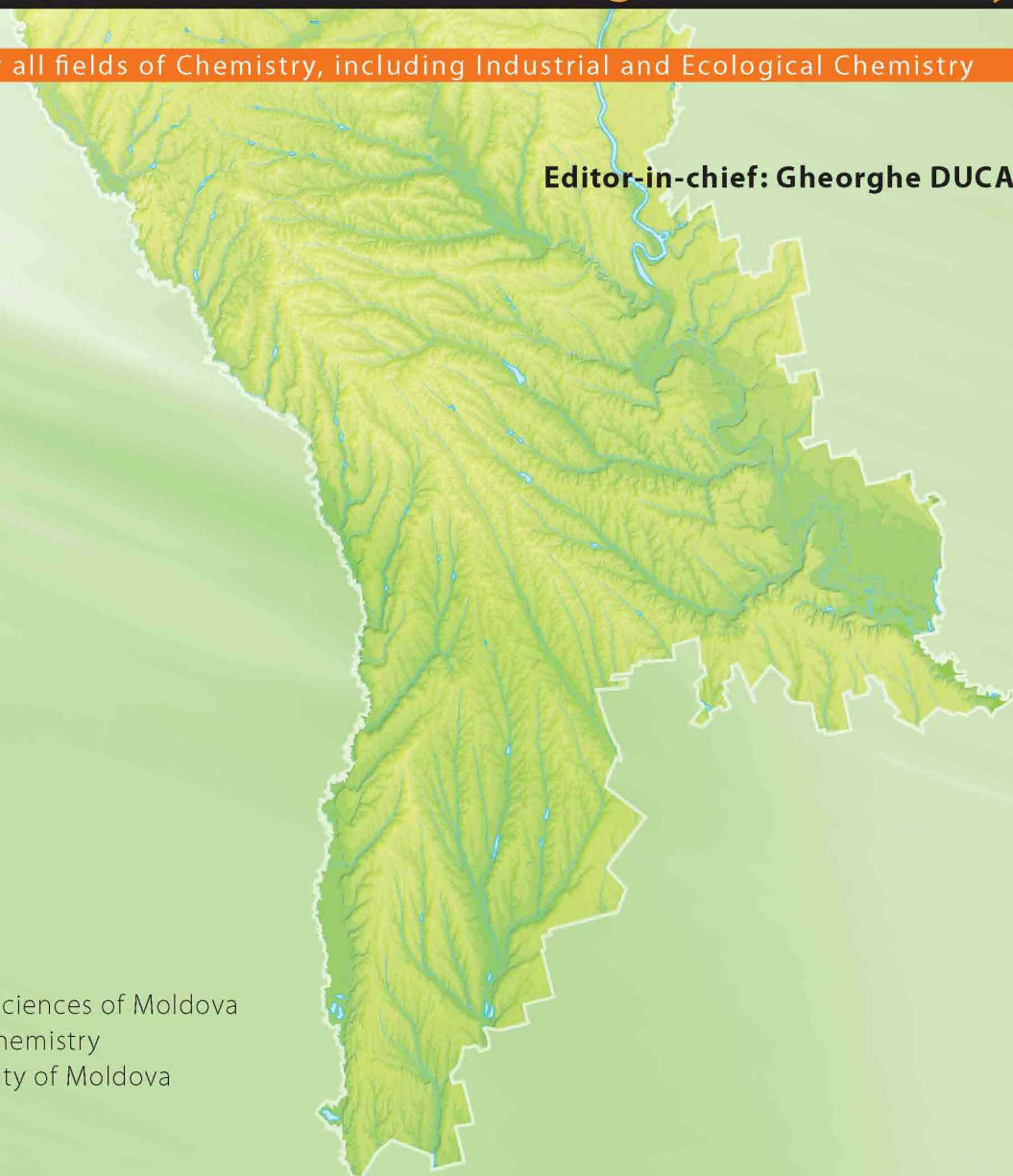# CHEMISTRY
JOURNAL OF MOLDOVA

General, Industrial and Ecological Chemistry

A journal for all fields of Chemistry, including Industrial and Ecological Chemistry

Editor-in-chief: Gheorghe DUCA

ISSUE CONTENT LIST WITH GRAPHICAL ABSTRACTS

A review of the synthesis of cyclic diterpenoids with different skeletons by electrophilic cyclization is provided.
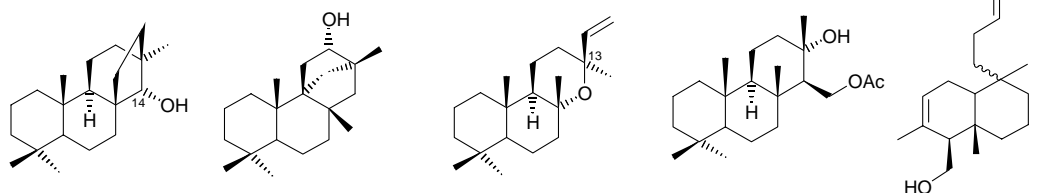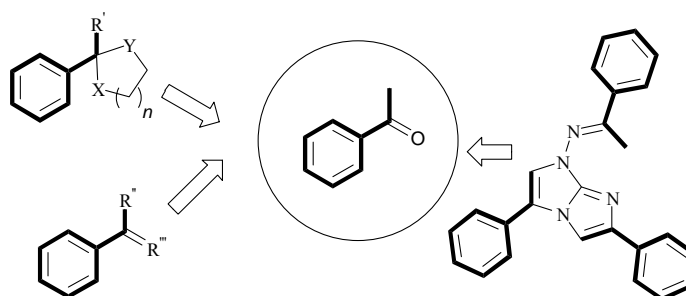
DEVELOPMENT OF NATIONAL EMISSION FACTORS FOR SOLID WASTE DISPOSAL ON LAND GREENHOUSE GAS SOURCE CATEGORY OF THE NATIONAL INVENTORY IN THE REPUBLIC OF MOLDOVA

Tatiana Tugui, Gheorghe Duca, Marius Taranu

The national GHGI is an essential link between science and policy making. Accurate tracking of GHGI play an important part in assessing overall national environmental performance and can be used as the basis for the abatement strategies.

	DOC	DOC_f	F
IPCC methodology	0,17	0,77	0,5
National data	0,146	0,585	0,6

ASSESSMENT OF KINETIC PARAMETERS IN THE WATERS OF THE NISTRU COURSE IN THE SECTION NASLAVCEA – DUBASARI

Elena Bunduchi, Gheorghe Duca, Viorica Gladchi, Nelli Goreaceva, Igor Mardari

The content of H2O2 and reductive substances in the Nistru water

september 2003
september 2005

1-Naslavcea;
2-Meresheuca;
3-Cosautsi;
4-Boshernitsa;
5-upstream the Dubasari barrage;
6-downstrean the Dubasari barrage
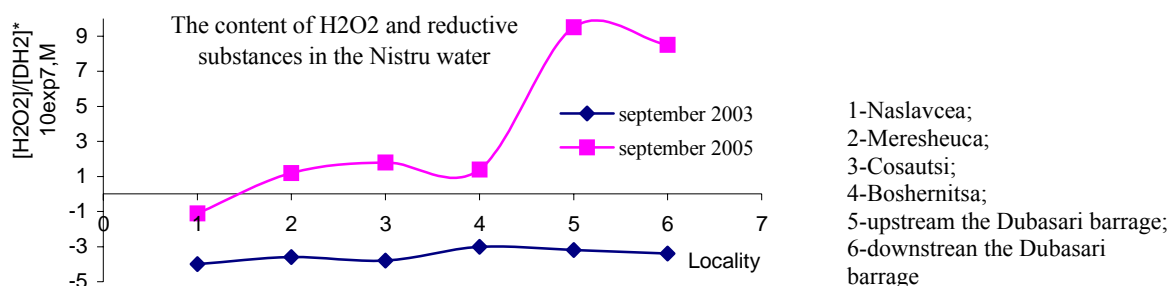
STUDIES ON THE SOLUBILIZATION PROCESSES IN WATER OF OENOTANNINS AND THEIR PHISICO-CHEMICAL PROPERTIES

T. Lupaşcu, Gh. Duca, P. Vlad, V. Kulciţki, R. Nastas

The results of investigation of oenotannins content in the seeds of different grape varieties are presented in the paper. It was demonstrated that the oenotannins content depends on the grape variety as well as on the geographycal zone of grape cultivation. A new procedure for water sollubilization of oenotannins has been elaborated. The mechanism of the oenotannins depolimerization has been reveiled by masss-spectrometric studies. It has been established, that the depolimerization process brings about formation of carboxilic acids and organic peroxides. The presence of the carboxilic and peroxidic groups was detremined on the basis of IR spectral analysis. It was demonstrated that the antioxidant properties of modified tannins are higher then those of initial unmodified ones.

IODINATION OF VEGETABLE OIL AS A METHOD FOR CORRECTING IODINE DEFICIENCY
Rodica Sturza

The aim of this work is the study made for obtaining iodized oil that would satisfy the requirements in iodine for human body. In the case of the iodination of the oil the addition of the iodine does not take place, but the fixation of molecular iodine to the double bond is performed with the formation of the clathrate type compounds, without the breakage of the double bond from the unsaturated fatty acids molecules. This allows the efficient incorporation of the molecular iodine in a large range of concentrations (1-100μg/ml) without a sensible modification of the physical-chemical properties of the product. This method, complementary with the iodinated salt, would allow the increase of the efficiency of the prophylactic undertaken measures.

HOMO- AND HETERONUCLEAR COMPLEXES OF COPPER(II) WITH SCHIFF BASE OBTAINED ON THE BASE OF 2-HYDROXY-3-CARBOXYNAPHTALDEHYDE

A.G.Lazarescu, T.C. Popa

The new polydentate Schiff base (H_4L) reacts stepwise with copper(II) and lanthanide (Nd^{3+}, Eu^{3+}, Gd^{3+}) ions to produce the heteronuclear complexes of composition $[CuLn(L)(NO_3)(H_2O)_n]$. The magnetic properties were studied.
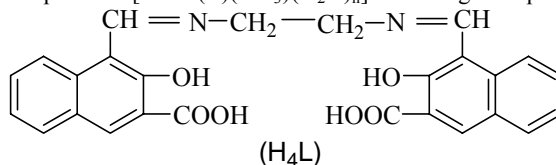
$$CH = N-CH_2-CH_2-N=CH$$

OH   HO

COOH   HOOC

(H_4L)

THE SYNTHESIS AND STUDY OF TETRANUCLEAR CLUSTER [Fe₄O₂(CCl₃COO)₈(THF)₂(DMF)(H₂O)]·THF

Denis Prodius, Valeriu Mereacre, Sergiu Shova, Maria Gdaniec, Yurii Simonov, Lorenzo Sorace, Andrea Caneschi, Nicolae Stanica, Ion Geru, Constantin Turta

The novel bis(μ_3-oxo) tetranuclear trichloracetate cluster, $[Fe_4O_2(CCl_3COO)_8(THF)_2(DMF)(H_2O)]\cdot THF$ (**1**), has been synthesised and subsequently characterised by X-ray structure analysis, magnetic measurements and infra red (IR). The structure of cluster is "butterfly" type. Magnetic studies reveal the presence of an antiferromagnetic exchange in the parallelogram skeletons of the tetranuclear species.
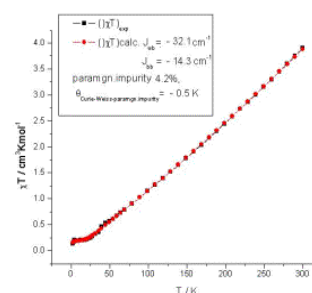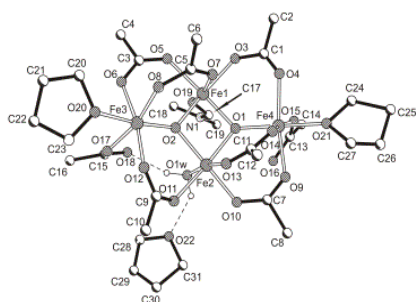
SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF HETEROMETALLIC NITRILOTRIACETATES OF CHROMIUM(III) WITH SOME *3d* METALS

Victor Ciornea, Aurelian Gulea

Heterometallic complexes of chromium (III) with some *3d* metals have been synthesized based on nitrilotriacetic acid (H_3nta), like $M(bpy)_2Cr_2(OH)_2(nta)_2\cdot nH_2O$, where M = Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}; *bpy* = α,α′-bipyridine; n = 8 or 9. Their chemical composition has been determined from the results of the elemental analysis and thermogravimetric study. The coordination modes of the *nta*$^{3-}$ ligand and the type of chemical bonds have been proposed basing on IR spectra.

[Cr$_3$O(CH$_3$COO)$_6$(H$_2$O)$_3$]NO$_3$·HNO$_3$·H$_2$O, TRIAQUA-HEXAKIS(μ-ACETATO)-μ$_3$-OXO-TRICHROMIUM(III) NITRATE NITRIC ACID SOLVATE MONOHYDRATE

Marco Bettinelli, Adolfo Speghini, Gabriele Bocelli, Olesea Gherco, Valeriu Mereacre, Denis Prodius, Constantin Turta

Reaction in methanol solution of the trinuclear 'basic' chromium(III) acetate with Pr(NO$_3$)$_3$·5H$_2$O and further extraction by chloroform-acetone mixture led to the formation of novel unusual [Cr$_3$O(CH$_3$COO)$_6$(H$_2$O)$_3$]NO$_3$·HNO$_3$·H$_2$O (**1**) cluster with one "free" molecule of nitric acid. Complex **1** crystallizes in the monoclinic space group *P*2$_1$/*c* with, at room temperature, *a* = 13.624(2), *b* = 15.032(2), *c* = 15.180(2) Å, *β* = 112.98(3) °, *Z* = 4, and *V* = 2862.09 Å^3. The obtained crystalline compound has been synthesized and characterized by IR and UV/Vis methods.

MAGNETIC INVESTIGATION OF AN UNUSUAL DISSYMMETRIC BINUCLEAR MANGANESE CARBOXYLATE COMPLEX

Ghenadie Novitchi, Jean-Pierre Costes, Lilia Popovschi, Sergiu Shova, Aurelian Gulea

The magnetic behaviour of an unusual dissymmetric μ- aqua binuclear manganese(II) corboxylate complex has been analysed. The magnetic data which have been fitted with spin-exchange Hamiltonian $\vec{H} = -J\vec{S}_1\vec{S}_2$, indicate that an antiferromagnetic interaction equal to *J* = -0.90(1) cm^{-1} is present. A correlation between *J* values and Mn-H$_2$O-Mn angles has been tempted.
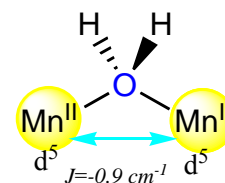
THREE SPIROSTANOL GLYCOSIDES FROM THE SEEDS OF HYOSCYAMUS NIGER L.

Irina Lunga, Pavel Kintia, Stepan Shvets, Carla Bassarelo, Cosimo Pizza and Sonia Piacente

Three steroidal glycosides of spirostane series have been isolated from the seeds of *Hyoscyamus niger L.* for the first time. Their structures were determined by physico-chemical methods.

1: R=Rha(1-2)Glc
3: R=Glc(1-2)Glc(1-4)Gal

2: R=Rha(1-2)Glc

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GUIDE FOR AUTHORS
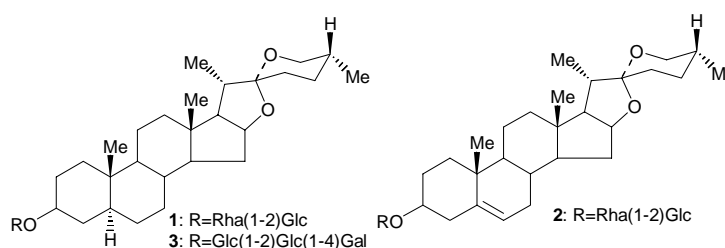
FOREWORD

Dear colleagues,

It is our pleasure to bring to life a new periodic publication devoted to chemists and chemical research.

The development of chemical research and its industrial applications has started in Moldova since the early 50-ies of the 20-th century. The most important and universally recognized achievements were made in several areas including Coordination Chemistry (Acad. A. Ablov, Acad. N. Garbalau), Natural Product Chemistry and Organic Chemistry (Acad. Gh. Lazurievski, Acad. P. Vlad), Analytical Chemistry and Electrochemistry (Prof. Yu. Lealikov, Dr. I. Vatamanu), Crystallography (Acad. T. Malinowski, Dr. Yu. Simonov), Physical Chemistry (Prof. A. Sychev, Prof. V. Isac), Quantum Chemistry (Acad. I. Bersuker), Ecological Chemistry (Acad. Gh. Duca, Dr. Hab. T. Lupascu, Dr. M. Gonta). Based on the earlier successes, chemical research has been continued currently in the Institute of Chemistry of the Academy of Sciences of Moldova, Department of Chemistry and Chemical Technology at Moldova State University, Medical University, Technical University, Agricultural University and at other research and educational institutions in Moldova.

The time has come to publish a journal in the research area to which so many efforts were made by Moldovan scientists and so many significant results were obtained. I am excited to note that this mutual decision was taken by the chemistry scientists of Moldova. Please let me greet all the chemists and experts in the adjacent areas with this new specialized periodical and the new possibilities opened for them: they are welcomed to present and discuss their latest results and find new information on its pages.

"CHEMISTRY JOURNAL OF MOLDOVA. General, Industrial and Ecological Chemistry" has several important goals. First of all we intend to focus this edition on the results of basic and applied chemical research, experimental and technological elaborations that are more likely to find implementation in Moldova. That's why we encourage publications related to traditional branches of the country's national economy, like food processing, crop protection, pharmaceutical, cosmetics industries, microelectronics, fiber processing and wine industry. Besides, we lay special emphasis on new processes and technologies aimed at sustainable development, rational use of resources and environmental protection.

It is also anticipated that this journal will contribute to strengthening the Chemical Society of Moldova, following development of research in Moldovan chemical institutions and promoting their collaboration with the international chemical community. Nowadays, the collaborative research represents the clue to competitive results and joint projects are always favored, especially those on the interfaces of different scientific areas. Moldovan chemists undertake concerted efforts to integrate in the global scientific environment and we would be extremely glad to have in our journal contributions originating from our research partners from all over the world.

And last, but not least we would like to provide an additional opportunity to the younger generation of Moldovan chemists to publish their research results in a journal close by format and style to the most recognized international journals.

I shall express my gratitude to the members of the editorial board who kindly agreed to support us and to the contributors of the journal's first issue who helped us to make it happen. Let's do hope that this is a good beginning of a fruitful activity.

Gheorghe DUCA
Editor-in-Chief

THE FORECAST AND THE STRATEGY OF CHEMISTRY DEVELOPMENT

Gheorghe Duca[a], Aurelian Gulea[b]

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[b]*State University of Moldova, 60 Mateevici str., Chişinău, Republic of Moldova*

Preliminaries

A lasting economy of the state requires continuous progress in technology based on novel scientific achievements. Science and innovation are the basic factors ensuring competitiveness of our industry and agriculture and provide for about 50-85% of economic growth.

Science is the nation's patrimony and it determines the future of the country.

The objectives of Science in Moldova are:
- to get new knowledge about nature and society;
- to create a wide scientific-technologic basis that would ensure:

(1) innovation activity in the country;
(2) technology progress;
(3) world competitiveness of our production.

The first pedagogic institution in our country specialized in chemistry was created in 1939 as a part of the Agronomy Department in Chisinau (a of the University of Jassy). Since 1946 till present graduate and undergraduate university training in chemistry in Moldova took place in the following institutions:
- Department of Chemistry and Technological Chemistry of Moldova State University;
- Department of Chemistry and Biology of Tiraspol State University (headquarter in Chisinau);
- Institute of Chemistry of the Academy of Sciences of Moldova.

At the Department of Chemistry and Technological Chemistry of Moldova State University there are three Divisions: inorganic and physical chemistry, organic and analytical chemistry, technological and ecological chemistry. In addition to these institutions there are Chemistry Departments in other high-educational institutions in Moldova that have university level training in chemistry, namely, "N.Testemitsanu" State University of Medicine and Pharmaceutics, Moldova Technical University and Moldova State Agrarian University.

The departments and divisions of these institutions provide for the country's needs in chemistry teachers, researchers and industry chemists. Biochemists are trained by the corresponding divisions in the Biology Department of Moldova State University and of "N.Testemitsianu" Moldovan State University of Medicine and Pharmaceutics.

At the Chemistry Institute of Moldova Academy of Sciences investigations are carried out in the following laboratories: coordination chemistry, bioinorganic chemistry, quantum and chemical kinetics chemistry, chemistry of terpenoides, organic synthesis, analytical chemistry and ecological chemistry. Since the onset of this institute the following laboratories were active during a limited time period: chemistry of regulators of plant growing, chemistry of mineral resources and water. Presently the Institute of Chemistry Moldova Academy of Sciences has 125 co-workers, 57 of them being scientific researchers (13 habilitatus doctors, 33 Ph doctors). The percentage of scientific researchers with scientific degree is 81%.

The chemical institution "Isomer" is also operative at Moldova Academy of Sciences.

The graduate studies that functions as a part of the mentioned institutions are aimed at training qualified experts in chemistry. During 1961-2005 Moldova Academy of Sciences prepared 181 doctors of philosophy and habilitatus doctors specialized in chemistry and physics. The distribution of the high qualified graduates on their majors is shown in the Table 1.

Table 1

The number of high qualified experts trained at the Chemistry Institute of Moldova Academy of Sciences during 1961-2005.

Specialty	Nr. of high qualified experts trained		Total
	Ph doctors	Habilitatus doctors	
Inorganic Chemistry	46	7	53
Quantum Chemistry	21	4	25
Organic Chemistry	39	6	45
Analytical Chemistry	29	1	30
Physical Chemistry	24	4	28
Ecological Chemistry		2*	2*
Total	159	22	181

*Thesis of habilitatus doctors defended at two specialties.

The research staff of the Institute of Chemistry of Moldova Academy of Sciences published over 2662 scientific works, 120 monographs, 10 handbooks, 240 patents. They took part at 330 national and international exhibitions.

Among the most important achievements of the Institute of Chemistry the following should be mentioned:
1. Perfumes and sauces for tobacco industry;
2. Odorous compounds with amber smell for perfumery and technologies for such compounds preparation;
3. New compositions for plastering;
4. Technology of surface water treatment;
5. Catalysts for epoxyde (rubbers) solidification;
6. Dyes for plastics;
7. *"Gajazot"* – product with anti-chlorosis properties for vineyards;
8. *"Virinil"* – growth stimulator for grafted vineyards;
9. Stomatologic preparations *"Fenglicol", "Fencarin"*;
10. *"Salivit"* – product for treating the inflammatory diseases or other diseases of locomotor's system;
11. *"Mobipan"* – antihypotensive product for treating the cardiovascular diseases.

Elaborations that can be applied in the national economy:
1. Preparation of active charcoal by chemical activation (the respective technology is implemented at "Isomer" Chemical institution);
2. Antidepressant *"Chetizal"*;
3. Anticancer product *"Setremed"* ;
4. *"Trifeden"* – growth stimulator for corn crops;
5. *"Difecoden"* – growth and productivity regulator;
6. *"Codiclogu"* – product with anticoccide properties;
7. *"Codimez"* – food intoxication antidote for bovine, particularly with pesticide;
8. *(Funghicide) products* – for cucumber flouring control, brown blight and wheat flouring control.

Table 2

Annual output of chemical products in Moldova

Chemical Industry				
Item	2001	2002	2003	2004
Number of companies	14	12	14	
Production volume, mln lei	78,0	81,3	99,6	
Annual average number of personnel, thous. pers.	1,1	1,1	1,1	
Cement, lime and plaster production				
Number of companies	5	5	3	
Production volume, mln lei	149,3	268,8	132,9	
Annual average number of personnel, thous. pers.	1,1	0,9	0,6	
Soap, detergents, maintenance products, perfumery and cosmetics products				
Number of companies	3	25	2	
Production volume, mln lei	27,2	20,4	24,6	
Annual average number of personnel, thous. pers.	0,4	0,4	0,4	
Glass and glass articles production				
Number of companies	4	4	4	
Production volume, mln lei	425,4	498,0	502,8	
Annual average number of personnel, thous. pers.	2,0	2,0	2,0	

The main research achievements of the "Industrial and Ecological Chemistry" Division at the Moldova State University involve the following:
- theory of oxidation chemical auto-purification of water and seasonal dynamics of redox condition specific to natural water;

- theory of fluid reactors, transformation of nitrogen compounds with micro-organisms immobilized on support;
- theory of environmental reduction-oxidation condition;
- methods of physical-chemical and biochemical treatment of solid wastes and waste waters;
- methods of inhibiting the formation process of N-nitrosamines using reductons;
- mechanisms of catalytic and photochemical oxidation of organic substances with oxygen, hydrogen peroxide and free radicals.

There is a modest output of chemical industry in Modova. However, according to statistical data, there exists certain chemical production in Moldova.

Chemistry as a science and as a branch of national economy will be developing in the following important areas:

- development of fundamental and applied science, development of applicative research oriented towards the production needs, in line with world's tendencies;
- exports, including high qualified ones;
- modernization of available chemical technologies, elaboration and implementation of new technologies for the obtaining of building materials;
- elaboration of efficient means for plants protection and increase in cultivated plant productivity;
- development of food products chemistry;
- elaboration of new multifunctional technologic materials;
- production of new pharmaceutical substances;
- elaboration of advanced technologies for the needs of cosmetics and tobacco industries;
- development of chemistry of oil and oil products;
- elaboration of advanced technologies for adsorbents production, waste and natural water treatment, soil and air protection, and also offals use in different areas of the country's economy.

The main objectives of chemistry development in the Republic of Moldova are:

- to maintain the high development level of fundamental chemical science;
- to create the efficient research and training system for chemistry development;
- to elaborate the advanced technologies for obtaining the adsorbents, using the available local raw material;
- to provide the scientific and technical control of cement, glass, ceramics materials, concrete production;
- to create the centre for physical methods application in chemistry;
to - create a screening and testing centre of active biologic substances synthesized and obtained by extraction;
- to create institutions for chemical substances production, necessary for national economy (agriculture, medicine, industry);
- to elaborate the efficient non-polluting technologies, and to elaborate the technologies for the treatment of contaminated environmental comportments;
- to create the suitable departments and corporations for offals use;
- to create the suitable departments and corporations for obtaining of competitive oil products;
- to create the institutions to produce the labor-saving devices using the local raw materials.

Inorganic and coordination chemistry

Being considered initially as a part of inorganic chemistry, and regarded as a special discipline nowadays, coordination chemistry is among the most important and actual areas of chemistry, an area that attracted and continues to attract the researchers from all around the world and from all chemistry's areas (inorganic chemistry, physical chemistry, organic chemistry, analytical chemistry, biological chemistry, etc.). This area have found rapid development within a short time period.

There is a world-recognized coordination chemistry school in Moldova, with old and solid traditions. The founder of this school was Academician Antonie Ablov.

The importance of this area consists in the following:

- coordination chemistry is a boundary discipline, that attracts inorganic chemists and other experts in theoretical and experimental areas;
- coordinative compounds, especially polynuclear ones, found broad applications in various fields;
- coordinative compounds are present in numerous natural and technological systems and living organisms (chlorophyll, hemul, vitamin B_{12}, hemocyanine, nitrogenase, etc.).

We should also add that coordination chemistry ensures chemistry progress, from both experimental and theoretic standpoint. The main development trends of coordination chemistry are specified in the chart below.

```
                                                    Methods of theoretical
Anchored          ┌─  ┌──────────┐      ┌──────────────────────┐  ─┐  Metal ions changing
Complex           │   │ Catalysis │      │ Methods of theoretical │  │  interactions
Combinations      └─  └──────────┘      │      chemistry       │  ─┘  Mixed valence systems
                         ▲                      ▲
                         │                      │
   ┌──────────────┐   ┌────────────────────────────┐   ┌──────────────────┐
   │ Super molecular │◄─│ POLYNUCLEAR COMPLEX      │─►│ New materials for │
   │   chemistry   │   │      COMBINATIONS          │   │ molecular electronics │
   └──────────────┘   └────────────────────────────┘   └──────────────────┘
                         │                      │                  │
                         ▼                      ▼                  ▼
Structural models  ┌─  ┌──────────────┐   ┌──────────────┐   Molecular iron magnets
Biomedical         │   │ Bioinorganic │   │ Materials science │  Information storage
 implications      └─  │   chemistry  │   └──────────────┘  ─►│ Magnetic materials
                       └──────────────┘          │             (mixed oxides)
                                                 ▼
```

Materials with super   a) oxide systems
conducting properties: b) oxocarbonates
                              c) mixed sulphides
                              d) mixed oxosulphides
                              e) complex polynuclear sulphides

Organic and bioorganic chemistry

Organic and bioorganic chemistry is the most important and large area of the modern chemistry. Organic compounds have are widespread in natural environment, practically providing the regulation of all vital processes specific to land flora and fauna.

Academician Gh. V. Lazurievschii was the founder of organic and bioorganic chemistry school in the Republic of Moldova. The works carried out under his leadership had significant impact on the study of such natural compounds as alkaloids, terpenoides, triterpenic and steroidal glycosides, cannabinoides and carbon hydrates. At the same time, thin organic synthesis found its development. Objects of these studies were natural compounds isolated from spontaneous local flora and some offals accumulated in agricultural and food industry.

The importance of this area of chemistry is evidenced by:
- revealing of the mechanisms of chemical reactions and developing the notions of stereochemistry;
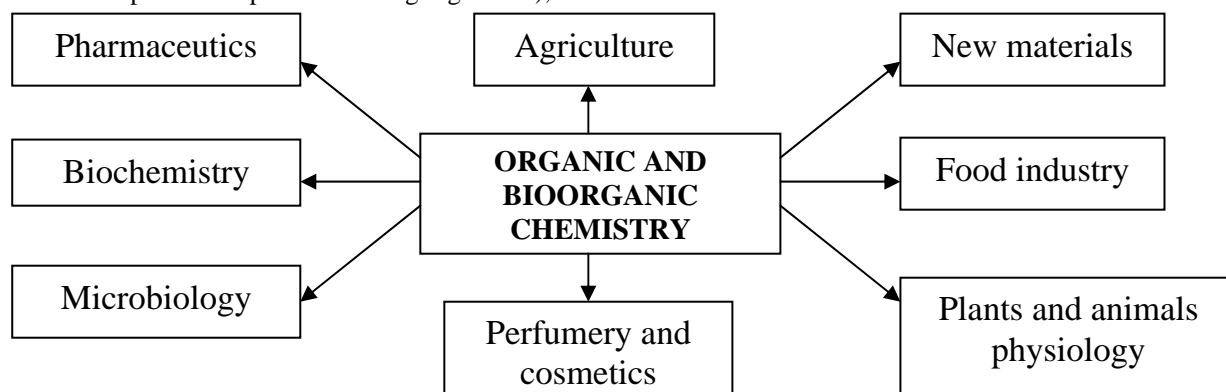- elaborating synthesis methods and technologies for producing a number of active biologic compounds, used on a large scale in medicine as pharmaceutical products and in agriculture to realize the regulation of processes of plant development and their protection against different diseases and damages;
- existence of renewable autochthonous sources for obtaining organic compounds, which can serve as raw materials for different industry branches;
- application in botany (chemotaxonomy), microbiology (establishing the structure of microorganisms metabolites), physiology (studying organic compounds which realize the regulation of different vital processes specific to living organisms);

```
┌──────────────┐        ┌──────────────┐        ┌──────────────┐
│ Pharmaceutics │        │  Agriculture  │        │ New materials │
└──────────────┘        └──────────────┘        └──────────────┘
        ▲                       ▲                       ▲
┌──────────────┐        ┌──────────────┐        ┌──────────────┐
│ Biochemistry  │◄──────│  ORGANIC AND  │──────►│ Food industry │
└──────────────┘        │  BIOORGANIC   │        └──────────────┘
        ▲               │  CHEMISTRY    │                ▲
┌──────────────┐        └──────────────┘        ┌──────────────┐
│ Microbiology  │               │                │ Plants and animals │
└──────────────┘               ▼                │  physiology   │
                        ┌──────────────┐        └──────────────┘
                        │ Perfumery and │
                        │   cosmetics   │
                        └──────────────┘
```

- large-tonnage production of plastics and fuel, inclusively of biofuel.

Objectives of organic and bioorganic chemistry are as follows:
- to isolate, identify and synthesize natural compounds representing an interest for different branches of national economy;
- to elaborate the directed synthesis methods of new organic compounds and their testing.

The scheme above shows the areas in which the results of scientific investigations are applied.

Analytical chemistry

The trends of analytical chemistry development in Moldova were justified by the scientific interests of the research school created by academician Yu. Lealikov. The research was focused on electrochemical methods elaboration to detect different elements (metals or non-metals) in non-ferrous metallurgy products, food products, electro-techniques (semiconductors), extra pure metals industry, and also in pesticides. Special attention was paid to preparation and testing of such materials.

Currently, the research in analytical chemistry is developing in two main areas which correlate with the research tendencies specific to the world science:
- elaboration the methods of trace amounts detection of toxic substances, biologically active substances, and their metabolites;
- elaboration of rapid ("express") analysis methods, including the field analysis techniques, which make it possible to provide the analytical control and large-scale monitoring of products quality.
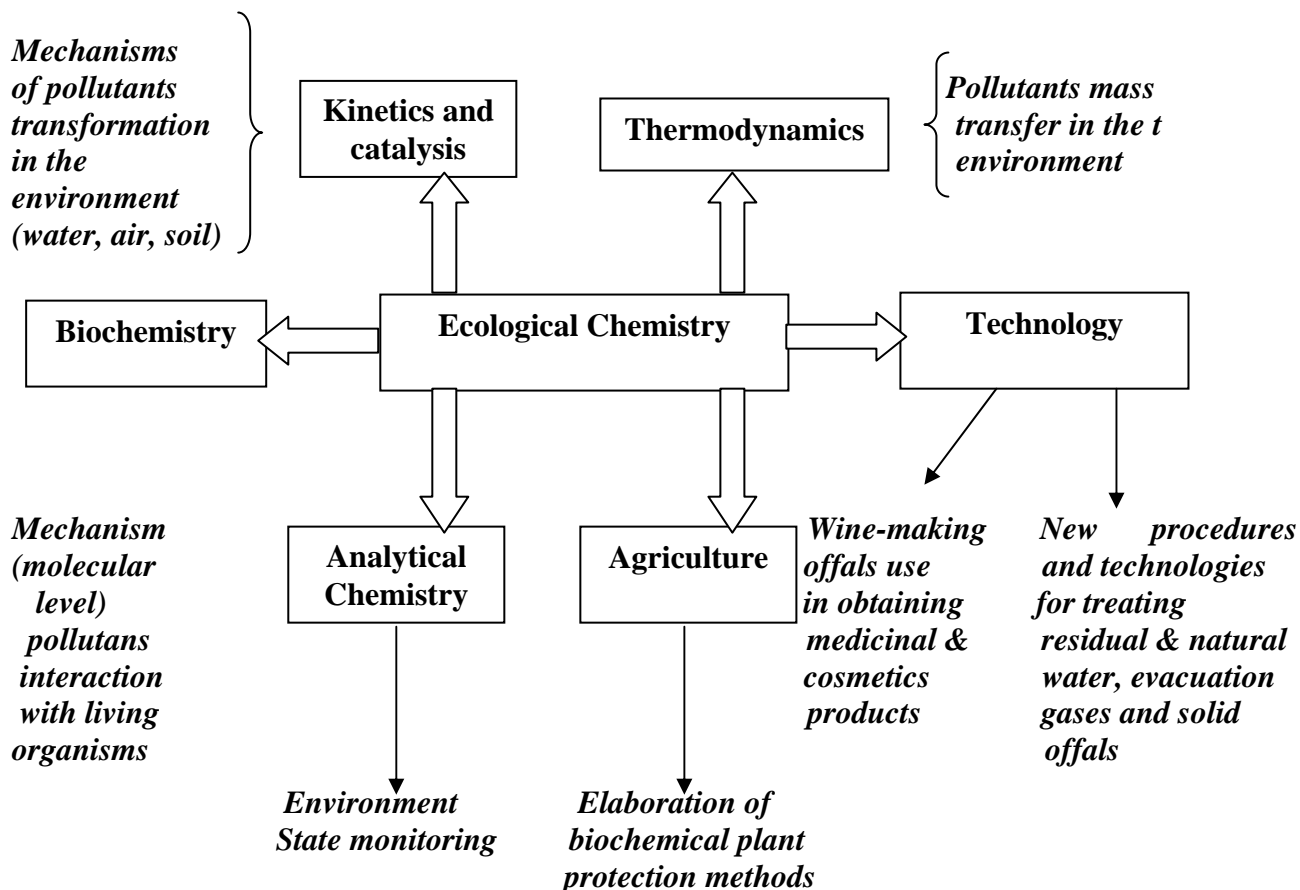
To reach these objectives, the electrochemical methods using the electrochemical or sorption accumulation processes and potentiometric, amperometric, optical, biologic sensors, will be applied.

Chromatography and molecular spectroscopy will be developed too, using new organic analytical chemicals. Elaboration and application on a large scale of new devices will be a good dam for the production of counterfeited, spoiled, with deviation from standards products.

Industrial and ecological chemistry

The environment is affected by the continuous anthropogenic loads. The concentration of toxic gases responsible for the greenhouse effect, leading to the destruction of ozone layer or generating the acid rains, is permanently increasing in the atmosphere.

The quality of fresh water is degrading; pollutants concentration (heavy metals, oil products, nitrogen compounds, surfactants, etc.) is increasing. The soil is also subjected to pollution (domestic, industrial discharges, pesticides) and its fertility decreases.

Mechanisms of pollutants transformation in the environment (water, air, soil)

Kinetics and catalysis

Thermodynamics

Pollutants mass transfer in the t environment

Biochemistry ← **Ecological Chemistry** → **Technology**

Mechanism (molecular level) pollutans interaction with living organisms

Analytical Chemistry

Agriculture

Wine-making offals use in obtaining medicinal & cosmetics products

New procedures and technologies for treating residual & natural water, evacuation gases and solid offals

Environment State monitoring

Elaboration of biochemical plant protection methods

The population health, which is affected by environmental pollution, is an important factor for economy development. Different pollutants may be modified yielding even more toxic metabolites in the environment.

Proceeding from the above considerations, we came to the conclusion that ecological chemistry and environment protection have a paramount significance. In the Republic of Moldova the scientific area of "Ecological chemistry" was founded and directed by academician Gh. Duca.

Fundamental and applied scientific research in this area are carried out at the Industrial and Ecological Chemistry Division at Moldova State University, Research Center on Applied and Ecological Chemistry, National Institute of Ecology and Institute of Chemistry of Moldova Academy of Sciences. The main achievements in ecological chemistry as fundamental science are presented above.

The main results achieved in chemical technology and environment protection research, are as follows:

- elaboration of electrochemical activation technology and conditioning of underground waters which contain fluorine and sulphury hydrogen;
- synthesis of adsorbents with modified surface for removing oil products, for wine demetallisation, etc;
- technology of anaerobic waste water treatment and hydrolytic destruction of persistent organic compounds using suspended and fixed microflora, and biogas obtaining;
- catalytic methods of gas emissions treatment from industry and auto transport;

In the above scheme the interrelated areas of ecological chemistry are given, which are the main research trends.

The main tendencies in industrial chemistry research are linked with the requirements of ecological chemistry and are determined by the national economy. They include:

- elaboration of new coagulant types and modified sorbents from secondary products for the water treatment containing oil products, dyes, for selective wine demetallisation;
- utilization and processing of secondary wine-making products by obtaining precious compounds for national economy;
- modernization of electrochemical technologies of water treatment and conditioning at rural zone;
- monitoring of surface and underground water quality in the Republic of Moldova and study of the reduction-oxidation state dynamics in natural waters;
- elaboration of kinetic methods for estimation of natural water quality and their correlation with the results of classical hydro-chemical investigations;
- intensification of catalytic combustion processes specific to fuel and emission gases treatment;
- elaboration of methods for N-nitrozo compounds formation inhibition in order to diminish the chemical risk of cancer occurrence;
- biogas obtaining, as alternative energy source, from industrial organic wastes and elaboration of individual systems for biogas production at the farms.

Quantum chemistry

Being a part of physical chemistry, quantum chemistry currently forms completely the theoretical base of modern chemistry. Various quantum-chemical aspects are discussed in the majority of chemistry papers published in the last decades.
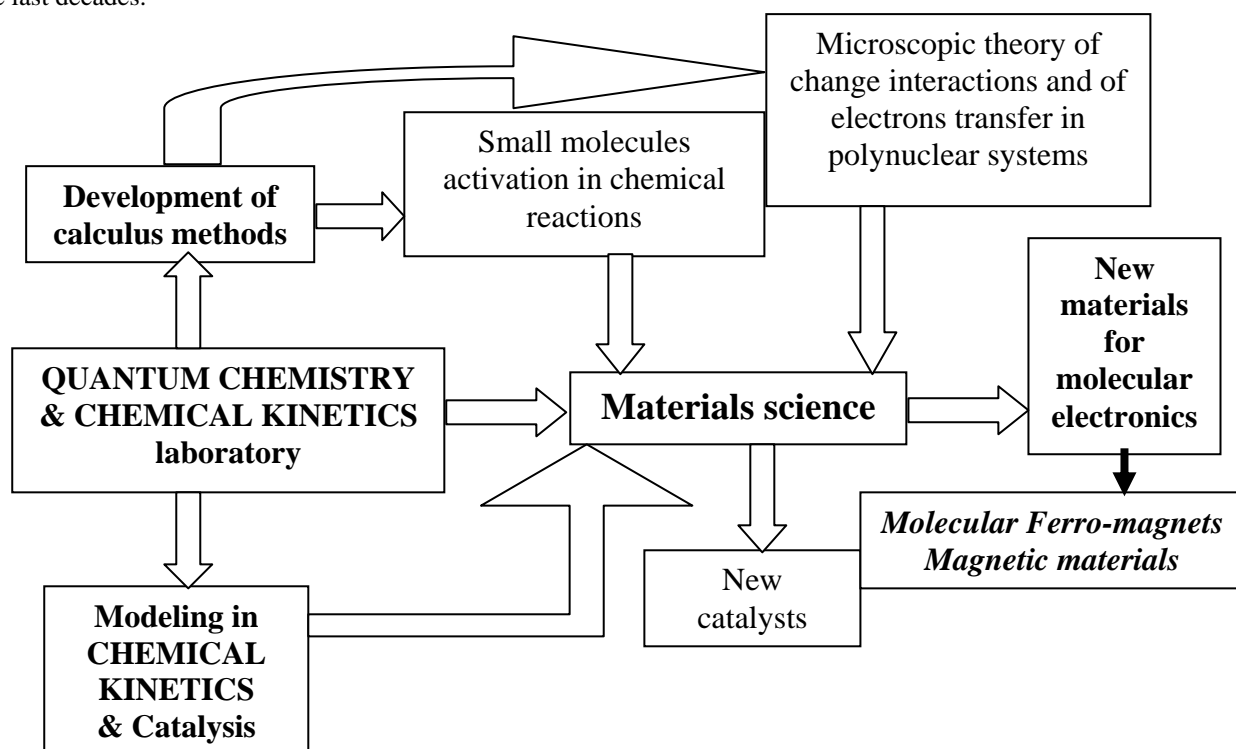
At the beginning of the year 1960 in the Republic of Moldova a specialized quantum chemistry school was established (the founder is academician I.Bersuker). The research on vibronic effects, chemical reactivity, electronography and spectroscopy, magnetic interactions of changing and transferring electrons into polynuclear clusters resulted in outstanding successes highly appreciated by the world scientific community. The following scheme shows the contribution of this research investigations to other areas.

Future research in this area will be focused on the following problems:

- activation of small molecules (oxygen, nitrogen, carbon oxide etc), which participate in different catalytic processes;
- study of molecular magnets;
- development of "structure – activity" scheme at different substances.

Academy of Sciences of R. Moldova
Institute of Chemistry
Institute of Applied Physics
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Institute of Physical Chemistry, Polish Academy of Sciences
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The XV-th Conference

"Physical Methods in Coordination and Supramolecular Chemistry"

and the XVII-th Reading in memory of Academician A. Ablov

September 27 - October 1, 2006, Chişinău, Moldova

The Organizing Committee is glad to invite you to participate in the **XV-th Conference "Physical Methods in Coordination and Supramolecular Chemistry"** *and the XVII-th Reading in memory of Academician A. Ablov*, which will be held in Chişinău, Republic Moldova on September 27 – October 1, 2006

The Program of the XV-th Conference will include lecture and poster presentations on a range of interdisciplinary topics connected with the study of coordination and supramolecular compounds by physical methods including optical, γ–resonance and radio-spectroscopy, diffraction methods, magnetochemistry. The special attention will be paid to the compounds with the library of useful properties, e.g., molecular magnets, switches, sensors, biologically important compounds.

HISTORICAL OVERVIEW

Beginning from 1962 Chişinău, hosted thirteen of a total of fourteen Conferences, on the applications of physical methods to the study of coordination compounds and beginning from 1999 to the study of supramolecular compounds also. These forums had brought a substantial contribution to the solution of fundamental problems of chemistry and enlarged the field of its practical applications.

Chişinău, was the host of these conferences not only by tradition, but also because of the high appreciation by the scientific community, earned by its school of coordination chemistry as well as by the wide use of physical methods in research of complex compounds. Previous conference editions had been attended by numerous specialists in the field, from the scientific centers of Belarus, Bulgaria, Baltic and Caucasian Republics, Czech Republic, Germany, Hungary, Poland, Romania, Russia, Ukraine, Yugoslavia. The event had an international resonance. At the last three conference session, researchers from scientific centers of Canada, France, Israel, Italy, Norway, Turkey, Spain, and U.S.A. have presented their papers.

The periodicity of these forums is once per three years. The last one, the XIV-th Conference held under this motto took place in September 2002 in Chisinau. In its framework there had been taken the decision to organize the XV-th edition of the Conference in 2006 in Chişinău.

The XV-th Conference is dedicated to memory of famous moldavian chemist academician Nicolae Gerbeleu (1931-2006).

SCIENTIFIC PROGRAM

The Conference program will include Plenary Lectures, Short Lectures and Poster Presentations. Scientific program will be organized around the following topics:

- Study of coordination compounds in the solid state and in solution by EPR, NMR, Mössbauer, laser and Röntgenoelectron spectroscopy.
- Relationship structure – property for the compounds with the library of useful properties (bioactive compounds, materials for molecular electronics).
- Magnetochemistry and single-molecule magnets (SMMs)
- Diffraction methods in study of coordination and supramolecular compounds
- Crystal engineering

English is the official Conference language. No translation will be provided.

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ACADEMICIAN PAVEL VLAD – A DISTINGUISHED RESEARCHER AND ARDENT PROMOTER OF SCIENCE

Names of some countries come to be famous owing to the deeds of their most devoted citizens. People are one of the main assets of a country. A very special and highly respected personality, a prominent Moldovan researcher in chemistry is academician Pavel Vlad. Academician Vlad has been one of those who laid the foundations of bioorganic chemistry, of chemistry of natural and biologically active compounds in Moldova. It is his commitment to scientific studies and research that has made the Republic of Moldova known in many countries.

Aristotle, an eminent Greek philosopher and scientist was supposed to say that friends were important to him, but even more important was the truth. Today we are firmly convinced that those words have become a credo for academician Pavel Vlad. Academician Vlad has always strived for the truth both in scientific activities and in social life. His many disciples, who have been happy to work under the guidance of this scientist, are thankful witnesses of putting into practice the Aristotle principle. Among the first subscribers here is the staff of the Laboratory of Chemistry of Essential Oils Plants, renamed as the Laboratory of Chemistry of Terpenoids, the Head of which academician Vlad has been for about 35 years. He has been a scrupulous but friendly mentor and reviewer of the works of his Ph.D. students and colleagues.

Nowadays when the society has realized that economic development, progress is very much dependent on advancement of science, when research or its results penetrate into every sphere of life, it is a hard task to build a scientific school recognized in many different countries, the task which only a renown figure can fulfill, a person whose scientific achievements are appreciated worldwide, a person who is an example of hard work, of life-time commitment to science, a person with an infinite creative potential. All these can be duly attributed to academician Pavel Vlad.

When being Director of the Institute of Chemistry, the Vice President of the Academy of Sciences of Moldova, academician Vlad was using the principle "truth above all" in his managerial activities, too. For quite a few years he was a good administrator of the institute and a fervent developer and promoter of Moldovan academic science, as Vice President.

The year 2006 marks the 70th anniversary of academician Vlad. Pavel Vlad was born on June 6, 1936, in the family of farmers in the village Lipnic, district Edineț.

In 1953 he left the local secondary school and applied for Chemistry Department at Moldova State University. He got a place there and graduated the university with Honors Degree in 1958. On the recommendation of the Department he started his Ph.D. research at the Sector of Organic Chemistry at the Moldovan Branch of the USSR Academy of Sciences. During hid postgraduate studies Pavel Vlad was sent to six-month training at the Institute of Organic Chemistry and Biochemistry in Prague. There, jointly with Milan Soucek, under the guidance of a prominent scientist Vlastimil Herout, Pavel Vlad carried out the investigation under the title of „The Establishment of Absolute Configuration of Linalool and Nerolidol", which was published in Europe. In Prague future academician got acquainted and learned to use several methods new for those times. First of all, column chromatography should be mentioned because it was that method which has greatly assisted in the development of chemistry research in Moldova.

Having successfully finished his postgraduate studies, Pavel Vlad was invited to work at the Institute of Chemistry of the Academy of Sciences of Moldova as a junior researcher (1961). In 1964 Pavel Vlad defended his doctoral thesis „Stereochemistry of Certain Diterpenoids of Labdanic Group". In 1984 the future academician Vlad defended the thesis for the higher degree of Doctor Habilitate (Chemistry) „Investigations of Labdanic Diterpenoids".

The employment record of academician Vlad is pretty long. He was Deputy Director for Research at the Institute of Chemistry (1974), and then he was appointed Director of the same institute (1975). In 1990 the rank of Full Professor was added to his name. In 1989 Pavel Vlad was elected Corresponding Member of the Moldovan Academy and in 1992 – Full Member (Academician) of the Academy of Sciences of Moldova.

In March 1995 academician Vlad was elected Vice President of the Academy of Sciences of Moldova, and he was holding that post till 2004. His profound knowledge not only in chemistry, his creative attitude, his enormous working capacity became extremely evident during those years.

At present academician Pavel Vlad continues his scientific work as the Head of the Laboratory of Chemistry of Terpenoids. Academician has been in this office since 1977.

His own research findings, as well as those of his school, have been shown to the world of science in a great many works published and patented not only in Moldova, but also abroad.

Academician Vlad has determined the priorities, new lines in studies of terpenic compounds, in working out methods of research into fine organic synthesis. Under his guidance and with his direct contribution new approaches to determining absolute configuration of a series of labdanic diterpenoids and of converting them into bi-, tri- and tetra-cyclic compounds have been designed. Novel universal methods for synthesizing tetrahydrofurans from 1,4-glycols, of nor-alcohols from cyclic olefins, of olefins from tertiary alcoholic acetates, of glycols from lactone, of unsaturated alcohols from monoacetates of bitertiary glycols, as well as of dienoneles by means of photodehydrogenation of unsaturated cyclic ketons.

The school founded by academician Pavel Vlad is the leader in the investigations of reaction of superacidic cyclisation of terpenoids, and also of the regularities of the reaction mentioned in different classes of terpenic compounds, such as alcohols, their acetates, acids, esters, phenylsulphones, etc. Efficient ozonolytic methods for norlabdanic compounds preparation as well as a new theory for evaluating their structure-ambra odor relationship have been also developed. The perfumery industry has received and started to implement original and efficient methods for obtaining familiar compounds, such as norambreinolide, sclareol, drimenone, ambroxide, as well the novel ones, such as ketoxide, ambrol, ionoxide. The local raw material has been used to prepare new fragrance compositions for tobacco, some of them have peen used at the Chişinău tobacco factory.

During his long and prolific life in science academician Vlad has published over 300 works, among them two monographs, two course books, 16 review articles, and have been patented 49 innovations. Academician Vlad has been a participant to 44 international conferences and symposia.

Academician Pavel Vlad has been the scientific adviser in two studies for the degree of Doctor Habilitate and 12 for the Degree of Doctor in Chemistry.

Academician was among those participants in International Innovation Saloons who were awarded various medals, among them: *Eureca 95, 96, 2001* – Gold Medals; Geneva 1996 – Gold Medals, 2001 – Silver Medals; Bucharest: *Inventa 9*9 – Gold Medal, to name but a few.

The colleagues have appreciated his outstanding abilities and results by inviting academician as a permanent member to many prestigious committees. Academician Vlad is the Chairman of the Specialized Scientific Council for Conferring the Degrees of Doctor and Doctor Habilitate, President of the Chemical Society of the Republic of Moldova, a member of the editorial boards of the journals "Химия Природных Соединений" (Chemistry of Natural Compounds), Tashkent; "Revista de Chimie" (Journal of Chemistry) and "Chimia" (Chemistry), Bucarest; and "Acta Universităţii Lucian Blaga" (Proceedings of Lucian Blaga University), Sibiu.

Academician Pavel Vlad has been the laureate of the State Prize in science, engineering and production (twice), the laureate of the prize of the World Organization for Intellectual Property. Special merits of academician Pavel Vlad have been confirmed with the „Order of the Republic", the URSS Order of the "Badge of Honor", the medal "For Distinguished Labour", the medal „Dimitrie Cantemir", and the silver medal of the International Foundation "Golden Fortune".

An eminent scientist, an outstanding personality, academician Pavel Vlad has a handful of wonderful personal qualities, which we are constantly witnessing, he is modest, honest considerate, openhearted, but there is not room enough to list all of them, for which his many colleagues pay him dully respect.

Direction of the Institute of Chemistry,
Academy of Sciences of Moldova

ACADEMICIAN NICOLAE V. GERBELEU - MANAGER OF THE METAL-PROMOTED REACTIONS

The name of the academician Nicolae V. Gerbeleu is associated with a number of fundamental ideas, which stimulated the basic and applied research and played a paramount role in tracing the general strategy of the development of Coordination Chemistry. Nicolae Gerbeleu was born on August 4, 1931 in the Moldavian city Balti. In 1949, after he completed his secondary education at a public school, he was accepted at the Faculty of Chemistry of the Kishinev State University. Being impressed by the outstanding courses taught by Prof. A.V. Ablov and Dr. C.B. Konunova at the Chair of Inorganic Chemistry, the young student chose Inorganic Chemistry as his specialty discipline. He graduated the University in 1955 and moved to Zaporojie, Ukraine to join the aircraft engine factory. The good professional background obtained at the University, the correct and respectful attitude towards his colleagues, as well as his responsible approach towards the work he was charged with, have promoted the young specialist to the position of deputy chief of the Central Laboratory of the factory and after three years he was appointed as the Head of this laboratory.

However, this fast carrier move has not overshadowed his passion for research and in 1958 N.V. Gerbeleu has begun his post-graduate PhD apprenticeship in the field of inorganic chemistry at the Academy of Sciences of Moldova. His mentor was Academician A.V. Ablov. The main topic of the PhD thesis was dealing with "Cobalt (III) dioximates with thiosemicarbazide derivatives". The PhD thesis was his main focus at that time, but very soon it became obvious that the interests of the young aspirant exceeded the area of metal dioximates. This was the time when in Kishinev a new direction in coordination chemistry was born – the chemistry of transition metal complexes with polydentate polyfunctional ligands based on thiosemicarbazide. The PhD thesis of N.V. Gerbeleu was one of the pioneer works in this field of research.

After the successful defence of the Candidate Dissertation (PhD) in 1964, N.V. Gerbeleu returns to the chemical industry in the position of deputy chief of the Central Laboratory of the Rare Metal Compounds Factory in the Sverdlovsk region of Russia (city Verkhnyaya Pyshma). However, the attraction towards research and especially towards the chemistry of coordination compounds prevented him from remaining in the industry for a longer time. In 1965 he was appointed as a senior researcher in the Laboratory of Coordination Chemistry at the Institute of Chemistry of the Academy of Sciences of Moldova. He continued the study of transition metal complexes with derivatives based on chalcogensemicarbazides, but at this stage the research involved more sophisticated ligands by taking into account the nature of the functional groups and substituents, their potential denticity and they ability to provide desired coordination geometry around the metal ions. In addition, the dependence of the structures and the reactivity of the synthesised metal complexes regarding to the nature of the metal ion and its oxidation state were investigated. These fundamental studies resulted in the defence of the Doctor Habilitat thesis at the Scientific Council of the Moscow State University. From 1972 to 1978 N.V. Gerbeleu headed the Chair of Inorganic Chemistry at the Kishinev State University where he received the title of Full Professor. After the death of Academician A.V. Ablov, in summer 1978, Prof. Gerbeleu was elected Chief of the Laboratory of Coordination Chemistry and headed this laboratory until February 20, 2006. In 1978 he also was appointed as Deputy Director of the Institute of Chemistry of the Academy of Sciences of Moldova and he remained in this position until 1988. Between 1995 and 2001 Professor Gerbaeleu was the Director of the abovementioned Institute.

The long-term experience of N.V. Gerbeleu in scientific and industrial administration allowed him to manage successfully and organize the work of Institute of Chemistry at a high academic level as well as to secure the effective research performance of his scientific group. This capacity of Prof Gerbeleu was extremely demanded after 1995, the most difficult period for science in Moldova then he become as a Guarantor for the survival of Chemistry in our country. In 1993 N.V. Gerbeleu was elected a Corresponding Member and in 1995 a Full Member of the Academy of Sciences of Moldova.

The research carried out by the school of Academician N.V. Gerbeleu is distinguished by novelty and originality, providing an excellent example of combining high quality advanced research with applied aspects of modern chemistry. The most significant achievements during his scientific activity include, but are not limited to:

- the metal-directed addition and redox reactions those allowing stabilization and isolation of the compounds with novel combinations of atoms and bonds;
- the development of original synthetic routes for organic and coordination compounds by exploring both the traditional and non-classic methodologies, e.g. the template syntheses, topochemical reactions, oligomerization in gaseous phase or in high-boiling inert solvents, etc.;
- the design and the syntheses of the metal complexes, based on the thiosemicarbazide and organic acids, with interesting magnetic, catalytic and biological properties.

The recognition of the scientific achievements of the school of Professor Gerbeleu by the scientific community is due to the versatility of the problems solved, the use of modern experimental and informational methods, the combination of different approaches and theoretical argumentation of the observed effects, high reproducibility of the discoveries and phenomena described by this school. His field of research was not only of local interest. This is corroborated by a number of joint projects and international grants where was involved Academician Gerbeleu and his group. Among them one can mention the INTAS projects, the projects of the American Society CRDF-MRDA, the Swiss Programme SCOPES, the Russian Fund RFFI, etc.

Academician Gerbeleu and his group have made a significant contribution to the Modern Coordination Chemistry in both the theoretical and applied aspects. Of a particular relevance are the following accomplishments:

- the development of effective synthetic routes for the metallomacrocyclic compounds and for their precursors, for polynuclear and for the supramolecular systems with a definite composition and with a controlled geometry;
- the use of modern analytical and spectroscopic techniques for determination of the composition and the structure of novel compounds and for the study of their reactivity;
- the search and the elucidation of useful properties of the metal complexes (e.g., catalysts of solidification of epoxy resins, dyes for textiles and plastics, corrosion inhibitors, magnetic materials, including molecular magnets and nanomaterials, electroactive species for membranes of the ion-selective electrodes, biological activity, etc.)

The scientific heritage of Academician N.V. Gerbeleu is enormous: he was the author of more than 600 academic works, including 4 monographs, 4 reviews and 30 patents. Professor Gerbeleu was well-known worldwide. The scientific school created by him includes today 2 Doctor Habilitat and 25 Doctors in Chemistry. His pupils are working today in the scientific institutions and Universities in Moldova, CIS, USA, France, Italy, United Kingdom, Austria, Switzerland, Germany, Serbia and Montenegro, Vietnam. He has been not only an active participant of numerous international chemical forums, conferences and congresses, but also an active member and the Chairman of the Organizing Committees of a number of meetings. He was one of the founders and since 1993 a permanent Chairman of the Organizing Committee of the International Conference "Physical Methods of Investigation of Coordination and Supramolecular Compounds", held every three years in Moldova. He was an invited Professor in a number of European Universities, a Doctor Honoris Causa of the Western Timisoara University (Romania), a member of the European Union of Mass-Spectrometry, the European Society "Euroscience", and a member of the Directorate of the International Union of Crystallographers. According to the data of the Institute of Scientific Information of Philadelphia (USA) Academician Gerbeleu was included in the list of the most cited chemists in the field of coordination chemistry. He was twice the winner of the Moldova State Prize in the field of Science and Technology (1985, 1994), earned a number of Prizes of the Academy of Sciences of Moldova and medals "N.S. Kurnakov", as well as the gold, silver and bronze medals of different international salons and workshops.

This year he would have had his 75th anniversary. Tragically, on February 20, 2006 he prematurely passed away. The death of N.V. Gerbeleu is an irretrievable loss for his family. It is an enormous loss for chemical science in general. His personality was a fusion of academic talent, broad scientific abilities, sharp organizing skills and humanism, kindness, delicacy and devotion. The conversations with him were always interesting and motivating. The memory of this outstanding scientist will fondly remain in the hearts of those who knew him, worked and discussed with him and, certainly, of those who will act further as "central ions" able to "coordinate" young people to continue the realization of his ideas.

Mihail.Revenco
Vladimir Arion
Grigore Timco

ELECTROPHILIC CYCLIZATION OF DITERPENOIDS[§]

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Abstract: A review of diterpenoid cyclization initiated by electrophilic reagents is provided. Conventional protonic and Lewis acids are examined along with superacids as initiators of cyclization cascade. An emphasis is placed on the use of cyclization reactions as a tool for the synthesis of compounds with potential practical utility. The review contains 74 references.

Keywords: isoprenoids, diterpenoids, electrophilic cyclization, superacids.

Introduction

Terpenoids, also referred to as isoprenoids, are a large and diverse group of naturally occurring organic compounds. These lipids-like substances have been isolated from all classes of living species, and are the largest group of natural products. They can be found everywhere: in humans and animals, in terrestrial plants and marine organisms, and even in fossil sediments. Plant terpenoids are extensively used for their flavoring action. They play an essential role in traditional herbal remedies, participate in the growth regulating processes of plants, insects' metamorphosis and are under investigation for a large spectrum of pharmacological activities, including antibacterial and anti-cancer properties. Terpenoids contribute to the scent of roses and eucalyptus, the flavors of cinnamon and peppermint, the odor of lavender and sage. The steroids in animals are also biosynthesized from terpenoid precursors. Sometimes terpenoids are found in living systems connected to compounds of different chemical nature, like proteins, quinones, heterocyclic compounds, playing a major role in the critical metabolitic steps of living beings.

From the chemical structure point of view, terpenoids derive from only a single precursor, the C-5 isoprene unit. But combining this unit in different ways and with different functional groups and stereochemical arrangement provides an infinite number of structures. The cyclic structures, formed in the living systems from open chain terpenic precursors after enzymatic cyclizations, provide additional opportunities for chemical diversity, due not only to the number of carbon atoms, cycles and their size but also to their junction mode, presence of different functional groups and their stereochemistry. That's why cyclic terpenoids have been always a challenging target for synthetic organic chemists. Different biogenetical schemes have been suggested to correlate the structure of cyclic terpenoids with their open chain "parents". The basis of all these schemes was the biogenetic isoprene rule formulated by Ruzicka [1, 2]. The methods of organic chemistry provided reliable tools to prove all biogenetical correlations and to provide efficient methods of access to valuable terpenoids in a biomimetic manner. The electrophilic cyclization appears to be one of the more efficient method for both modeling the biochemical processes and target oriented synthesis of natural products that are hardly accessible by other means. These investigations contributed to the elucidation of a number of biogenetic processes mechanisms, confirmed by efficient biomimetical synthesis, which are as a rule the most efficient, short and economical. As external electrophyles both conventional acids and superacids have been broadly used. We will focus our attention only to the cyclization of diterpenoids, which consist of four isoprenic units and have bold representative among compounds with high practical utility. Besides, diterpenoids are widely distributed in Moldovan flora and represent a high potential for efficient exploration.

## Cyclizations induced by conventional protonic and Lewis acids

One of the first papers related to the cyclization of diterpenoids was the work of Ruzicka and Hosking [3]. The cyclization of agathic acid **1** was investigated under the action of formic acid (Scheme 1).
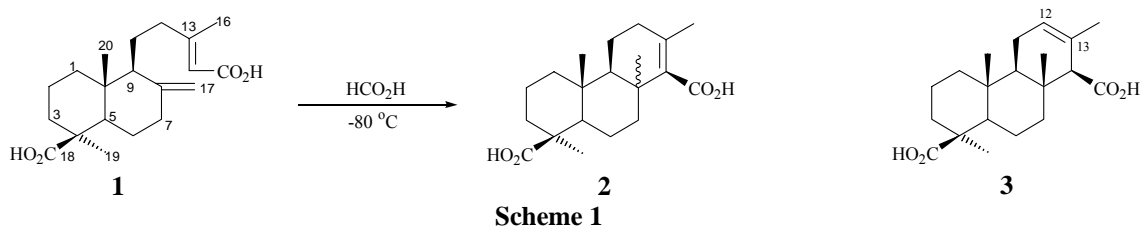
Scheme 1

It was shown, that **1** is converted to isoagathic acid **2**. The structure **2** was assigned in the original paper on the basis of chemical transformations. But the definitive structure of this compound was established by French chemists [4, 5]. Investigating the IR and NMR spectra of dimethyl ester of isoagathic acid, they came to the conclusion that the double bond is trisubstituted and is located between C_{12}-C_{13} carbon atoms. Consequently, isoagathic acid is represented by formula **3** (Scheme 1). In such a way the cyclization reaction takes place in a structure- and stereoselective manner, providing the α-isomer of the tricyclic product.

The structural and stereochemical outcome of electrophilic cyclization of compounds related to agathic acid was investigated in detail [5-7]. The substrates of choice were the stereoisomeric hydroxi-esters **4** and **5**, as well as their dehydration products **6** and **7**. The later ones were obtained using as a dehydration agent phosphorus oxychloride in pyridine [5, 7] that gave as predominant products olefins with exocyclic double bond (Scheme 2).

Scheme 2
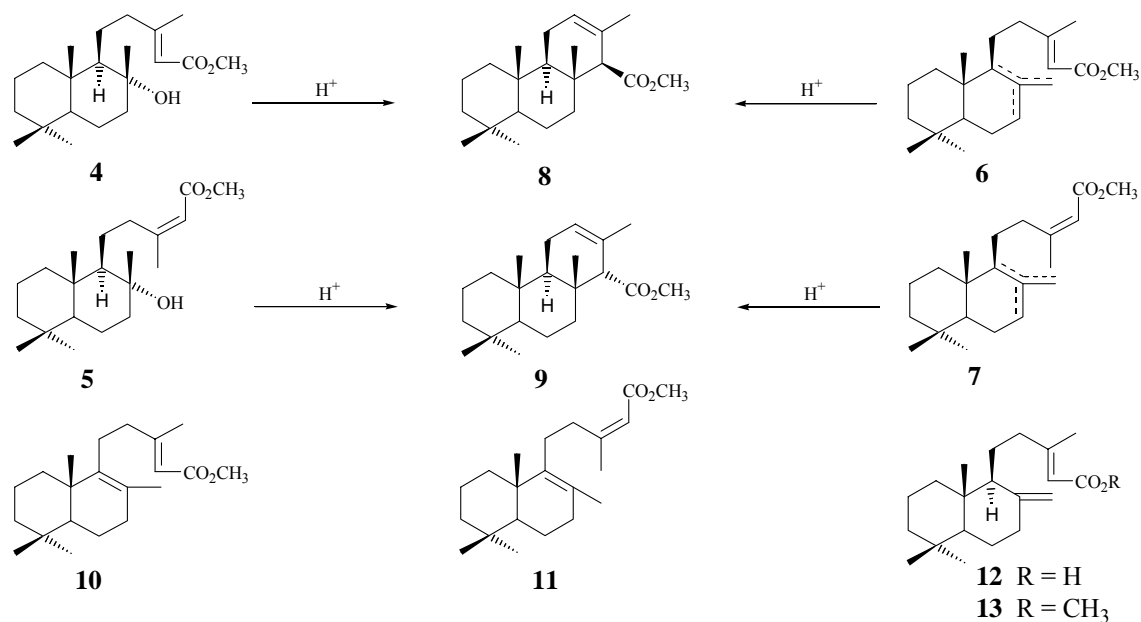
It was established, that all bicyclic compounds with the same configuration of the lateral chain provide the same tricyclic α-isoagathic ester under the action of formic acid. It was concluded that as an initial step in the cyclization process of **4** and **5** is their dehydration followed by cyclization. This cyclization is initiated by a stereospecific protonation of the $\Delta^{8(9)}$-double bond at C_9 from the less hindered α-face of the molecule which generates the carbonium ion at C_8. It was shown that cyclization of Δ^{13}-trans and Δ^{13}-cis mixtures of esters **6** and **7**, as well as of individual isomers with $\Delta^{8(9)}$- and $\Delta^{8(17)}$ double bonds leads in a stereospecific way to isoagathic esters **8** and **9**.

Synthesis of tricyclic isoagathic esters **8** and **9** was reported in a series of following papers [8-12]. Cimino et al. [8] obtained these compounds by cyclization of stereoisomeric esters **10** and **11** of labdanic structure with concentrated formic acid (Scheme 2).
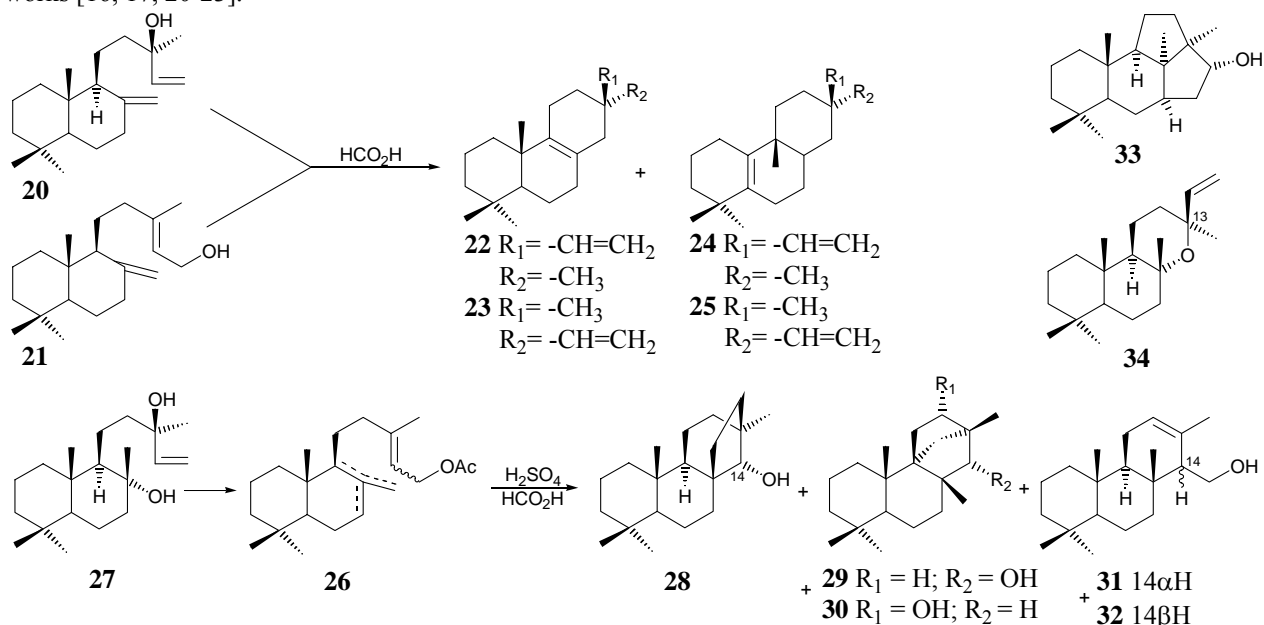
Ester **8** is the main reaction product of the cyclization of the acid **12** with concentrated formic acid, followed by methylation with diazomethane. Direct cyclization of the ester **13** provides also the tricyclic ester **8** [4-7]. Consequently, positioning of the double bond in cycle B does not influence the structure and stereochemistry of the formed cyclic products.
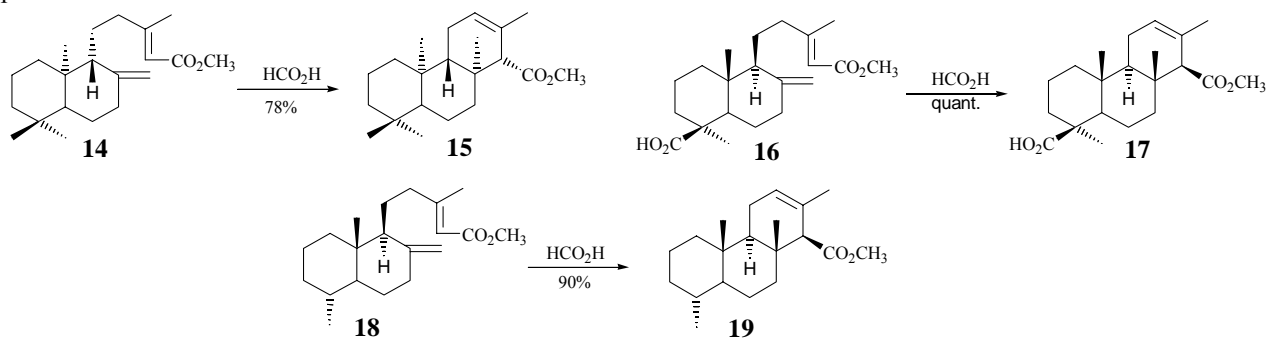
Scheme 3

The cyclization of *ent*-labdadienoic acid methyl ester **14** has been also performed (Scheme 3). On interaction of **14** with concentrated formic acid *ent*-isoagathic ester **15** was formed in a 78% yield [13].

The isoagathic acid monomethyl ester **17** was obtained in a quantitative yield on cyclization of agathic acid monomethyl ester **16** in the same reaction conditions [14]. The absence of one methyl group at C_4 in the norlabdanic ester **18** does not influence the cyclization reaction course [15]. In this case the tricyclic 19-norisoagathic ester **19** was obtained in a 90% yield (Scheme 3).

Manool **20** and isomeric labdadienol **21** were reported to cyclize also on treatment with protonic acids [17, 21]. Hydrocarbons **22**-**25** along with hibanol **28** were isolated, but the oxygenated reaction products were not investigated in detail, though they constituted cca. 50% of the reaction products mixture. In an attempt to fill this gap, related to labdanic derivatives, the mixture of allylic labdanylacetates **26**, readily available from sclareol **27**, was submitted to cyclization under the action of a mixture of concentrated sulfuric and formic acids [18, 19]. The reaction product composition was very complex (Scheme 4) and consisted of hydrocarbon fraction, formates and alcohols. In this case only the oxygenated fraction was investigated, since the hydrocarbon fraction was studied in detail in the previous works [16, 17, 20-23].

22 R_1= -CH=CH$_2$ **24** R_1= -CH=CH$_2$
    R_2= -CH$_3$ R_2= -CH$_3$
23 R_1= -CH$_3$ **25** R_1= -CH$_3$
    R_2= -CH=CH$_2$ R_2= -CH=CH$_2$

29 R_1 = H; R_2 = OH   **31** 14αH
30 R_1 = OH; R_2 = H   **32** 14βH

Scheme 4

The alcoholic fraction consisted of five components **28**-**32**, which were formed also on hydrolysis of the formiates fraction, but in different relative ratio. The structure of these components was elucidated by chemical transformations and spectral analysis. One of the reaction products, alcohol **30** was found identical with the alcohol obtained in good yield on the cyclization of sclareol **27** with perchloric acid [24]. Basing on experiments with deuterated substrates [19] the structure **33**, originally assigned in [24] was found not correct and the alcohol obtained on sclareol cyclization was represented by formula **30**.
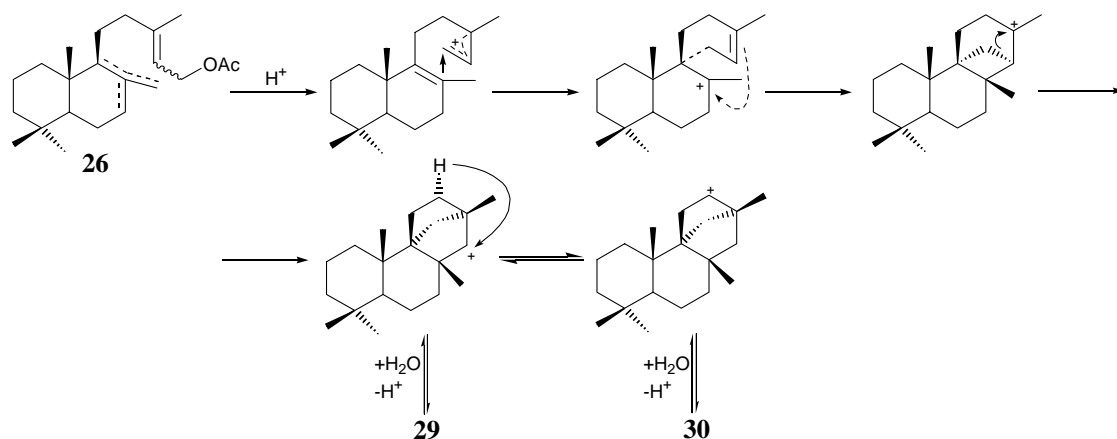

Scheme 5

It was also established, that compounds **28**-**32** are formed on cyclization of different labdanes (manool **20**, sclareol **27**, 13-epimanoiloxide **34** and others) with conventional acids or their mixtures [19]. Moreover, some hydrocarbons

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obtained in these reactions were found to be identical with the hydrocarbons obtained on treatment of alcohols **31** and **32** with the same reagents [25]. It was a proof, that initially formed alcohols are cyclized further in the acidic media to provide the corresponding hydrocarbons.

The reaction mechanism that brings about formation of tetracyclic compounds **29** and **30** with the new carbon skeleton is shown in Scheme 5. This mechanism was proved by experiments with deuterated substrates, as well as by the investigation of the cyclization of 13*Z*-labda-8(9),13-dien-15-ol **35** initiated by titanium chloride-N-methylaniline complex [26]. On performing the cyclization reaction in a wide range of temperature conditions, the predominating isolated product was the chloride **40**. It's structure was elucidated on the basis of spectral data, as well as after its preparation from alcohol **30**, followed by its reduction to provide the known hydrocarbon **41** (Scheme 6). The absence of the hypothetical chloride **39** among the reaction products proves that the initially formed carbonium ion rearranges to the new skeletons and finally leads to alcohols **29** and **30** or chloride **40**.

Scheme 6
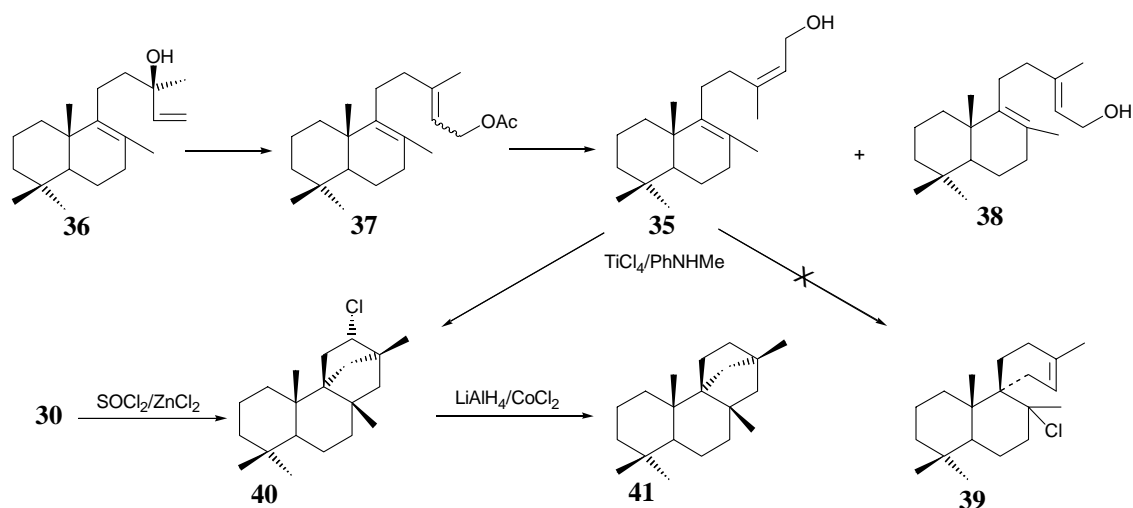
On the other hand, the information on the cyclization of open chain aliphatic diterpenic acids and their esters is rather scarce. Caliezi and Schinz [27] reported cyclization of geranylgeranic acid **42** under the action of a mixture of sulfuric and formic acids. A fraction of tricyclic compounds was isolated in a 40% yield, consisting according to authors of α- and β-tricycloizoagathic acids **43** and **44** (Scheme 7).

Scheme 7
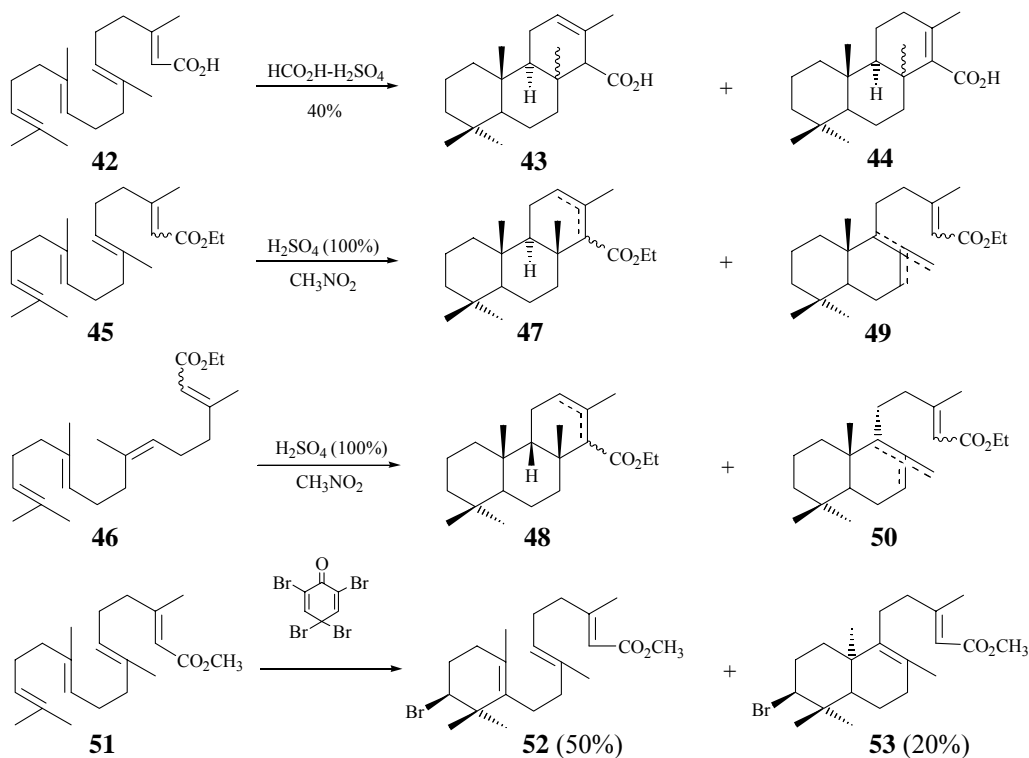
But the attempts to separate this fraction into individual compounds failed. Besides, the stereochemistry of the initial compound was still unclear, as well as the structure and stereochemistry of the reaction products.

Authors [28] performed the cyclization reaction of the mixture of esters **45** and **46** under the action of 100% sulfuric acid in nitromethane. A complex mixture of tricyclic **47**, **48** and bicyclic products **49** and **50** has been obtained (Scheme 7). It was concluded on the basis of spectral data that the reaction is stereospecific, though structural nonselective. Due to the high complexity of the reaction products composition it was not possible to isolate individual compounds and to prove their structure and stereochemistry univocally.

Japanese chemists [29] investigated the cyclization of the geranylgeranic acid methyl ester **51** under the action of 2,4,4,6-tetrabromocyclohexa-2,5-diene in acetonitrile to obtain a mixture of mono- and bicyclobromoesters **52** and **53** (corresponding yields 50% and 20%). Although the monocyclic derivative **52** predominates (Scheme 7), the structural selectivity of the reaction is low.
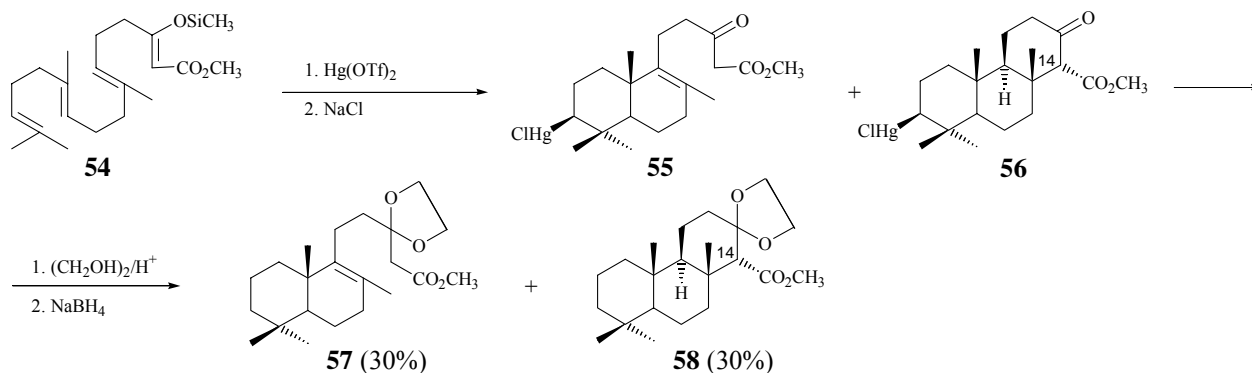
Scheme 8

Corey and Burk [30] studied the cyclization of the norditerpenic silylenolether **54** promoted by mercury trifluoroacetate in nitromethane (Scheme 8). A mixture (1:1) of bi- and tricyclic mercurated ketoesters **55** and **56** was obtained. This mixture was subjected to ketalization with a subsequent sodium borohydride reduction. As a result, the mixture of compounds **57** and **58** was obtained (yield 30% for each compound) and separated chromatographically. The stereochemical outcome of the reaction, in particular the configuration at the C_{14} asymmetric center in **56** and **58** is determined by termodinamical control. In this case the cyclization reaction is not structurally selective and the yields of cyclic products are low.

Electrophilic cyclization of labdanic alcohols and esters has been discussed in detail in a former review [31]. Cyclization of similar diterpenic substrates has been reported in the following period. Authors [32] investigated cyclization of geranylgeraniol esters **59** and **60** with the complex of mercury triflate-N,N-dimethylaniline. The results of this work showed that the cyclization in this case is not a univocal process. On the cyclization of the *p*-nitrobenzoate **59** in nitromethane with the subsequent reduction of the mercurated products with sodium borohydride a mixture of isomeric bicyclic labdadienols **61** and **62** (28%) and tricyclic isoagath-12-en-15-ol **25** (22%) was obtained (Scheme 9).
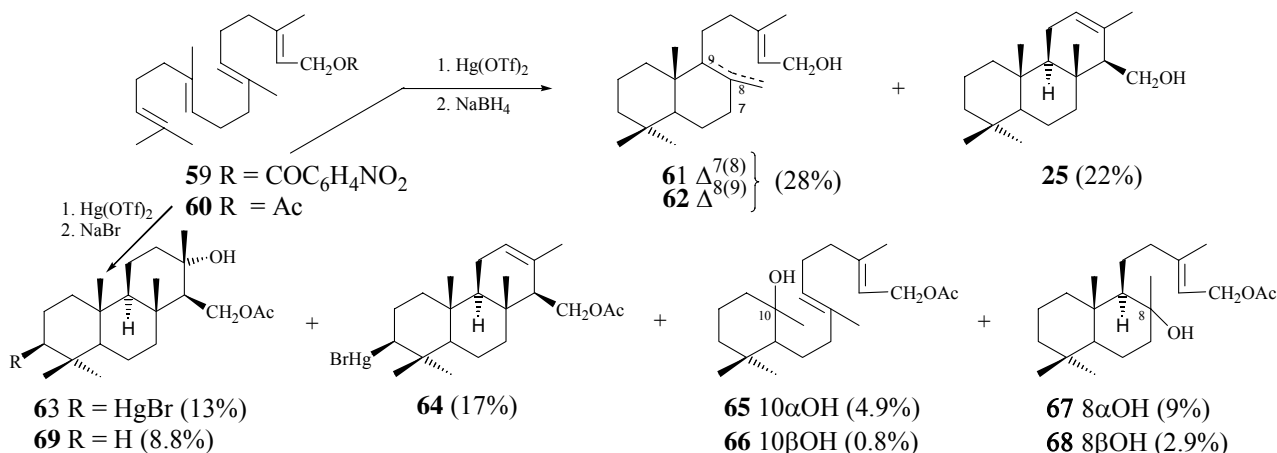
Scheme 9

On the other hand, the cyclization of geranylgeranylacetate **60** with the same reagent [33-35] followed by substitution of the triflate residue for bromine brings about formation of the mixture of mercurated isoagathanyl acetates **63** (13%) and **64** (17%). On performing the reaction with the same mercury complex, but in the presence of 12 equivalents of water in nitromethane with subsequent borohydride reduction of the reaction products, a complex mixture of

monocyclic **65** (4.9%) and **66** (0.8%), bicyclic **67** (9%) and **68** (2.9%) and tricyclic **69** (8.8%) hydroxiacetates was formed [33, 35]. A substantial portion (40%) of initial geranylgeranylacetate **60** remains unreacted. In such a way the structural selectivity of the reaction is extremely low in this case and as a consequence the reaction products represent a complex mixture of compounds.

According to the first conceptions, the cationic cyclization of polienic compounds was considered a concerted process [36-42]. But other data [43, 44], including above mentioned mercury-induced cyclizations in particular [33, 35], showed that this is a stepwise sequence. This conclusion was quite important for biomimethic-like cyclization of open chain substrates. In this case a complete cyclization cascade leads in a spectacular manner to complex molecules incorporating several asymmetric centers. Performing these reactions with optically active substrates leads to single enantiomeric products. In this line, authors [45] showed that the cyclization of the optically active terminal epoxide of trimethylsilyl derivative of geranylgeranylacetate **70** with Lewis acids provide a mixture of (+)-3-hydroxi-9,10-*sin*- and (+)-9,10-*anti*-copalols **71** and **72** (Scheme 10). The reaction is not stereospecific in this case. Formation of **71** and **72** is explained by two boat and chair equilibrium conformations **73** and **74** adopted by the substrate on the stage of reaction initiation.
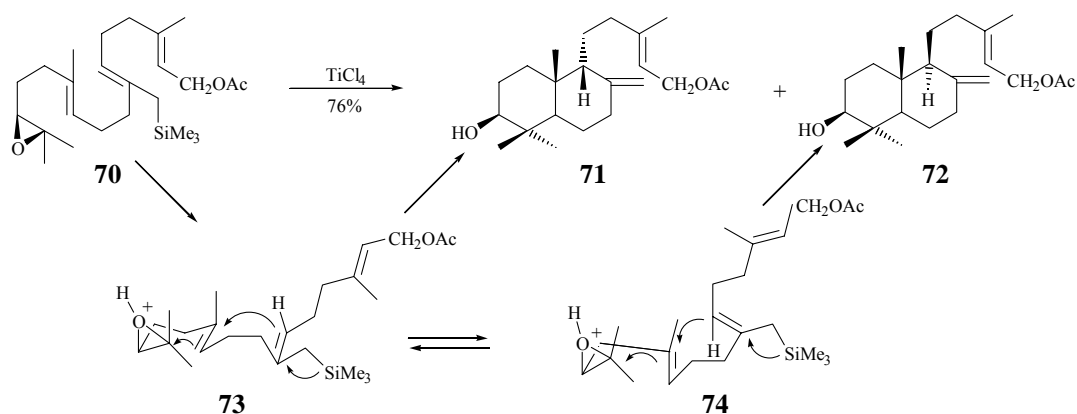
Scheme 10

On the interaction of 13-epimanool **75** with mercury acetate in aqueous nitromethane with the subsequent reduction of the reaction product with sodium borohydride a mixture of strobane oxide **76** is formed [46] (Scheme 11). Quite unexpectedly, in the same reaction conditions manool **20** gave manoyloxide **77**. This fact could be explained only assuming that due to conformational effects and steric hindrance the mercury salt attack on vinyl group of **20** is hampered and as a consequence reaction is initiated from the mercury salt attack on the C_8-C_{17} double bond on the C_{17} atom.

Scheme 11
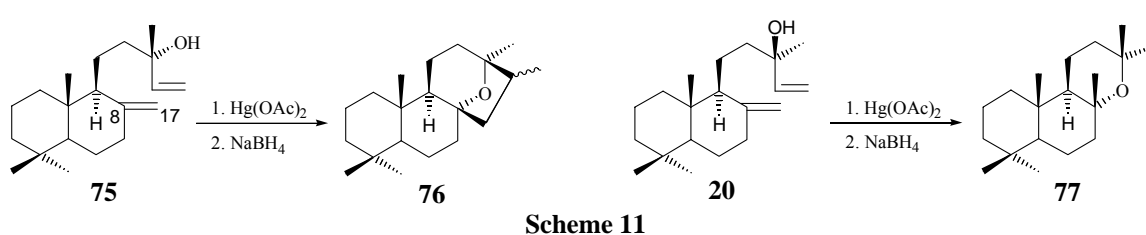
All the above mentioned data show that cyclization of diterpenoids initiated by conventional acids (both protonic and Lewis acids) was not investigated so frequently. Cyclization of bicyclic labdanic compounds with protonic acids has been paid more attention, due to relatively high availability of starting substrates from natural sources. The data on cyclization of open chain diterpenoids are relatively scarce. The available data show that in this case the cyclization reaction does not proceed univocally and structure-selectively, the reaction products are complex mixtures of compounds and its preparative value is not relevant, although it is stereospecific.

Cyclization induced by superacids

Unlike the usual protonic and Lewis acids, superacids showed more superior cyclization properties in terms of selectivity and mildness of the reaction conditions. The pioneering work of Semenovsky and Smit [47, 48] showed that fluorosulfonic acid can be a very efficient cyclization agent for terpenoids. This reagent proved to be more successful in promoting olefinic cyclization even compared to solvolitic methods of initiation that was broadly used in the synthesis of steroidal compounds [40-42].

The first interest towards superacidic cyclization of diterpenoids was due to the necessity of solving the particular question concerning the transformation of labdanes. As it was mentioned in the first part of this review, electrophilic cyclization of labdanic derivatives under the action of usual acids is not selective and provides complex mixtures of bi-, tri- and tetracyclic compounds. But it appeared interesting to get access to natural compounds of izoagathanic structure and it was found that superacids are efficient reagents for transformations of readily available labdanoids into izoagathans. On treatment of a mixture of labdadienol acetates **21** with fluorosulfonic acid [51] a mixture (3:1) of hydroxiacetates **69** and **78** was formed in a respectable 76% yield (Scheme 12). The unsaturated acetates **79** and **80** were also isolated as minor byproducts (10%). Cyclization of individual isomers **81** and **82** in the same reaction conditions led to the same hydroxiacetates **69** and **78** in high yields. The structure of these compounds was elucidated both on the basis of spectral data and several chemical transformations.
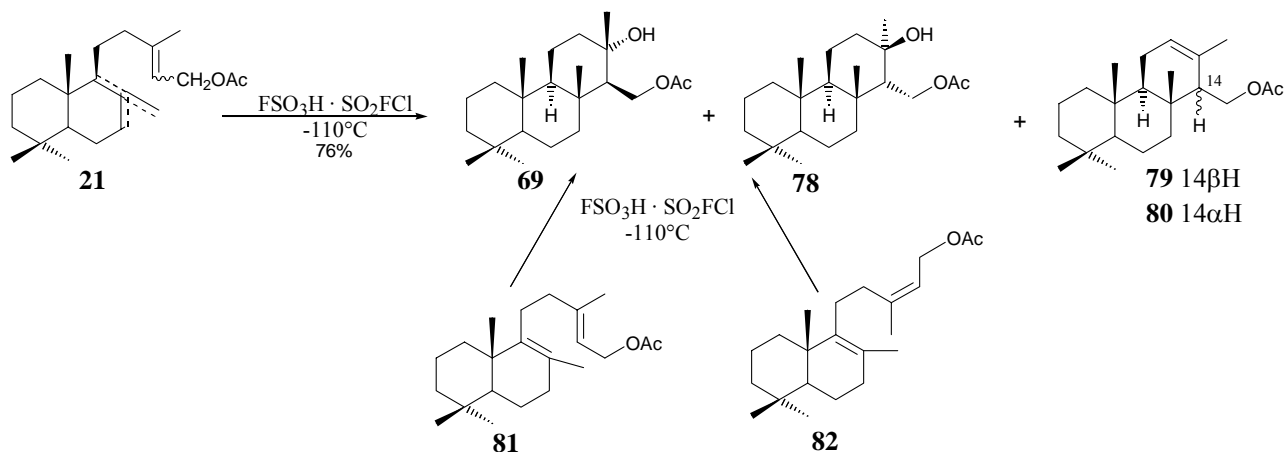
Scheme 12

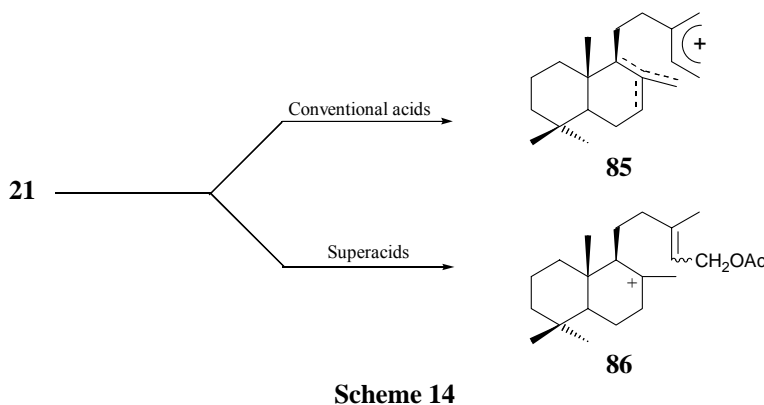Superacidic cyclization of the mixture of *ent*-copalols **83** provides also the mixture of isoagathic alcohols **25** and **26** (85%) and a minor hydrocarbon fraction (10%) where the basic component is the isoagathadiene **84** (Scheme 13).

Scheme 13
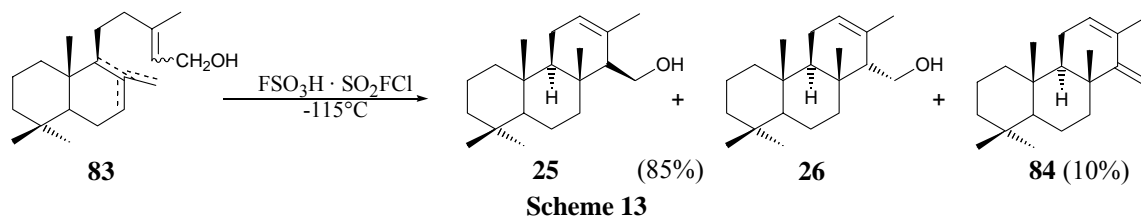
Basing on this result, it was established that superacidic cyclization of primary labdanic alcohols and their acetates is a convenient path towards isoagathic diterpenoids. The cyclization reaction is chemoselective and stereospecific. It's course differs essentially from conventional acids induced cyclization of labdanes. On the action of the latter ones the solvolisis of the C_{15}-O bond takes place to form the carbonium ion **85** in the lateral chain, which transforms then into tricyclic pimaranic hydrocarbons and tetracyclic compounds [19]. In the superacidic media, protonation of the double bond in the cycle B is favored and this leads to C_8 carbonium ion **86** which cyclises to isoagathanes (Scheme 14).

Scheme 14

Unlike alcohols with primary allylic functional groups **83** and their acetates **21**, superacidic cyclization of labdanes with functional groups at C_{13} – sclareol **27**, manool **20** and isomanool **87** proceeds by a solvolitic generation of the carbonium ion in the lateral chain. The reaction products are tetracyclic hydrocarbons with new carbon skeletons **88** and **89** [51, 52] (Scheme 15).

These results were somehow unexpected and they showed for the first time that the behavior of labdanoids with primary and tertiary allylic oxygen containing functional group in the lateral chain differs in superacidic media. A possible reason for such reactivity could be found in a lower protonation rate of the double bond in cycle B then the solvolysis of the tertiary hydroxyl group in the lateral chain.
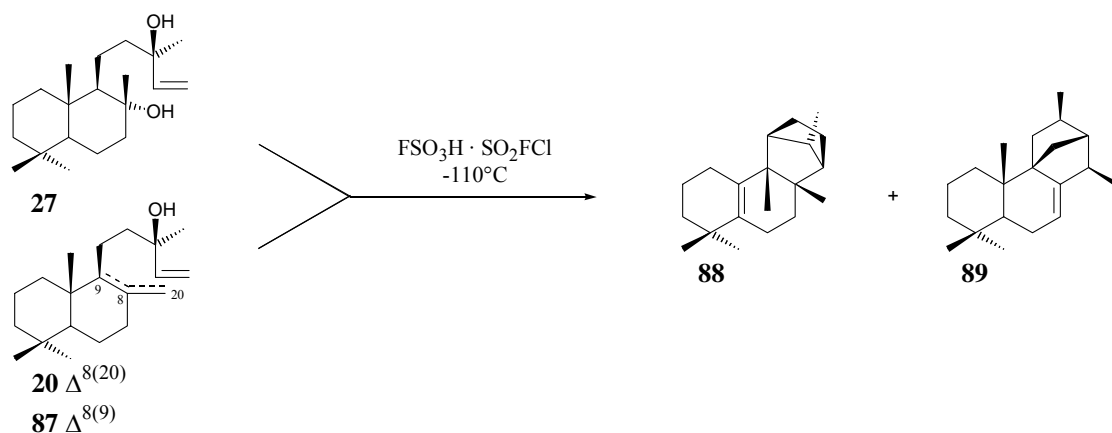
Scheme 15

The first successful results of superacidic cyclization of labdanoids promoted investigation of other diterpenic substrata. Cyclization of open chain diterpenoids was an eloquent example of a biomimetic approach in the synthesis of complex polycyclic diterpenoids. Substrates of choice were E,E,E- and Z,E,E-geranylgeraniols **90** and **91**, as well as their acetates **60** and **92**. On the cyclization of alcohols **90** and **91** with fluorosulfonic acid in 2-nitropropane at -78°C [53, 54] racemic isoagathic alcohols **30** and **31** were obtained respectively in high yields (Scheme 16). The main products of the cyclization of acetates **60** and **92** were racemic hydroxiacetates **69** (72% yield) and **78** (65% yield). The reaction yields were better in the case of cyclization of α-isomers the E,E,E- geranylgeraniol and its acetate **93** and **94** [55]. The terminal isobutenylic group in these substrates is more accessible for protonation [56] and both **93** and **94** provided isoagathanes **30** and **69** in 85% and 78% yields, that is slightly higher compared to the corresponding β-isomers **90** and **60**.
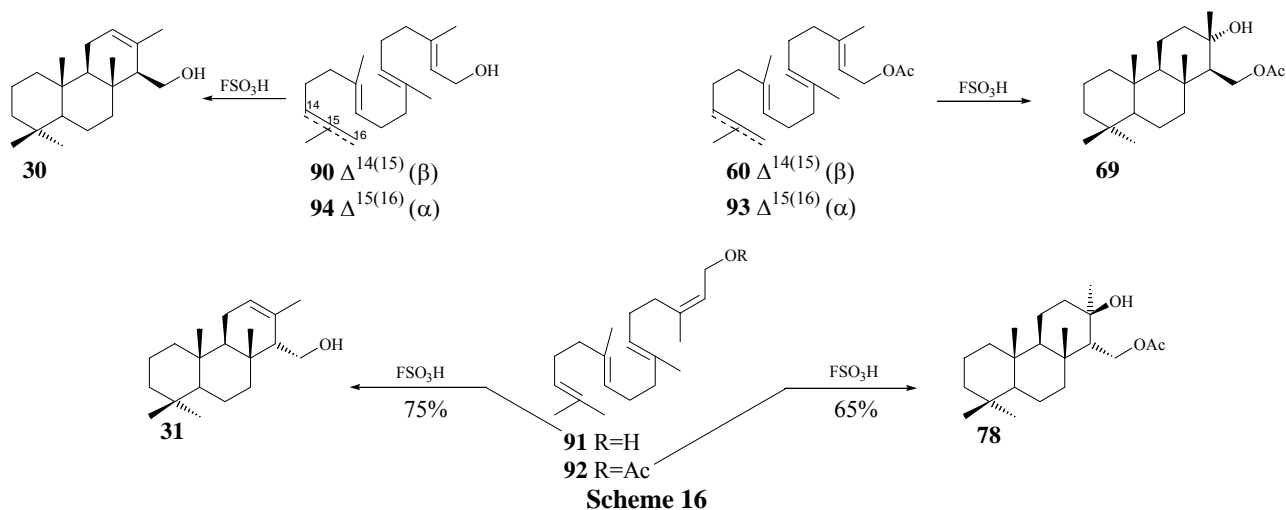
Scheme 16

The range of functional groups compatible with superacidic conditions has been broadened, providing a better flexibility of this cyclization method from the synthetic point of view. As it was mentioned, cyclization of diterpenic acids and their esters has been performed under the action of usual acids. Good results were obtained only in the case of cyclization of bicyclic compounds into tricyclic. The cyclization of open chain diterpenic acids and corresponding esters was not studied at all. On the contrary, superacidic cyclization of these substrata provided very good results [57, 58]. Cyclization of 13E- and 13Z-acids **95** and **96** with fluorosulfonic acid (-80°C), followed by methylation with diazomethane provided the known [4] optically active esters **8** and **9** (yields 92% and 91% respectively) with isoagathic structure (Scheme 17). These esters were also obtained by direct cyclization of bicyclic esters **10** and **11** (yields 95% and 91% respectively). The free acid **97** was prepared on direct cyclization of **95** and used in a following work connected to the synthesis of naturally occurring acylglicerols of marine origine [59]. The following development of this work [60, 61] included an efficient superacidic cyclization of copalic acid **99** (Scheme 18) and the obtained optically active isocopalic acid **100** served as a very convenient template in the synthesis of acylglicerols from the same series. It is noteworthy mentioning, that diterpenoid 1,2-diacyl-sn-glycerols are much more potent activators of protein

kinase C than the linear long chain analogs, such as 1,2-dioleoyl-*sn*-glycerol [62] These enzymes are very relevant regulators of important biochemical events, including gene expression, cell proliferation and down-regulation of receptors [63].

The open chain *E,E,E*- and *Z,E,E*-geranylgeranic acids **42** and **101** were cyclized biomimetically with fluorosulfonic acid and provided after methylation the racemic isoagathic esters **8** and **9** (yields 85% and 81% respectively). Conversion of the open chain esters **51** and **102** has been also reported to provide the same products **8** and **9** in excellent yields (92% and 85% respectively) [57, 64].

Scheme 17
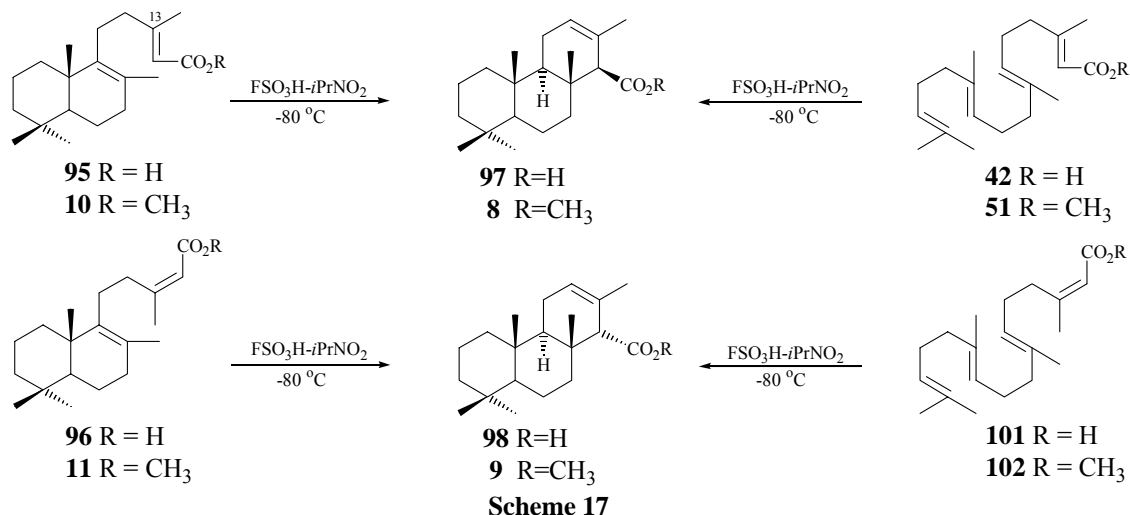
A very interesting effect was observed on cyclization of bishomo- and bisnorditerpenoids. It was established, that superacidic cyclization of an isomeric mixture of bicyclogeranylacetic acids **103** leeds to a mixture (5:1) of δ-lactones **104** and **105** (Scheme 18) in a 95% yield [65]. The carboxylic group plays a role of an efficient terminator of cyclization sequence by closing the lactone cycle. For the corresponding ethyl ester **106**, the absence of such an efficient terminator leads to a dramatical effect in selectivity: lactones **104** and **105** are formed only in a minor yield (14%), predominating hydroxyester **107** was isolated in a 35% yield, along with 32% of unsaturated tricyclic esters **108** and **109** [66].

Scheme 18
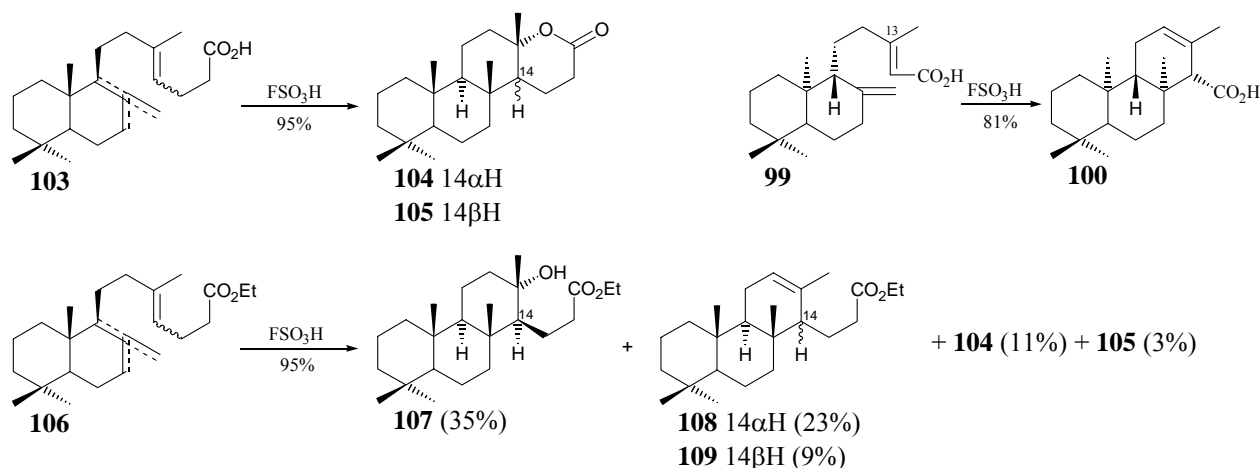
Cyclization of *E,E*- and *Z,E*-farnesylacetones **110** and **111** was found to provide *trans,trans* sclareoloxide **112** (67%) and *cis,trans*-sclareoloxide **113** (65%) respectively [48]. In this case, the configuration of the internal double bond determines the stereochemistry of ring juncture in the cyclic products (Scheme 19).

Scheme 19

30
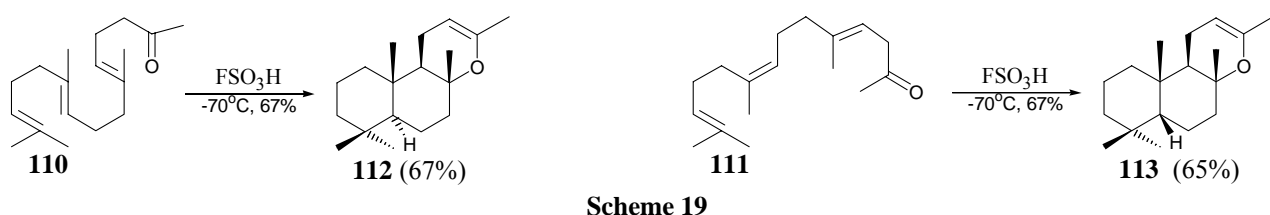
These examples show that bishomo- and bisnorditerpenoids cyclization provides a convenient synthetic access to important compounds with biological activity and practical importance [65, 67]. On the other hand, it was revealed that the presence of an oxygenated functional group in the cycle B of bicyclo-bishomoditerpenes **114-117** inhibits initiation of the carbocyclization sequence [66]. The reaction products are a mixture of lactones **118**, **119** and hydroxyesters **120-122** (Scheme 20).

Scheme 20
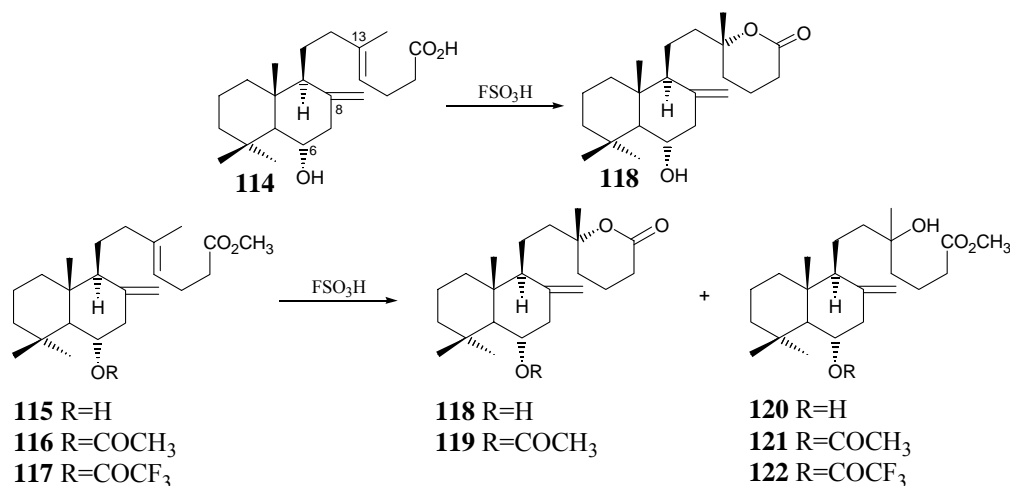
Diterpenic phenylsulfones are potential synthons in the synthesis of more complex compounds and their superacidic cyclization has been also investigated [68]. The character of the reaction products was similar to those obtained on cyclization of diterpenic alcohols, acids and esters. Both bicyclic- and open chain substrata provided the same products. 2E,6E,10E-geranylgeranylsulfone **123** and the corresponding bicyclic counterpart **124** cyclized efficiently (Scheme 21) with fluorosulfonic acid under standardized reaction conditions into the tricyclic sulfone **125** (yields 71% and 85% respectively). But in the case of α-Z isomeric phenylsulfones a specific effect of the phenylsulfonyl group on the outcome of the cyclization reaction was observed. Both 2Z,6E,10E-geranylgeranylsulfone **126** and the bicyclic sulfone **127** formed on treatment with fluorosulfonic acid under standard conditions the exocyclic isomer **128**, along with a minor amount of trisubstituted tricyclic compound **129**.

Scheme 21
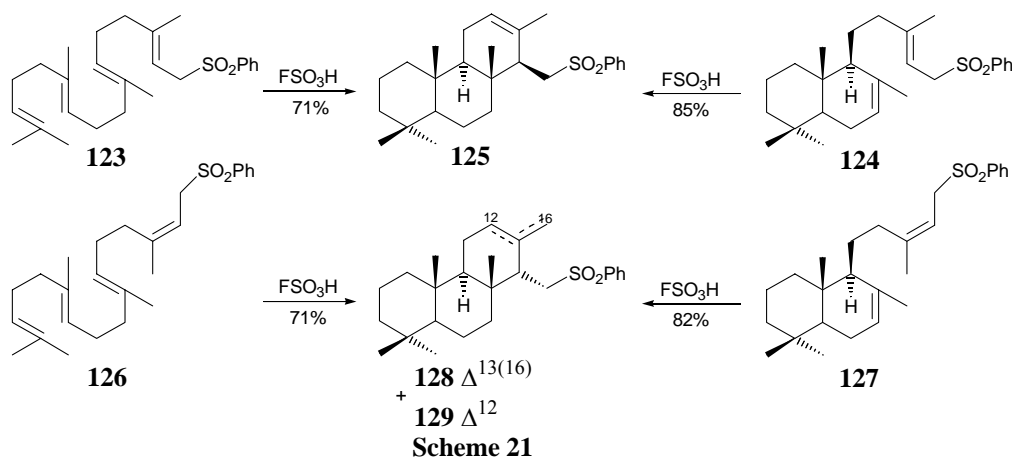
The explanation of this unusual selectivity, caused by the α-double bond configuration was given on the basis of a specific interaction of the phenylsulfonyl group with the tricyclic skeleton on the stage of carbonium ion formation. Molecular models simulations showed a specific anchimeric assistance of the phenylsulfonyl residue on the deprotonation process by facilitating the elimination of a proton from a suitable spatially disposed position.

It is noteworthy mentioning that the bicyclic sulfones similar with **124** could be prepared from abundantly occurring sclareol **27** or manool **20**. This is a very convenient way to get access to optically active synthons in preparative amounts.
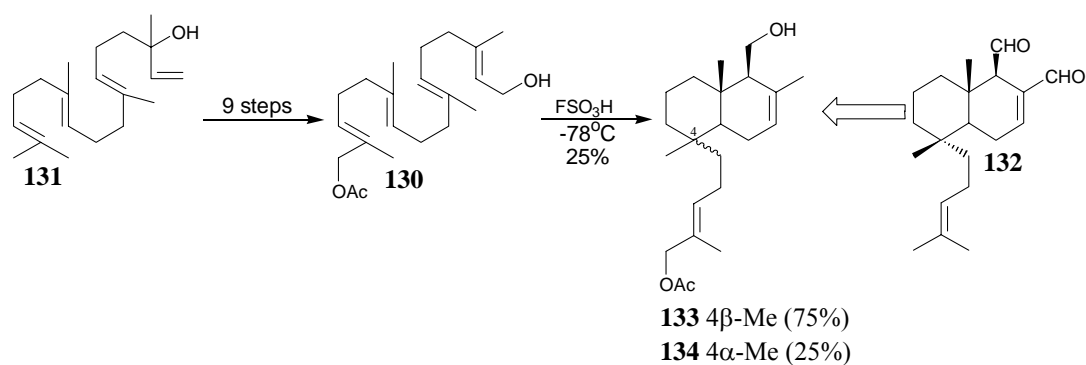
Scheme 22

Superacidic cyclization of more complex diterpenic substrates was reported recently by us and relates to α,ω-bifunctionalized substrate **130** [69] obtained from geranyllinalool **131**. Basing on the data obtained for similar sesquiterpenic α,ω-bifunctionalized substrate [70], we have expected a specific initiation of the cyclization sequence from the internal double bond to give naturally occurring sacculatane skeleton like sacculatadial **132**. Under standard cyclization conditions substrate **130** provided the desired sacculatane skeleton **133** along with its C_4-epimer **131** in a 25% overall yield, resolved successfully by HPLC (Scheme 22). The structure of **133** and **134** was elucidated on the basis of spectral data, including 2D-NMR experiments.
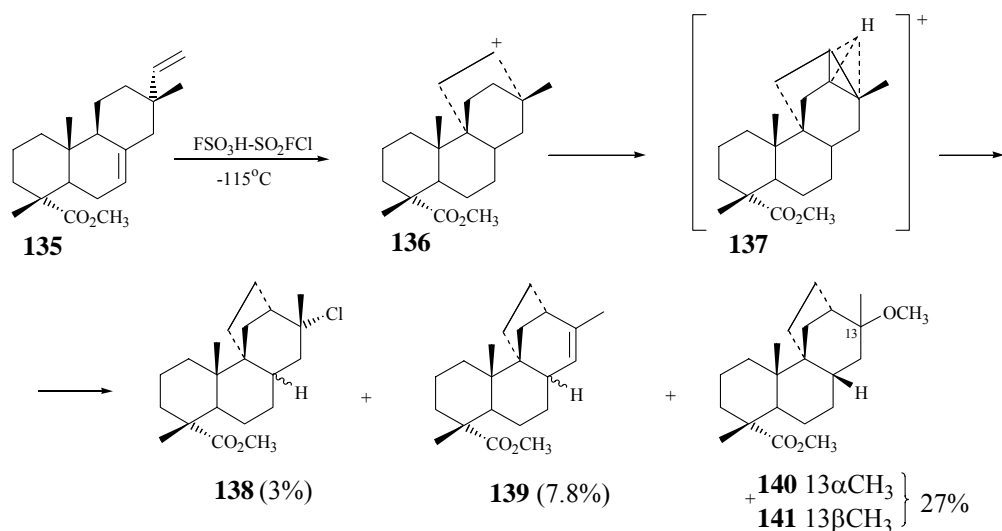
Scheme 23

More complex cyclization reactions were observed on superacidic treatment of tricyclic diterpenoids. Methylpimarate **135** was treated with fluorosulfonic acid in sulfuryl chloride-fluoride at -120°C [71, 72]. It was established that cyclization reaction takes place via carbonium ions **136** and **137** to form after quenching the neutral tetracyclic diterpenoids of stemodanic structure **138-139** (Scheme 23). Earlier attempts to convert pimaranic compounds into tetracyclic diterpenoids under the action of conventional or Lewis acids failed [31].

All above mentioned results show that fluorosulfonic acid is a highly effective reagent for a biomimetic stereospecific and structurally selective transformation of diterpenic substrates into isoagathic tricyclic compounds. Morover, our results suggested a development of this synthetic tool by combining the superacidic cyclisation with acetylation and following enzymatic hydrolysis to get access to the enantiomerically pure compounds. Our first results in this direction [73] demonstrated that this protocol is synthetically useful. Its optimisation by the known biocatalytic methods [74] seems to be a feasible task.

Conclusions

All presented data on cyclization of diterpenoids provide an additional confirmation that the electrophilic cyclization, initiated by both conventional and especially superacids represent a general, highly selective and efficient tool for the synthesis of cyclic terpenoids. Superacidic cyclization of open chain and partially cyclized diterpenic alconols, acids and esters, as well as phenylsulfones leads predominantly to α-isomers of the corresponding cyclic homoallylic alcohols, acids and esters, where the configuration of the functional group is determined by the stereochemistry of the

double bond at the α-extremity of the initial substrate (Scheme 24). The phenylsulfonyl group shows an anchimeric asistence in the deprotonation process of the cyclic carbonium ion. Superacidic cyclization of primary acetates provides cyclic hydroxiacetates of the diastereomeric 1,3-diols. Their stereochemistry is also determined by the configuration of the initial acetates at C_2 (Scheme 24).

Alcohols with primary and tertiary allylic hydroxi-group give different cyclization products under the action of superacids compared to conventional acids.

Cyclization of tricyclic pimaranic compounds leads to products with stemodanic structure.

Superacidic cyclization of bishomo- and bisnorditerpenes is accompanied by a specific interaction of the corresponding functional group and cyclic carbonium ions that brings about formation of lactones and oxides. The oxygenated functional group plays the role of an efficient terminator of the cyclization sequence.

R=CH$_2$OH, CO$_2$H, CO$_2$CH$_3$, CH$_2$SO$_2$Ph
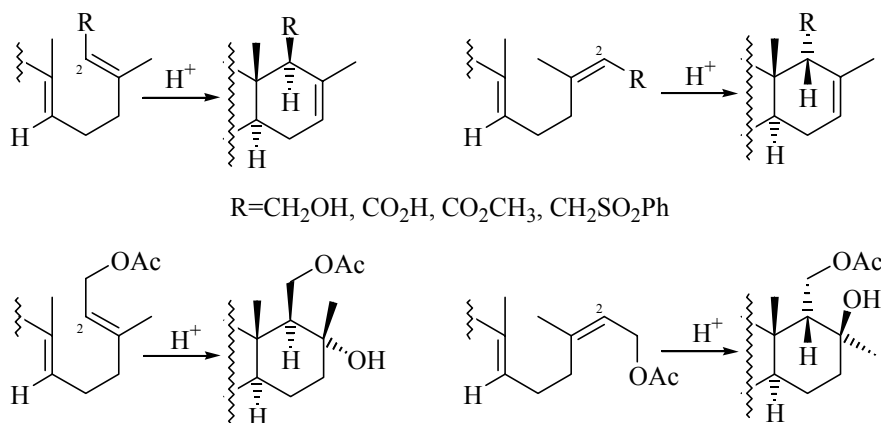
Scheme 24

Cyclization of α,ω-bifunctionalized open chain diterpenoids is initiated predominantly from the internal C10-C11 double bond and provides in a one step sacculatane derivatives – compounds with high biological activity.

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WHAT CAN BE DONE WITH THE ACETYL GROUP OF ARYL-1-ETHANONES?

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Dedicated to academician Vlad Pavel on his 70th birthday

Abstract: Literature data on utilization of acetyl group of aryl-1-ethanones (acetophenones) for the synthesis of organic compounds is generalized. Different approaches of preparation of aromatic compounds by chemical transformations of methyl as well as keto- group of titled compounds are systematized. Examples of the synthesis of organic compounds based on products of primary transformations of aryl-1-ethanones are considered.

Keyword: organic synthesis, aryl-1-ethanones, acetyl group

Content

1. Introduction

Aryl-1-ethanones (acetophenones) **1** are convenient starting substances for the synthesis of various classes of organic compounds. Their acetyl group can be subjected to various transformations leading to formation of a number of substances, including heterocyclic compounds with various dimensions of cycles, number and nature of heteroatoms. Moreover, different substituents in the aromatic ring of **1** can significantly increase the diversification of synthesized products.

Acetophenones are useful models for the development of different synthetic methods. The syntheses of heterocyclic compounds, based on products of primary transformation of aryl-1-ethanones, are considered in a number of monographs [1,2] and reviews [3,4].

Current review is concentrated mostly on data, published in last 15 years, and investigations, which are not included in the earlier articles [1-4].

Based on the structure of aryl-1-ethanones, usually, reagents interact with methyl or carbonyl group. Further transformation of obtained substances leads to products with a larger or smaller amount of carbon atoms than starting compounds, and this overview will be presented as four main parts: a) syntheses with retention of methyl group; b) syntheses where keto group is retained; c) syntheses where both groups of acetyl fragment are transformed; d) synthetic schemes based on the products of primary transformation of acetyl group.

2. Syntheses with retention of methyl group

Among the large number of products of transformations of **1** with retention of methyl group, the first to be mentioned are 1,3-dioxolanes **3**, which are stable under neutral and basic condition. The most convenient and practical method for their synthesis is the reaction of ketones **1** with 1,2-diols **2** in presence of an appropriate catalyst.

Scheme 1
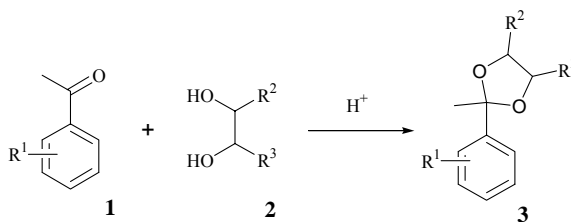
It should be mentioned that the reaction is reversible and proceeds at the presence of acid catalysts [5]. Good yields of 1,3-dioxolanes have been obtained in the presence of an oxalic acid, benzene or toluene sulfonic acids, $HClO_4$, $ZnCl_2$, BF_3-etherate, $SnCl_4$ etc. For example, the synthesis of **3** in the presence of the Ti^{4+}-exchanged montmorillonite as a strong solid acid catalyst is described [6]. Other different heterogeneous catalytic systems are used also: natural kaolinic clay, zeolite HSZ-360, sulfated polystyrene clays, polymers corporate with different metals, triphenylphosphine iodide

[7-10]. Such catalysts have been separated by simple filtration and the possibility for the recycling process was indicated.

The cyclization of substituted benzene derivatives is an important strategy for the synthesis of benzanellated heterocyclic compounds [11]. The synthetic introduction of electrophilic substituents into position 2 (R^2=H) or 6 (R^2=Me) of **4** have led to compounds **7**, and carried out via preliminary prepared of ketals **5,6**.

Scheme 2

R^1= H, Cl, Me; R^2= H, Me; R^3=CO_2H, SO_2Cl
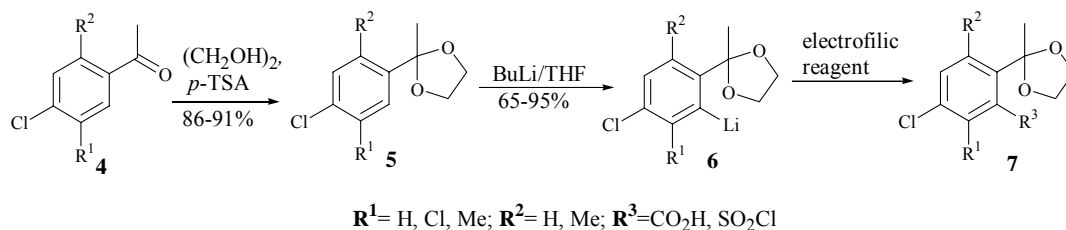
Thiosemicarbazones of aryl-1-ethanones are well known to form stable complexes with transition elements and heavy metal ions. Synthesis and applications of these chelating ligands were also reported [12-14]. The similar strategy was employed for the preparation of thio-derivatives **9** from 1-(2-hydroxyphenyl)-1-ethanone **8** [15].

Scheme 3
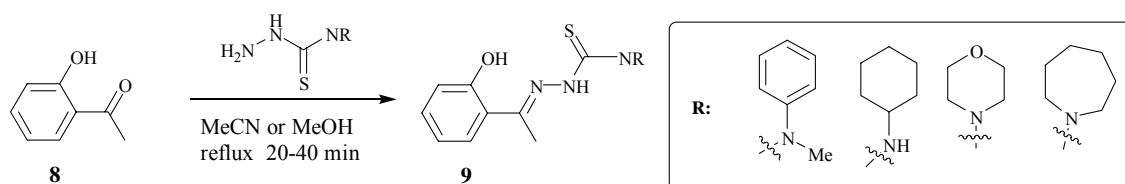
The aryl-1-ethanol chemistry has proved a powerful tool for obtaining C-C, C-N, C-Hal bonds in organic synthesis. Tremendous progresses have been made in the area of asymmetric reduction of discussed ketones to aryl-1-ethanols. Due to extensive body of work carried   out in the area of transformation of **1**, emphasis here is focused on data that were not overviewed in the past and will be presented in the fourth part of the review.

3. Syntheses where keto group is retained
The transformations of methyl group of acetophenones provides an obvious entry to further synthesis of practically important heteroatomic compounds [3,4].

Scheme 4
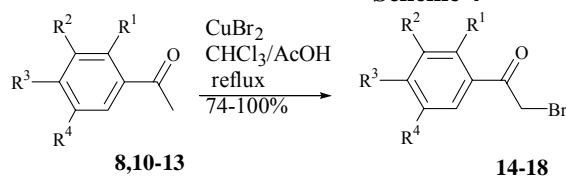
8,14: R^1=OH, R^2=R^3=R^4=H; **10,15**: R^2=OH, R^1=R^3=R^4=H; **11,16**: R^3=OH, R^1=R^2=R^4=H
12,17: R^1=R^3=OH, R^2=R^4=H; **13,18**: R^1=R^4=OH, R^2=R^3=H

Scheme 5
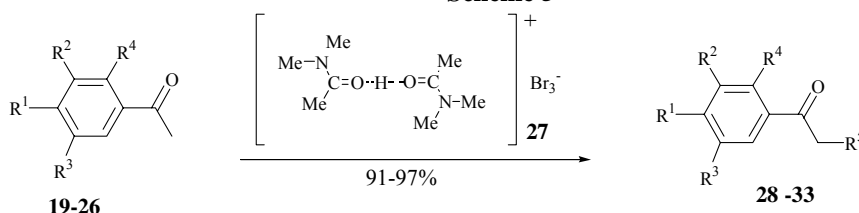
19, 28: R^1=Cl, R^2=R^3=R^4=H; **20, 29**: R^1=Br, R^2=R^3=R^4=H; **21, 30**: R^1=OMe, R^2=R^3=R^4=H;
22, 31: R^1=R^2=Cl, R^3=R^4=H; **23, 32**: R^1=R^2=OMe, R^3=H, R^4=Me; **24** R^1=OMe, R^2=NO_2, R^3=R^4=H;
25 R^1=NH_2, R^2=R^3=R^4=H; **26** R^1=NO_2, R^2=R^3=R^4=H; **33** R^1=NH_2, R^2=R^3=Br, R^4=R^5=H

α-Bromoketones art as important intermediates in many synthetic schemes. They can be prepared by direct bromination of acetophenones in various solvents (H_2O, $CHCl_3$, CCl_4, AcOH, EtOH, MeOH, DMF) or on free solvent conditions [16]. Chemoselective bromination of 1-(hydroxyphenyl)-1-ethanones **8,10-13** into bromides **14-18** is achieved by treatment with $CuBr_2$ (scheme 4) [17]. According to another report [18], the system: Br_2-$CO(NH_2)_2$-CH_3COOH has been used as a bromination's reagent, but **27** was more effective [19].

High-yielding protocol for exclusive formation **28-32** from **19-23** using complex **27** was reported. It should be mentioned, that 1-(4-aminophenyl)-1-ethanone **25** has produced 1-(3,5-dibromo-4-aminophenyl)-1-ethanone **33** (yield not indicated) as well as the bromination of **24,26** doesn't place. This problem was solved by use of tribromine of 2,4-diamino-1,3-thiazole **36** [20].

Scheme 6

26,38: $R^1=NO_2$, $R^2=H$; **34,39**: $R^1=H$, $R^2=NO_2$; **35,37**: $R^1=R^2=H$;
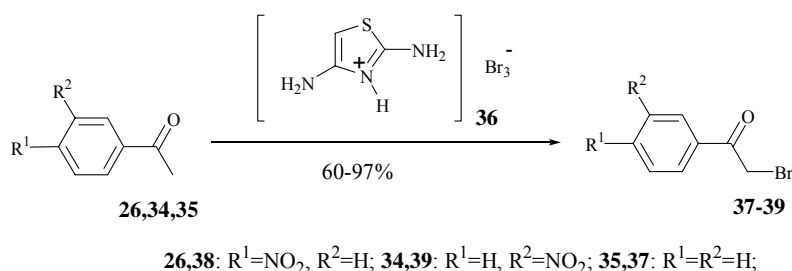
The target products **37-39** from **26, 34** and **35** have been prepared according scheme 6.

It is well known that treatment of methylketones with bromine covalent bonding reagents leads to α-bromoketo derivatives. For example, hexabromocyclopentadiene has shown good properties as reagent for selective bromination of **35** to **37** (yield 80%) [21]. A different approach to **37** using the polymer supported bromine Amberlyst-A26 Br_3^- was described [22], but the yield in this reaction did not exceed 55%.

Chemists still carries out their reactions in solution, even when a special reason for the use of solvent cannot be found. During the last two decades it was found out that many reactions proceed efficiently in solid state. Indeed, in many cases, solid-state organic reaction occurs more efficiently and more selectively than its solution counterpart does, since the molecules in a crystal are arranged tightly and regularly [16]. The investigation of the solvent-free microwave-induced bromination of **19-21, 26, 34, 35** to **28-30, 37-39** with dioxane-dibromide **40** on the surface of SiO_2 was performed. Acidic silica gel has play twofold roles: promoting enol formation from ketone and inducing electrophilic assistance to Br-Br bond breaking.

Scheme 7

19, 28: $R^1=Cl$, $R^2=H$; **20, 29**: $R^1=Br$, $R^2=H$; **21, 30**: $R^1=OMe$, $R^2=H$
26, 38: $R^1=NO_2$, $R^2=H$; **34, 39**: $R^1=H$, $R^2=NO_2$; **35, 37**: $R^1=R^2=H$
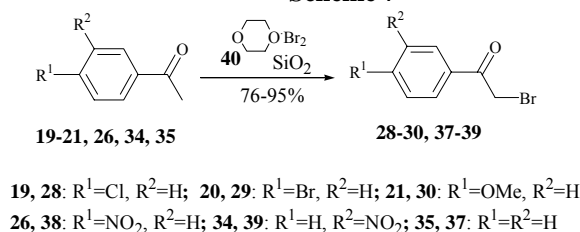
Under photochemical conditions, the bromination of compounds **19, 21, 35, 41** with N-bromosuccinimide was performed, and the α-bromoketones **28, 30, 37, 42** were obtained [23]. A mixture **37**, **43** was synthesized by treatment of acetophenone **35** with NBS in the presence of *p*-toluenesulfonic acid.

Scheme 8

19, 28: R=Cl; **21, 30**: R=OMe; **35, 37**: R=H; **41, 42**: R=Me
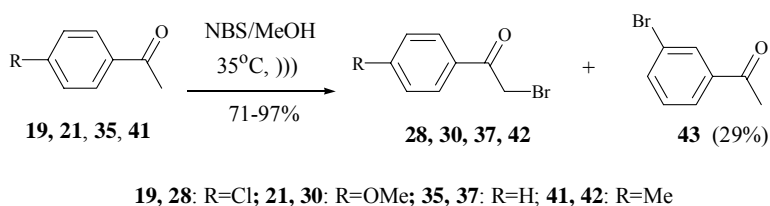
Benzylideneacetophenones present a class of naturally and synthetic occurring pigments, which are often referred to as "chalcones" [1, 2, 24-28]. The simplest method of synthesis of chalcones is involving the Claisen-Schmidt reaction. This is a two step reaction of acetophenones **21, 26, 35, 41** with benzaldehyde in the presence of base and result the aldols **44-47** followed by formation α,β-unsaturated ketones **48-51** (scheme 9). The water formed in this reaction is azeotropically distilled off with xylene.

38

Scheme 9
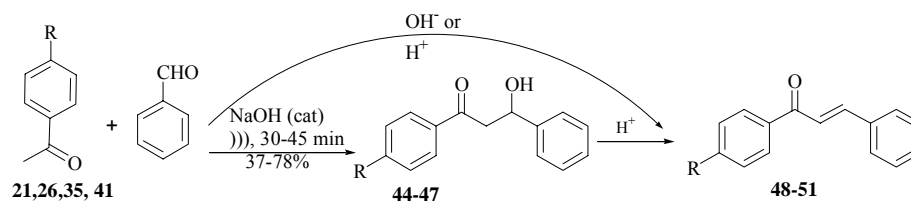
21, 44, 48 : R= 4-OMe; **26, 45, 49** : R=4-NO$_2$; **35, 46, 50**: R=H; **41, 47, 51**: R= 4-Me

The concentration of alkali used for this reaction usually ranges between 10-60%, but in case of fluoro acetophenones it should not be higher than 1,5% [29].   The use of an acid catalyst has been recommended for prepation of hydroxychalcones [30]. Synthesis of chalcones on the surface of SiO$_2$ was also reported [31]. Selective synthesis of aldols should be performed by use of ultrasound irradiation [32,33].

Another strategy was employed for the preparation of chiral aldol **53** from acetophenone **35** and 1*H*-indole-2,3-dione **52.** The condition of Knoevenagel reaction was recommended [34].

Scheme 10
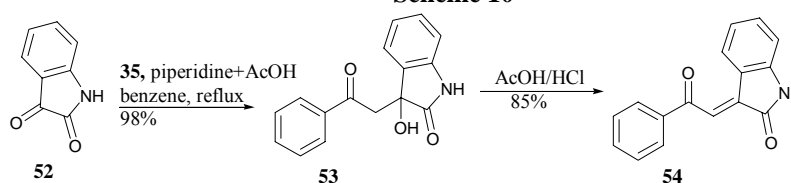
Dehydration of **53** leads to **54** – homolog of inhibitor of *Plasmodium falciparum* [35].

4. Syntheses where both groups of acetyl fragment are transformed

The α-hydroxylation of methyl group of **35, 41** is based on the initial oxidation of enol ethers **55, 56** with 3-chlorobenzenecarboperoxoic acid, chromyl chloride or iodosylbenzene [36-38].

Scheme 11
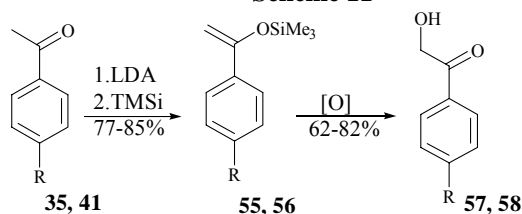
35, 55, 57: R=H; **41, 56, 58**: R=Me

Yields of products **57, 58** are moderate (from 48 up to 70 %).

Scheme 12

61 R^1=H,R^2=OH

62 R^1=OH,R^2=H
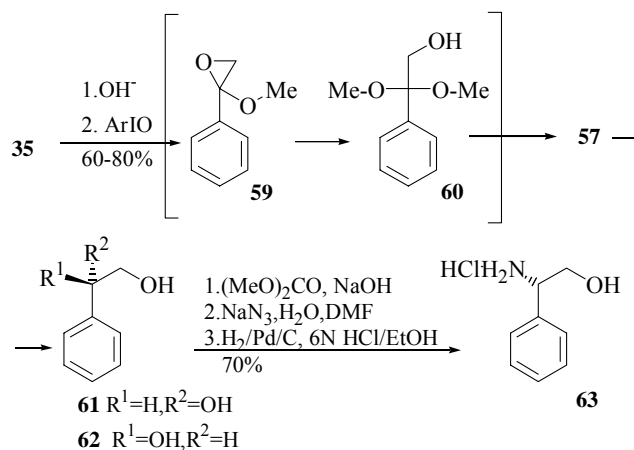
The direct hydroxylation of acetophenone **35** to **57** is illustrated on the scheme 12 and includes the preliminary formation of enolate anion [39-41]. The elimination of phenyl iodide or - iodo-benzoic acid has accompanied by

addition of anion MeO- to carbonyl group with formation of epoxide **59**, hydroximethylacetal **60**, and ketol **57**, respectively. The reduction of **57** led to a mixture of epimeric 1,2-diols **61, 62** separated by the use of lipases [42].

The synthesis of the enantiomeric pure amino alcohol **63** from **61** was also reported [43].

Conversion of ketone **35** to the alcohol **64**, styrene **65**, epoxides **66, 67** and 1,2-diols **68, 69** is presented on the scheme 13 [43-47].

Scheme 13

35, 64-69: R^1=H; **70, 71** : R^1=F; **72** : R^1=Cl; **73** : R^1=Br
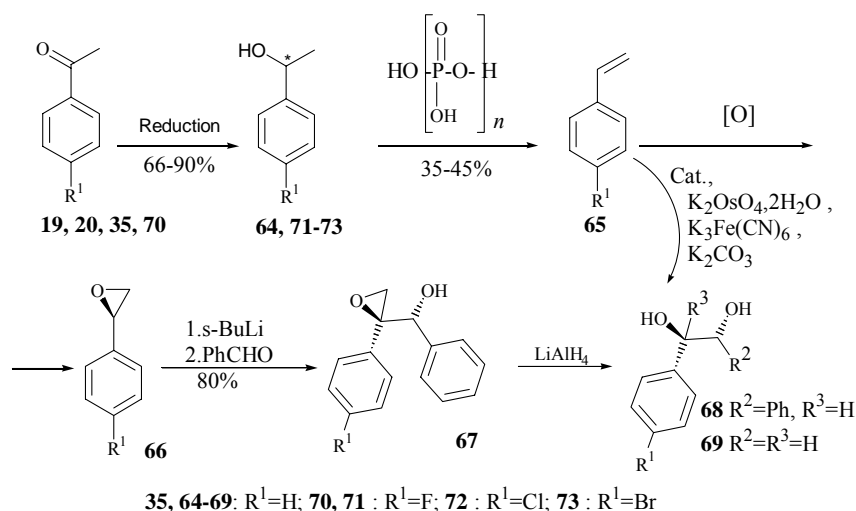
The reduction of unsymmetrical ketone to alcohols is one of the most common reactions in organic synthesis. During the reduction, nucleophile can approach both the faces of a carbonyl group of aryl-1-ethanones with an angle close to 109° giving rise to a mixture of two isomers. The asymmetric metal complex catalysis is one of the fast developing fields of modern chemistry [48]. Not only academic but also ever growing practical and industrial interest prompts researchers to make more efforts to develop the catalytic synthesis of various enantiomerically pure **64, 71-73** [49]. It is mentioned that many research groups put most their efforts onto catalytic testings of ligands, for example for the separation of **64** via specific palladium catalysed oxidation [50]. On the other hand, the reduction of aryl-1-ethanones **19, 20, 35, 70** with complex sodium borohydride- β-cyclodextrin leads to enantio-enriched alcohols [51]. The epoxide **66** serves as a starting point in the synthesis of alcohols **67**, **68** and **69** [47]. The last compound can be synthesized (yield 94 %, 93 ee) directly from **65** by hydroxylation using optically active catalyst [52].

Scheme 14
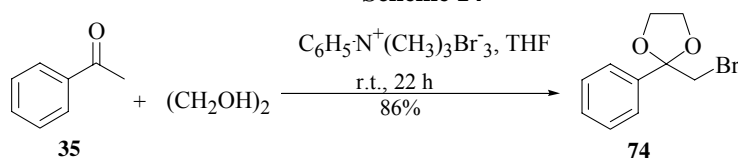
α-Bromoketals are useful precursors in the synthesis of different organic compounds, including agrochemicals [53-56]. They can be readily prepared by a number of methods: 1) bromination of methylketones followed by protection of carbonyl group; 2) ketalization with 1,2-diols and then bromination; 3) when bromination and ketalisation going together. The synthesis of phenacylbromides as well as 1,3-dioxolanes has already been overviewed by us, and so just the one pot reaction for formation of α-bromoketals will be discussed.

Scheme 15

78-89
78 : R=OTs, n=1; **79** : R=OH, n=1;
80 : R=CO$_2$H, n=1; **81** : R=Ph, n=0;
82 : R=2,4-Cl$_2$-C$_6$H$_3$, n=0; **83** : R=2,4-Cl$_2$-C$_6$H$_3$, n=1
84 : R=4-Cl-C$_6$H$_4$, n=1; **85** : R=2,4-C$_6$H$_3$, n=2
86: R=4-Cl-C$_6$H$_4$, n=0; **87** : R=4-Cl-C$_6$H$_4$, n=1
88: R=4-Cl-C$_6$H$_4$, n=2; **89** : R=Cl, n=1
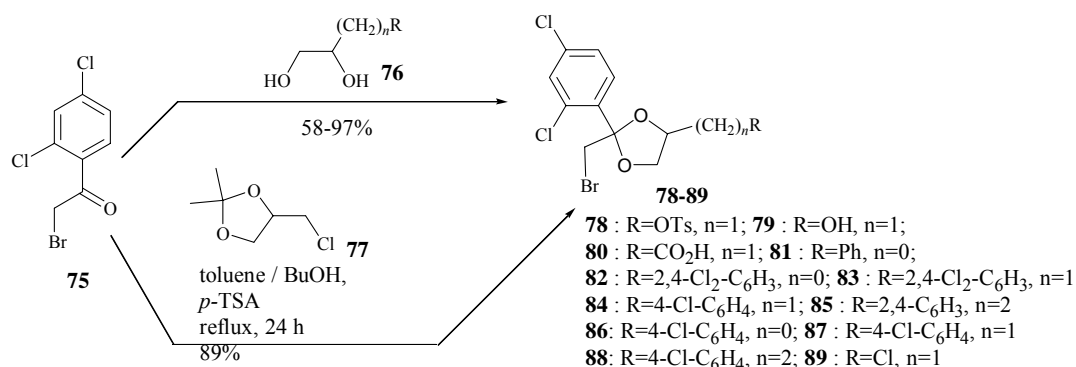
Environmental and economical considerations prompt an urgent need to redesign there important processes. In this context, an example of preparation of 2-bromomethyl-2-phenyl-1,3-dioxolane **74** is presented on scheme 14 [57].

The related bromides **78-89** could be prepared in one step from 2-bromo-1-(2,4-dichlorophenyl)-1-ethanone **75** and 1,2-dioles **76** [58]. It was established that the acetalization performs in the presence of *p*-toluenesulfonic acid in a mixture of 1-butanol - benzene. Notably, in absence of 1-butanol the reaction doesn't take place or the yields are usually low [59].

The separation of diastereomeric products **79** as well as **80** can be done by use of lipase [60].

The synthesis of optically active compounds **89** from R- and S-isomers of **77** was also carried out [55]. All the attempts of ketalization **75** with enantiomerically pure epichlohydrines by method [61] have been burst.

The convergent of total synthesis of (2*R*,4*S*,2'*S*,3'*R*)-hydroxyitraconazole **95** was previously reported [62]. The described process includes the conversion of ketone **90** and 1,2-diol **91** to the corresponding acetonide **92**. Palladium-catalyzed coupling of **93** with **94** followed by deprotection was burnished **95**.
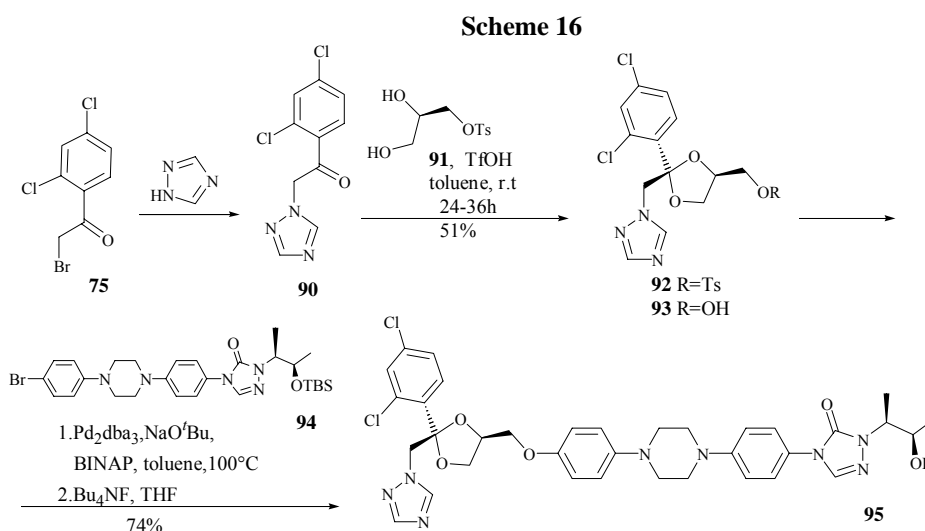
Scheme 16

5. Synthetic schemes based on the products of primary transformation of acetyl group

Heterocyclic compounds are the basis of many pharmaceutical, agrochemical and veterinary products. A large amount of references on synthetic methods of elaboration of heterocycle ring structures based on the products of primary transformation of the acetyl group of acetophenones were early summarized [1-3], however, time passes and new results have been published.

The selective transformation of bromohydrines **98, 99** obtained from 2-bromoacetophenones **37, 96** by chiral catalyst **97** reduction, to enantiomerically-pure epoxides **66** and **100** can be achieved by using K_2CO_3 as a base [63].

Scheme 17

37, 66, 98 : R=H; **96, 99, 100** : R=OCH$_2$Ph
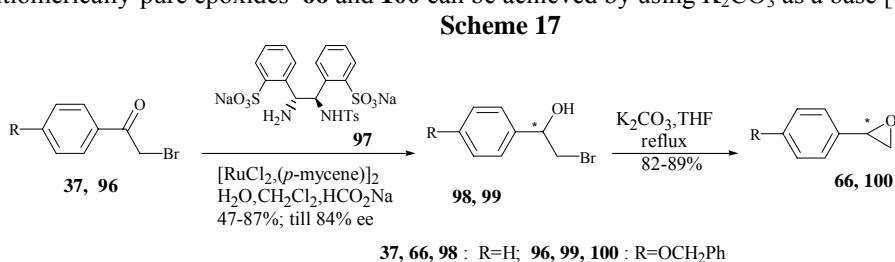
Chalcones still remain the subjects for the studing of structure-bioactivity properties [25,64,65], but most efforts involve the generation of functional chiral molecular diversity using their α,β-unsaturated system as illustrated in Scheme 18.

Scheme 18

101 : R=-CH$_2$NO$_2$; **102** : R=C(O)-CH=CMe$_2$; **103** : R=C(O)-(CH$_2$)$_4$Me; **104** : R=C(O)-3-Br-C$_6$H$_4$;
105 : R=CH(Me)-C(O)-Ph; **106** : R=CH(CO$_2$Et)-COMe; **107** : R=CH(CO$_2$Et)-COMe; **108** : R=H
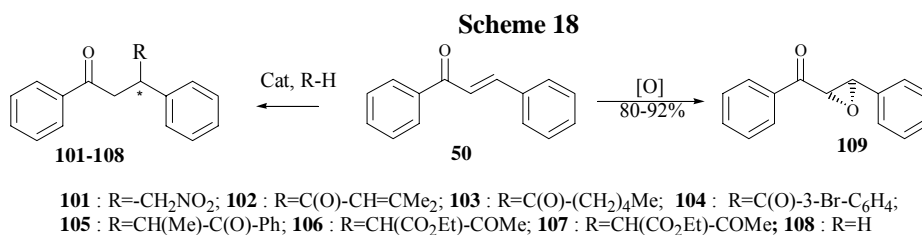
For example, the synthesis of enantio-enriched (3S)-ketone **101** was based on the mediated asymmetric catalyst conjugated 1,4-addition reaction of MeNO$_2$ to **50** [66]. The solvent-free microwave-induced reaction of **50** with wide range of aliphatic and aromatic aldehydes on the surface of SiO$_2$ gave adducts **102-104** [67]. According to another

report, lithium alkoxides was employed as a catalyst for the Michael addition of silyl enol ethers to **50** leading product **105** [68]. The reaction of acetoacetic ester with **50** in the presence of K_2CO_3 produced mixture stereo isomers **106, 107** [69]. Selective reduction of **50** to **108** as well as asymmetric epoxidation to **109** was reviewed recently [70], and published also [71,72].

Chalcone **50** was used as a model for the studing of possibility of synthesis of 1,2-dibenzoyl-3-methyl-3-phenylcyclopropanes. It was found out that cyclopropanation by sulfur ilide, generated from salt **110**, leads to a mixture of isomers **111, 112**, although the selectivity in this reaction was not good [73].
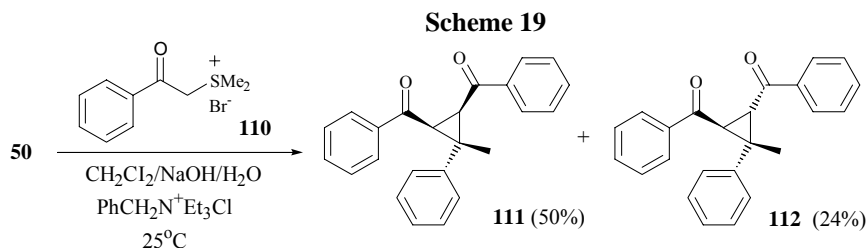
Scheme 19

Dihydroisoxazoles **114** and dihydropyrazoles **115-119** can be prepared by the reaction of chalcones **113** with hydroxylamine, hydrazine hydrate, monosubstituted hydrazines, and thiosemicarbazide according scheme 20 [74-80].

Scheme 20
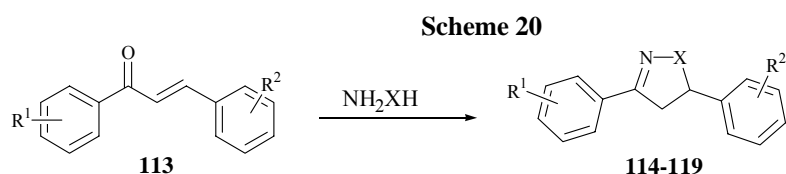
114 : X=O; **115** : X=NH; **116** : X=NAr; **117** : X=NC(S)NH$_2$; **118** : X=Nalkyl; **119** : X=NAc

One pot synthesis of N-acetyl-substituted dihydropyrazoles **119** was carried out in AcOH [81,82]. 1,3,5-Triphenyl-4,5-dihydro-1*H*-pyrazoles **116** can be prepared it two steps from chalcones **113** and phenyl hydrazine via hydrazone followed by the heterocyclization in boiling acetic acid. The influence of nature of the substituent in chalcone's ring on isolation of intermediate hydrazone is discussed [83]. Formation of N-carbamoyl, N-carbonyl as well as N-sulfanyl dihydropyrazoles by reaction with polymer-bound reagents was also described [84]. Synthesis of 3,5-diaryl-N-alkyldihydropyrazoles **118** from 3,5-diaryldihydropyrazoles **115** can be done by use of the phase transfer catalysis reaction [85]. Some derivatives of 3,5-diaryl-2- dihydropyrazoles **114** and 1,3,5-triphenyl-2- dihydropyrazoles **116** were found to exhibit the antidepressant activity [78,79].

4-Substituted dihydroizoxazole **121** and dihydropyrazoles **122, 123** were prepared from oxides **120** or dibromides **124** (Scheme 21) [2,86].

Scheme 21

121 X=O, R^3=OH
122 X=NH, R^3=OH
123 X=NH, R^3=Br
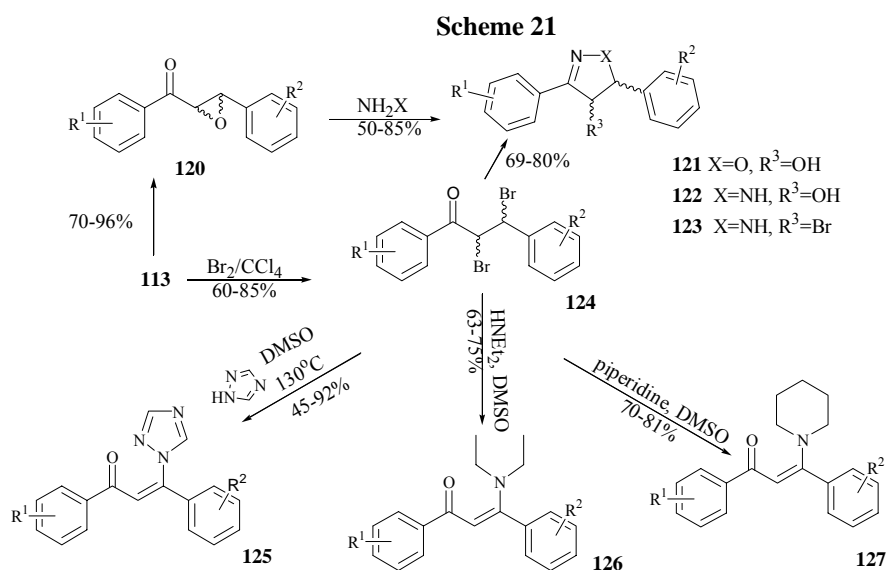
Compounds **121-123** represent an unstable mixture of isomers resulting diphenylisoxazoles and diphenylpyrazoles. The treatment of the **124** with secondary amines furnished enamines **125-127** [87,88].

Antimicrobial agents **129a-c** have to be synthesized by reaction of 1-aryl-3-(5-aryl-2-furyl)-2-propen-1-ones **128a-c** with hydrazine hydrate or phenyl hydrazine [89].

Scheme 22

a: R^1=NO$_2$, R^2=Cl, R^3=H; **b**: R^1=Cl, R^2=H, R^3=Ph; **c**: R^1=Br, R^2=Me, R^3=H
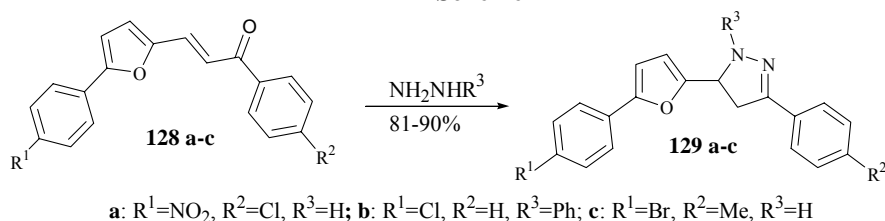
The stead of spiran stems among natural and synthetic products arouses a great interest in there. A special position among these compounds is occupied by spiro-indolin-2-ones. There are many methods of synthesis of such type derivatives, which are discussed in review [90].

α,β-Unsaturated ketone **54** can be readily transformed into spiro-products **130** and **133** upon treatment with hydroxylamine, hydrazine hydrate [74,91,92].

Scheme 23
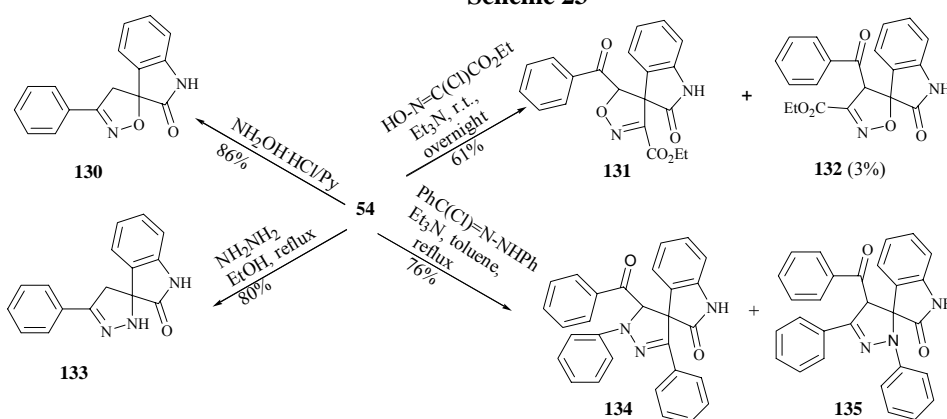
Regioselective cycloaddition of carboethoxyformonitrile oxide (generated *in situ* from hydroxamoyl chloride) to **54** could be regarded as one of the approaches to spiroproducts **131** [93]. The content of regioisomer **132** is not more than 3%. The same author reported the synthesis of mixture of **134** and **135**.

The syntheses of organic compounds starting from α-halogeno ketones were overviewed [3,94]. Based on this information, new data for the synthesis of heterocyclic systems will be reviewed. For example, N-substituted 2-aminothiazoles **136** are synthesized in one-pot procedure using **38** and amines (Scheme 24) [95].

Scheme 24
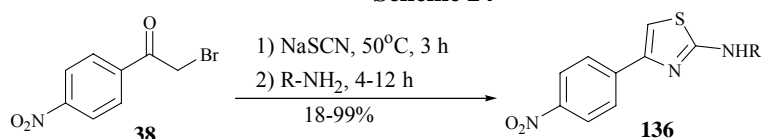
Selectivity of the reaction decreases for α,α-disubstituted amines, and with α,α,α'-trisubstituted amines no reaction occurs. Only ethanol proved to be a suitable solvent for the described above transformation; the yield of target compound was very poor in DMF or acetonitrile.

Authors [96] have reported the solid support synthesis of 2,4-disubstituted aminothiazoles. Rink amide resin with loaded 3-iodobenzoic acid was involved in Pd(0) coupling reaction with tributyl(1-ethoxyvinyl)tin followed by bromination leads to bromoketones. Last were condensed with thiourea and thioamide, followed by trifluoroacetic acid cleavage from resin, to give targets **137 a-e** (total yields 61-90%).

Scheme 25

a: R=Me; **b**: R=Ph; **c**: R=NH-Ph; **d**: R=3-Py; **e** R=NH$_2$
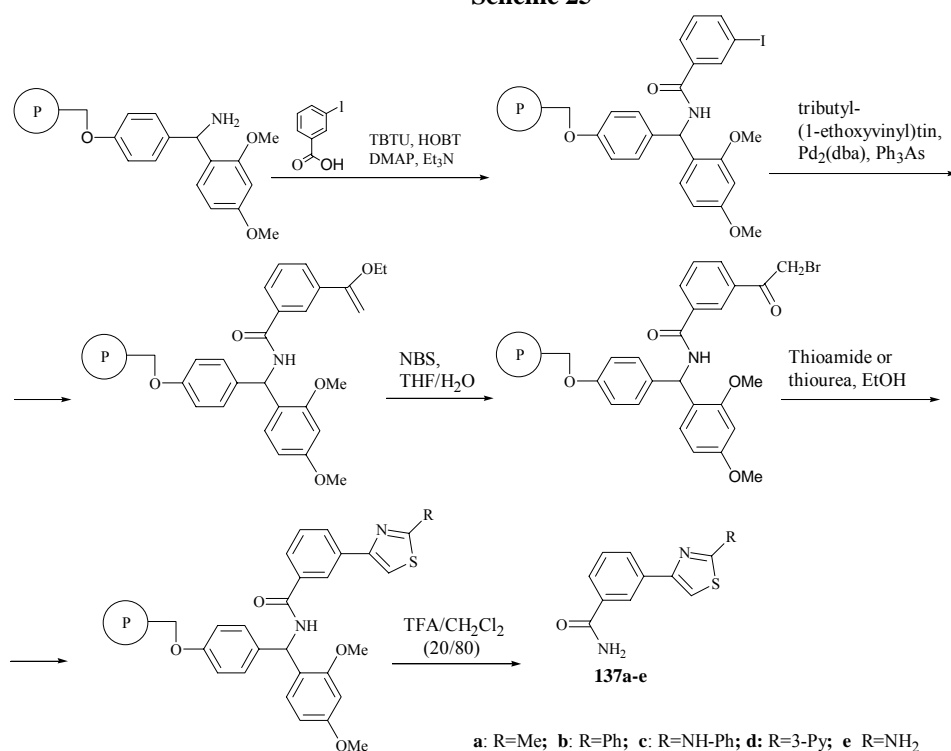
2-Aminothiazole **139** was obtained from the **37** in one-pot reaction, using supported reagents systems KSCN/SiO$_2$-NH$_4$Oac/Al$_2$O$_3$ (Scheme 26) [97].

Scheme 26

142 : Ar=2-NO$_2$-C$_6$H$_4$; **143** : Ar=3-NO$_2$-C$_6$H$_4$; **144** : Ar=2-Cl-C$_6$H$_4$
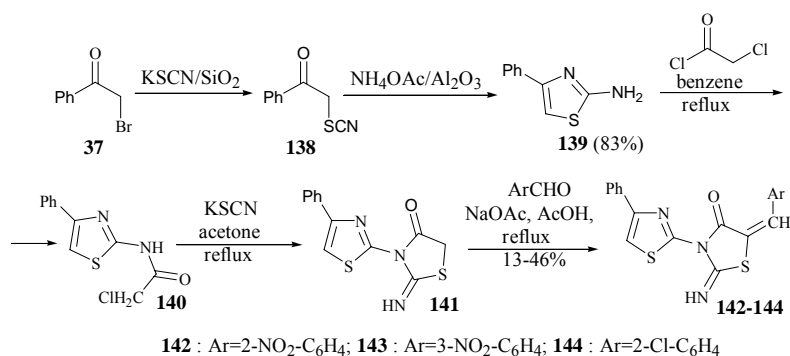
First, 2'-bromoacetophenone **37** reacts with KSCN/SiO$_2$, and then the obtained α-thiocyanatoketone **138** reacts with NH$_4$Oac/Al$_2$O$_3$ to afford final product **139**. Fungicides **142-144** could be prepared via aminothiazoles **140**, **141** [98].

As a new variant of Hantzsch thiazole synthesis, the reactions of 1-alkyl-2-thiobiureas **145** with 2-bromo-1-phenyl-1-ethanone **37** yielded 3-alkyl-4-aryl-2-semicarbazono-Δ^4-dihydrothiazoles **146a,b** was presented [99].

Scheme 27

146a : R=Me
146b : R=Pr
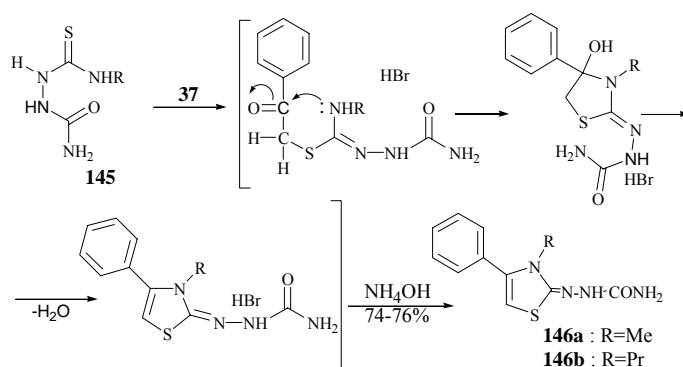
The combinatoric method for synthesis the molecular libraries of 2-aminothiazoles **149-153** is based on use of DMF as a solvent and dimethylamine as acceptor of HBr [100].

Scheme 28
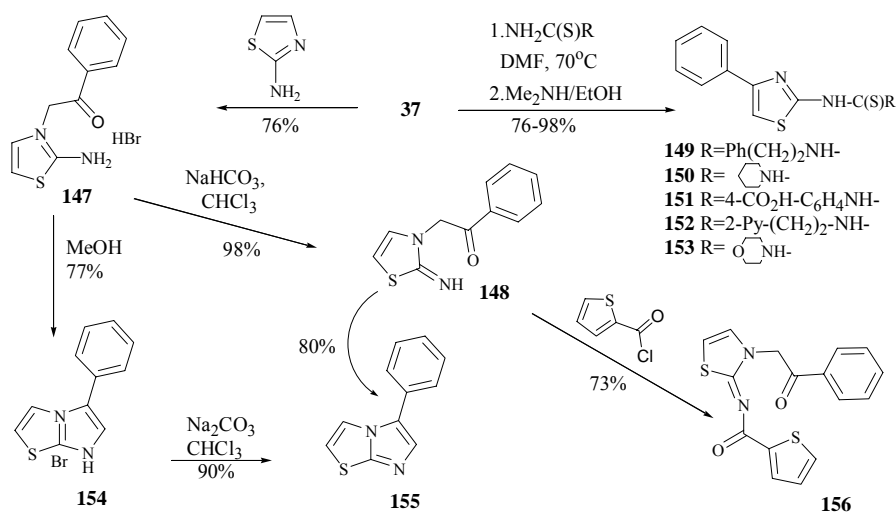
The imidazo[2,1-*b*]thiazoles **154,155** were prepared from 2-aminothiazole and **37** [101]. The adduct **147** was used for the synthesis of ketones **148, 156**.

We established that 2-amino-1-arylideneaminoimidazoles **158** and 1-arylideneaminoimidazo[1,2-*a*]imidazoles **159** can be synthesized through combination of hydrazones **157** as well as 2-bromo-1-aryl-1-ethanones [102].

Scheme 29
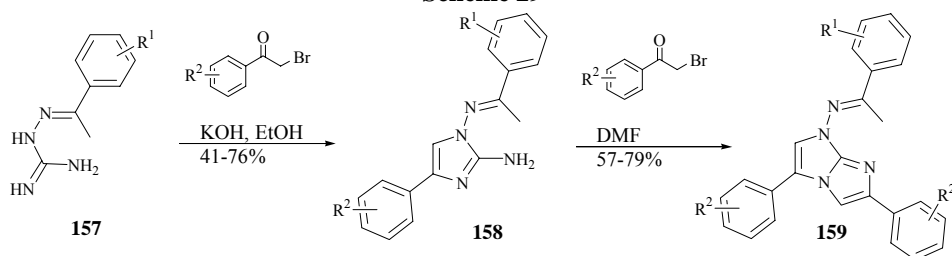
One-pot procedure for the rapid synthesis of 5,11-dioxa- and 5-oxa-11-thiabenzo[*b*]fluoren-10-ones **162a,b** via condensation of esters of salicylic and thio-salicylic acids **160a,b** with α-bromoketone **161** was discovered [103].

Scheme 30

a : X=O; **b** : X=S
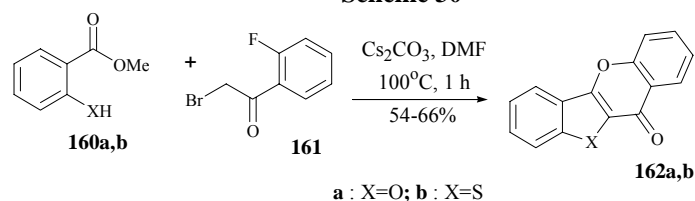
The preparation of 1,2,4-triazolechlorohydrine **166** has involved three step process transformation of chloroketone **163** via alkynes **164, 165** as illustrated in Scheme 31 [103].

Scheme 31
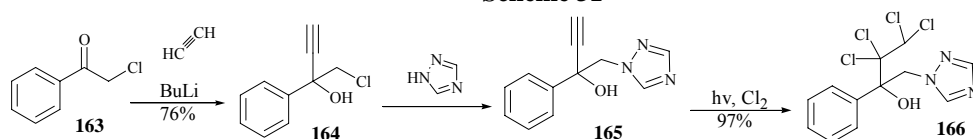
We reported our efforts to find the relationship of the bioactivity from the nature of substituents in 1,2,4-triazoles **167-178** [104,105]. Condensation of ketone **90** and aldehydes (Knoevenagel reaction) gives the specific formation of *Z*-isomer of N-vinyl-1,2,4-triazoles **171-177**. Synthesized allylic alcohols **178-184** and its precursors exhibit anti-fungal and anti-bacterial activity. The selective synthesis of 2,4-bis(azolylmethyl)-2-(2,4-dichlorophenyl)-1,3-dioxolanes **169, 170** has to be carried out via preliminary preparation of alcohols **167** and corresponding mesylates **168** [59].

Scheme 32

167 : R=OH; **168** : R=OMs; **169** : R=-1,2,4-Tr; **170** : R=Im; **171, 178** : R=-n-C$_3$H$_7$; **172, 179** : R=-i-C$_3$H$_7$; **173, 180** : R=-n-C$_4$H$_9$; **174, 181** : R=-i-C$_4$H$_9$; **175, 182** : R=-3-Py; **176, 183** : R=-Ph; **177, 184** : R=-4-Cl-C$_6$H$_4$
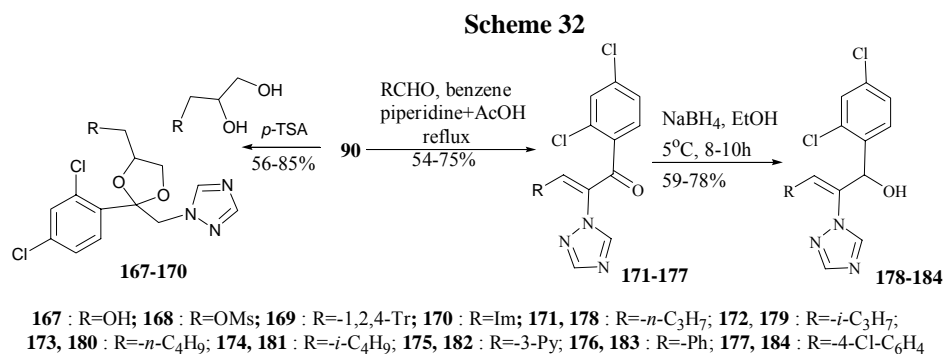
The computer-aided study "structure-activity" of synthesized compounds was also reported [106].

Recently, we have select 2-bromo-1-(4-halogenophenyl)-1-ethanones **29**, **185** as an intermediates for the synthesis of new anxiolytics **186, 187** (Scheme 33) [107].

Scheme 33

29, 186 : R=Br; **185, 187** : R=F
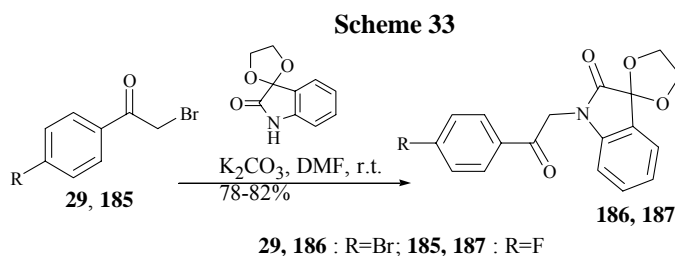
Also, a series of 2,5-disubstituted-1,3,4-thiadiazoles **188-192** aws designed and synthesized, and these compounds were screened for anti-tuberculosis activity against *Mycobacterium tuberculosis* H37Rv [108].

Scheme 34
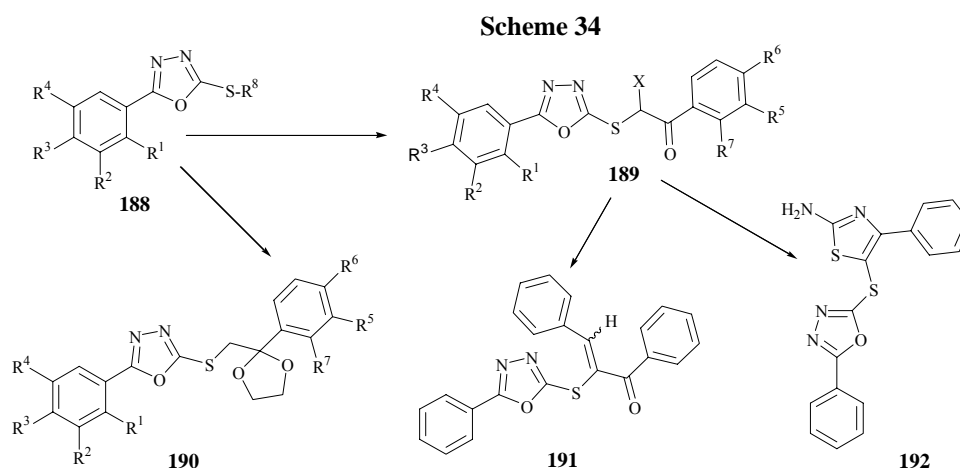
It was found that 1,3-dioxolane derivatives **190** are less active than the corresponding keto-precursor compounds **189**. Compound **190** (R^1=R^2=R^3=R^4=R^5=R^6=R^7=H) is a notable exception. The last compound showed the highest target activity (82%) among all the 5-aryl-2-thio-1,3,4-oxadiazoles.

6. Conclusions

The present compilation showed clearly the diversity in the field of synthetic organic chemistry by use of the acetyl group of aryl-1-ethanones. In the future, more complex target compounds, new methodology will be required for rapid construction of molecules bearing unusual substitution patterns. Thus, work is being continued in an effort to elucidate innovative new regio-, stereo- and enantio-selectively processes using the acetophenones to obtain products with target properties.

7. Acknowledgments

8. References

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DEVELOPMENT OF NATIONAL EMISSION FACTORS FOR SOLID WASTE DISPOSAL ON LAND GREENHOUSE GAS SOURCE CATEGORY OF THE NATIONAL INVENTORY IN THE REPUBLIC OF MOLDOVA

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Abstract: The paper summarizes the research results on development national emissions factor for the Greenhouse Gas Inventory (GHGI) Source Category "6A Solid Waste Disposal on Land". The obtained results offer the opportunity to improve the Intergovernmental Panel for Climate Change (IPCC) methodologies and Emission Factors for assessing the GHG emissions originated from waste sector. The article contains relevant information on composition of landfill gases at managed and unmanaged solid waste disposal sites, as well as the municipal solid waste composition results, investigated during one year in the Republic of Moldova: from autumn, 2004 to summer, 2005.

Keywords: solid waste disposal, greenhouse gas, methane emissions, landfill gas measurements.

Introduction

Urbanization and economic development have increased waste generation in whole world. In the 21st century, the treatment of waste has become a serious environmental concern and waste management continues to be an important environmental challenge. Waste management and climate change are closely related. For instance, solid waste disposal sites are one of the largest sources of greenhouse gas (GHG) - methane emissions. The methodology used to estimate emissions from waste activities requires country–specific knowledge on waste generation, composition and management practice. In this context the main objective for this study has been to compile results of the municipal solid waste composition, as well as landfills gas (LFG) measurements on managed and unmanaged landfills in the Republic of Moldova. These studies were carried out during one year, monthly for landfill gas measurements and seasonally for waste composition analyses.

Results and Discussions

The obtained results from field studies indicated that solid waste composition slightly varied seasonally and is indicated in the table 1.

Table 1: Seasonable waste composition results in the Republic of Moldova, 2004-2005

Waste categories	Autumn 2004			Winter 2005			Spring 2005			Summer 2005		
	09. XI	19. XI	Ave-rage	02. II	28. II	Ave-rage	23. III	15. IV	Ave-rage	13. VII	09. VIII	Ave-rage
	%	%	%	%	%	%	%	%	%	%	%	%
Paper	5.7	4.5	5.1	8.7	8.3	8.5	9.5	6.6	8.0	5.3	7.3	6.3
Glass	5.2	2.9	4.1	6.2	11	8.6	7.6	7.7	7.7	8.4	7.6	8.0
Plastic	10.8	8.6	9.7	11.5	15.4	13.4	13.4	10.5	12.0	11.1	16.2	13.7
Metals	3.9	2.2	3.1	4.0	3.7	3.9	2.7	5.4	4.0	5.0	6.2	5.6
Food remains	63.1	66.5	64.8	48.1	53.2	50.7	53.5	56.6	55.1	54.8	51.6	53.2
Garden waste	1.4	3.7	2.5	1.0	0.8	0.9	1.2	0.9	1.0	3.7	1.0	2.4
Textile	4.3	5.5	4.9	12.2	3.5	7.8	4.5	2.5	3.5	2.6	3.1	2.8
Wood	1.8	1.6	1.7	1.3	1.4	1.4	0.6	2.4	1.5	2.1	2.6	2.3
Construction	2.2	3.6	2.9	6.4	1.6	4.0	6.5	6.3	6.4	5.5	3.3	4.4
Leather	1.6	0.9	1.2	0.6	1.1	0.8	0.4	1.1	0.8	1.5	1.1	1.3

It should be mention that we consider householders generate the composition of waste, which is disposed at landfill and not that. MSW are collected in the open containers and scavengers recover usually recyclable fractions. This fact led to reduction of paper fraction in the MSW, but does not affect fraction of plastic packaging, which counted about 13% by weighing and even more times by volume. The food wastes represent almost 50% of the waste stream.

Data on municipal solid waste composition is used for the estimation of national value for DOC, which represents the value of 0.146. The same value of 0.146 can be obtained if the Extended Buswell Equation is used as well (Table 3).

First measurements of biogas composition have been undertaken at Straseni landfill weekly during one month. As no fluctuation of biogas components was observed, it was decided to monitories emissions monthly. Researches and

LFG measuring on this landfill have revealed that the depth of a landfill and the thickness of the waste layer are very important for the formation of LFG. It was demonstrated that a landfill with the thickness of waste layer around 5-8 m generate a low concentration (around 20 per cent) of CH_4 (Figure 1).
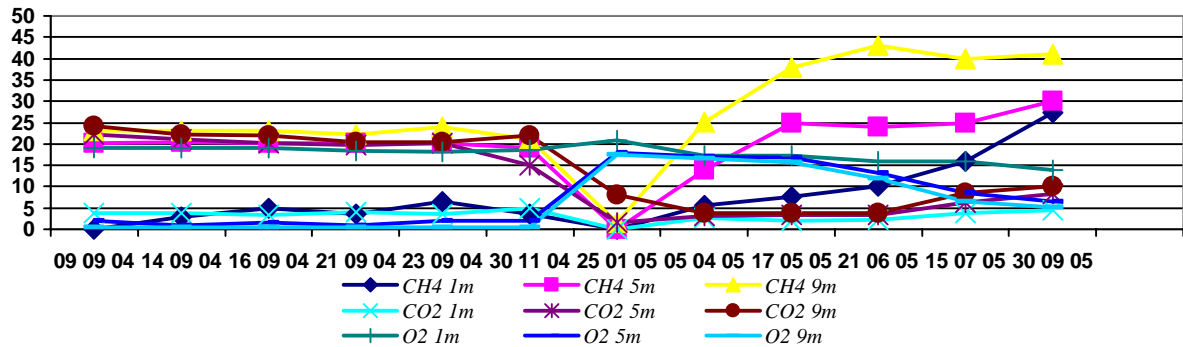
Figure 1: Dynamics of biogas measurement at Straseni landfill

In order to verify the results of chromatography analysis, using measuring devices «GASOTEST» TU 4215-001-17763771-95 performed an additional measurement of CO2 and O2 concentrations. The graphic below illustrated the results of both analyses (Figure 2).
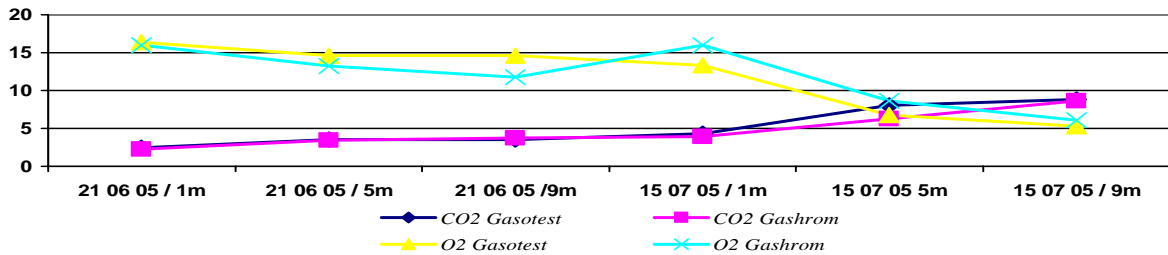
Figure 2: Comparison between express analysis and chromatograph of O_2 and CO_2 emissions at Străşeni landfill

During the research period at Balti landfill the CH_4 emissions are constantly produced, their concentration had fluctuated between 45-80%, depending by the level of taking measurements. For a deeper level like 5-9 m, the CH_4 concentration practically is not influenced by seasonal temperature fluctuation, but at the level of 1 m it was observed a reduction of CH_4 in the cold period of year (Figure 3).
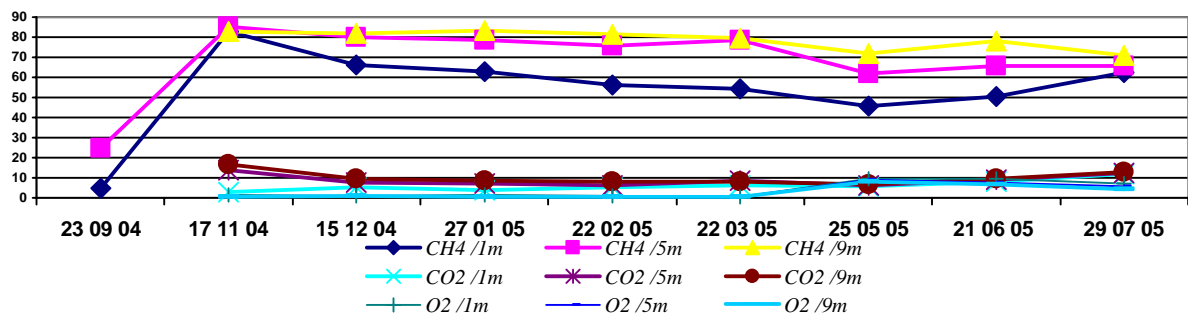
Figure 3: Dynamics of biogas measurement at Bălţi landfill

In addition, the CO_2 emissions have been measured by using the device „GAZOTEST" TU 4215-001-17763771-95. For the first measurement, the biogas concentration (it was collected on 22.03.2005) was analyzed in laboratory conditions. The obtained results revealed the following: the concentration of O_2 is 0.5-0.4%, while the CO_2 concentration remained constant (11.6%) for all the taken samples: from 1, 5 and 9 meter levels (Figure 4).
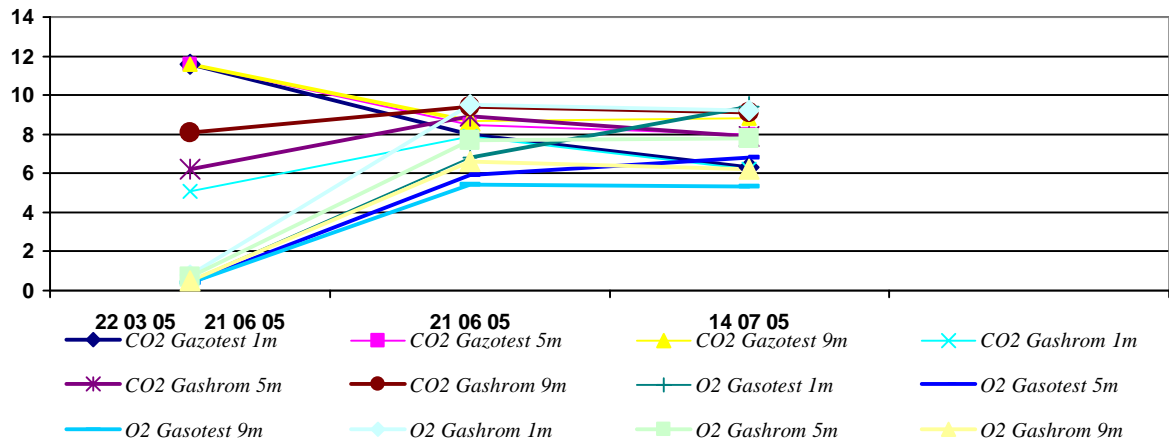
Figure 4: Comparison between express analysis and chromatograph of O_2 and CO_2 emissions at Bălți landfill

Samples collected on 21.06.05 and 14.07.05 have been analyzed directly at well, at the landfill. The obtained results defer from the previous one. First of all, the O_2 concentration has changed in dependence of the level, from 1m to 9m (6.8% and 5.4%, respectively), also the CO_2 concentration has increased from 8.0% to 8.7% for the 9-meter level. At the same time, the obtained results are comparable with the results of the chromatography analyzes of the biogas (Figure 5).
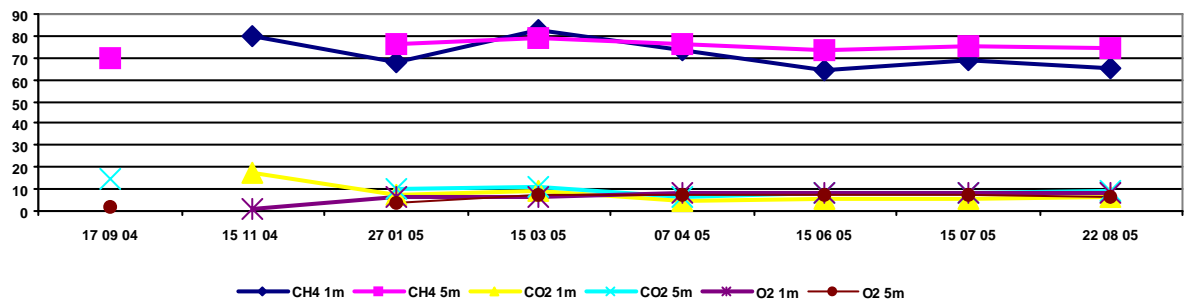
Figure 5: Dynamics of biogas measurement at Chisinau landfill

Nevertheless the concentration of CH_4 at Chisinau landfill is lower than at Balti landfill, this fact might be explained by the using of the technique of landfilling with separate waste layers at the first one. Generally it is expected that the production of LFG on landfills with separate waste layers is less than on landfills with one waste layer, because layers of covering materials has significant impact on the forming of LFG [1]. This assumption was confirmed by our results what is indicated in the Table 2.

In addition to the chromatograph analysis, other measuring device (GAZOTEST TU 4215-001-17763771-95) has been used on 15.07.2005 with the scope of detecting the presence of CO_2 and O_2 at Chisinau landfill. The obtained results are presented below (Figure 6).
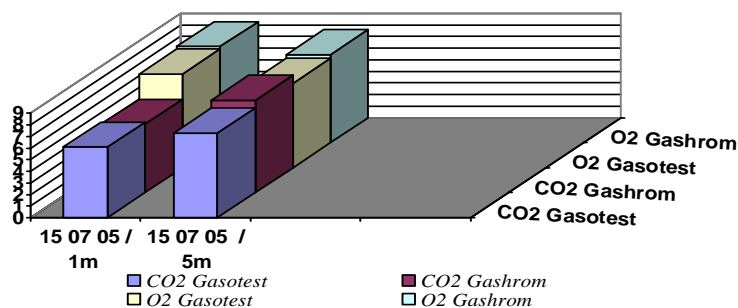
Figure 6: Comparison between express and chromatograph analysis of O_2 and CO_2 at Chisinau landfill

The results of measurements at three landfills from the republic of Moldova revealed the variability of landfill gas composition from one site to another. This fact might be explained, first of all, by landfill characteristics: in the case of Balti and Chilinau, they are managed landfill while the last one, from Straseni town, it is unmanaged. The table below contains the usual biogas composition and the obtained results characteristic for the Republic of Moldova [2].

Table 2: Obtained results on composition of gases at three landfills in the Republic of Moldova (h=5-9 meters)

Gases	Usual LFG composition, %	LFG composition Chisinau landfill *, %	LFG composition Balti landfill, %	LFG composition Straseni landfill, %	Average LFG composition, in RM, %
CH_4	50-60	71–75 / 63–65	74–79	23–45	56–66
CO_2	30-40	8–10 / 32–34	9–10	12–14	10–12
N_2	5-32	10–16	10–16	50–60	15–30
O_2	0-2	5–6 / 0.5–1	3–5	7–8	5–7

* Alternative results have obtained from CDM Projects "Landfill gas utilization at Chisinau landfill" (donor: DEPA, Denmark Kingdom, beneficiary: Mayoralty of Chisinau).

It should be mentioned, that CH_4 generation depends also on the quantities of MSW disposed at landfill, in the case of Straseni landfill the MSW it is many times less then at the landfills from Balti and Chisinau. The Extended Buswell Equation was used for the estimation of methane fraction in landfill gas (the obtained results are presented in Table 3).

Table 3: Fraction of methane in landfill gas (F)

$$C_\alpha H_\beta O_\gamma N_\delta S_\sigma + A_1 H_2O \rightarrow A_2 CH_4 + A_3 CO_2 + A_4 NH_3 + A_5 H_2S$$

$$A_1 = \alpha - \beta/4 - \gamma/2 + 3\delta/4 + \sigma/2, \; A_2 = \alpha/2 + \beta/8 - \gamma/4 - 3\delta/8 - \sigma/4, \; A_3 = \alpha/2 - \beta/8 + \gamma/4 + 3\delta/8 + \sigma/4, \; A_4 = \delta, \; A_5 = \sigma.$$

$\alpha=$ 17.933	$\delta=$ 545	$A_1=$ 6953,0	$A_4=$ 545
$\beta=$ 27.841	$\sigma=$ 29	$A_2=$ 10.013,5	$A_5=$ 29
$\gamma=$ 8.886		$A_3=$ 7919,5	

Factor of SH$_2$	1

Component	Composition %	Dry/wet %	Percent by weight (dry basis)					Content (g/Mg wet waste)				
			C	H	O	N	S	C	H	O	N	S
Food wastes	56,10	30	0,458	0,064	0,376	0,026	0,004	77.081	10.771	63.281	4.376	673
Paper	7,00	94	0,425	0,060	0,440	0,003	0,002	27.965	3.948	28.952	197	132
Cardboard		95	0,440	0,059	0,446	0,003	0,002					
Plastics	12,10	99	0,600	0,072	0,228			71.874	8.625	27.312		
Textiles	4,70	90	0,550	0,066	0,312	0,046	0,002	23.265	2.792	13.198	1.946	63
Rubber		100	0,78	0,10		0,02						
Leather	1,10	80	0,600	0,080	0,116	0,100	0,004	5.280	704	1.021	880	35
Yard wastes	1,70	35	0,478	0,060	0,380	0,034	0,003	2.844	357	2.261	202	18
Wood	1,80	80	0,492	0,060	0,427	0,002	0,001	7.085	864	6.149	29	14
Total								215.394	28.061	142.173	7.630	936
Molar mass (g/mole)								12,011	1,008	15,9994	14,0067	32,060
Total moles								17.933	27.841	8.886	545	29

Test (balance)

C	17.933	0,0
H	41.747	0,0
O	15.839	0,0

CH_4 production per Mg wet waste

kg	m³
160,64	225,05

C --> CH_4	10.013,5	**55,8**	**%**
C --> CO_2	7.919,5	44,2	%
C total	17.933,0	100,0	%

Conclusions

The main conclusion and findings related to the consolidating data from landfill gas measurements and solid waste composition at national level are presented below:

1. Data on composition of municipal solid waste have been used for the estimation of national parameter of DOC=0.146 and DOC$_f$=0.585, based on IPCC methodology and the Extended Buswell Equation.

2. Based on the comparison between express and chromatography analyses it could be concluded what the chromatography analyses might be accepted for using, as the differences between the two methods is around ±10%, which is in frame of limited errors for measurement devices.

3. The obtained results for the LFG measurements during a year, offer the opportunity to update the IPCC EFs for CH$_4$ emissions from landfills for the Republic of Moldova, by using the 0.6 instead of 0.5 value, which was used before in the First National Communication to the UNFCCC [3].

4. The decision on using the value of 0.6 as EFs for CH$_4$ is confirmed also by the results presented into the Table 3 (the fraction of CH$_4$ in biogas is 55.8%, which is close to the average value of the LFG composition presented in Table 2).

Experimental

Municipal solid waste (MSW) composition surveys were performed at transfer station in Chisinau municipality and humidity analyzes at Central Ecological Laboratory of the State Ecological Inspectorate of the Republic of Moldova. Waste characterization surveys provide the percentage by weight of each major category of waste in the overall waste stream. Relevant details on the used methodology can be found in the article [4]. The obtained results are summarized as well in the table 1 above. Based on the Revised 1996 IPCC methodology and by using the data obtained, the national value for DOC (degradable organic carbon) was estimated.

Under UNDP/GEF Regional Project "Capacity Building for Improving the Quality of Greenhouse Gas Inventories (Europe and CIS region)", Georgia prepared and proposed the new methodology (approach) to estimate degradable organic carbon (DOC) and fraction of degradable organic carbon dissimilated (DOC$_F$) for waste components and for total waste taking into account lignin content in waste (for both cases including and excluding lignin). The Approach (Methodology) is based on results of the laboratory experiments conducted by Dr. Morton Barlaz [5-7] and on investigations of I.Chandler et al. [8] and Van Soest [9]. "MSW Learning Tool" of the University of Central Florida [10] also was used. In the methodology also is presented the method (based on the Extended Buswell Equation) for estimating fraction of CH$_4$ in landfill gas (F).

Follow this model and using national data on solid waste composition, there were estimated the DOC, DOCf values and biogas composition at managed and unmanaged landfills from the Republic of Moldova. Table 4 reveals the obtained results [11].

Table 4: Degradable Organic Carbon and Fraction of Degradable Organic Carbon Dissimilated (DOC and DOC$_F$)

Material	DOC	DOC$_F$	%	DOC$_i$	DOC$_i$ * DOC$_F$
	g C/g wet waste	g C/g wet waste		g C/g wet waste	g C/g wet waste
A	B	C	D	E	F
Second food	0,137	0,70	56,1	0,077	0,054
Leaves	0,326	0,15	1,7	0,006	0,001
Wood	0,393	0,36	1,8	0,007	0,003
Mixed Paper from Residential sources	0,400	0,45	7	0,028	0,013
Textile	0,495	0,55	4,7	0,023	0,013
Leather	0,480	0,55	1,1	0,005	0,003
				0,146	0,085
		DOC$_F$			0,585
		DOC			0,146

Landfill gas measurements were performed at three landfills from Straseni and Balti towns and Chisinau Municipality (the landfill is located near the Cretoaiea village). Landfill biogas was collected from special wells installed in 2004 and investigated chromatographically at the Central Ecological Laboratory of the State Ecological Inspectorate, which has a respective accreditation [12, 13]. Also, express analysis for CO$_2$ and CH$_4$ were conducted directly at landfills. The following equipments were used during measurements: aspirator "AM-5", "GIAM–305" portable gas analyzer, chromatograph "GAZHROM-3101" and „GAZOTEST" TU 4215-001-17763771-95.

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ASSESSMENT OF KINETIC PARAMETERS IN THE WATERS OF THE NISTRU COURSE IN THE SECTION NASLAVCEA – DUBASARI

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Abstract: The current work represents the results of a monitoring executed on Nistru River waters between October 2003 and September 2005. The water quality was evaluated on the basis of such kinetic indicators as redox state and capacity of inhibition. The obtained results shows that Nistru River water in the segment Naslavcea village – Dubasari barrage are continuously polluted with reducing substances that diminish the H_2O_2 content, that actually determines the redox state of natural waters and the content of free radicals

Keywords: kinetic indicators, hydrogen peroxide, redox state, free radicals, inhibition capacity.

Introduction

As a system of environmental supervision and control, monitoring is intended to perform a supervision, assessment of the practical environment and the forecasting of eventual changes. The main constituent part of monitoring is environmental assessment.

Aimed at the assessment and control over content of substances in the aquatic medium the existing hydrochemical and hydrobiological methods of monitoring are built upon the principle of comparison of the values observed in the natural medium with the maximum permissible concentrations (MPC). It is not always that these measurements can reflect water quality by criteria that are adequate to its *biological value*. Therefore, in water quality assessment *kinetic indicators* and *biotesting methods* should be a priority, as being integral values that characterize the efficiency of self-purification processes [1]. The quality of environmental water should by stated not only by the content of certain substances in it, but by its *biological value*. In waters of adequate biological value there are normally carried processes of vital activity and reproduction of biological forms at different trophic levels in such a way that the cycle of chemical substances with the participation of all members of the ecosystem is closed..

The kinetic surface water quality indicators characterize the content and the dynamics of the products of *single-electron activation* of molecular oxygen, among which there stand up particular redox agents of very high activity: hydroxide radical, singlet oxygen, superoxide anions and hydrogen peroxide. These values and the dynamics of these indicators enable the determination of the degree of quality of the water body, its biological value and self-purification capacity.

The content of hydrogen peroxide in natural waters is the result of the influence of a number of biotic and abiotic factors that define the dynamic water redox state. From the ecological point of view the water body quality is assessed based on the analysis of the redox state dynamics.

The biologically valuable state of the natural waters is considered to be their oxidative state when hydrogen peroxide is present in concentrations physiologically favorable for aquatic forms, of the order of 10^{-6}mol/l.

The cycle of hydrogen peroxide in the natural aquatic medium is influenced by the human factor, which often leads to a decrease in the concentration of the substance. The decrease in concentration of hydrogen peroxide in water is caused not only by the discharge of biologically treated waste waters loaded with reductive substances that react with H_2O_2 but also by a boost of the green-blue algae that emit toxic reductive metabolites in the outer medium. The discharge of waters containing biogenic elements (N and P) and water course regulation are the main human factors stimulating the flourishing of the green-blue algae in the natural algae community [2].

The phenomenon of importance of the free radicals in natural waters has become a subject of discussion and study not so long ago. Among the products of monoelectric reduction of the molecular oxygen the *OH* radicals tend to have higher oxidative properties. According to the results of investigations from literature sources the permanent concentration of OH radicals, the strongest oxidant of the natural waters, is very low ($\approx 10^{-15} – 10^{-17}$ M), that is why at the beginning there were doubts on whether they can have a significant role in the self-purification processes of natural waters. A parameter that characterizes the capacity of natural waters for inhibition of radical self-purification processes with the participation of *OH* radicals is the *inhibition capacity* ($\Sigma k_i[S_i]$) [2]**.** The value and physical sense of the inhibition capacity enable us to treat it as an effective interruption constant of the radical chain in the processes of oxidation in the natural waters.

According to the capacity of inhibition of self-purification by radicals all natural waters can be classified in three categories:
1) if $\Sigma k_i[S_i] < 10^4 s^{-1}$ – the water is considered pure
2) if $\Sigma k_i[S_i] \approx 10^5 s^{-1}$ – the natural water is in normal state
3) $\Sigma k_i[S_i] > 10^6 s^{-1}$ – the water is highly polluted

The monitoring of processes with the participation of free radicals in aquatic systems is necessary for both the evaluation of the self-purification capacity and prevention of the appearance of the phenomenon of toxicity for aquatic forms. From the point of view of efficiency of the self-purification processes with the participation of free radicals the

growth of permanent concentration of the OH radicals represents a positive factor. However, together with the growth of radical's concentration there appears the threat of involvement in the radical processes not only of pollutants, but also of natural environmental components parts of the biological cycle of substances, as well as of interruption of biogeochemical cycle of manganese ions. The growth of the permanent concentration of the OH radicals may be a result of either the growth of the initiation rate, or of decrease of the OH radicals reaction constant through various "traps". The radical initiation rate grows in polluted medium, especially with nitrates and nitrites (particularly during abundant precipitations) or as a result of radioactive pollution.

Results

The Nistru river represents an important aquatic arteria for the Republic of Moldova at the same time being a source of drinking water and fishery products and playing the role of a valuable recreation zone. Monitoring of the Nistru water quality has always been a priority in the investigations in the Republic of Moldova [3-5]. With the purpose of estimation of the human impact on the Nistru water quality using the classical indicators and the kinetic ones (the content of hydrogen peroxide, redox state, concentration of OH radicals, the inhibition capacity) many expeditions have been carried out.

In the framework of an expedition along the segment between the Byk river and Dnestrovsk liman (1987), nearly all the samples of water did not show the presence of H_2O_2, but only of reductants in concentrations in the range of values $(0.5-120) \cdot 10^{-7}$ mol/l. Higher levels of concentrations were observed in points of waste water disposal: the Bic river firth ($120 \cdot 10^{-7}$ mol/l), the Olanesti tinned food factory ($4 \cdot 10^{-7}$ mol/l), the Belgorod-Dnestrovsk meet factory [3].
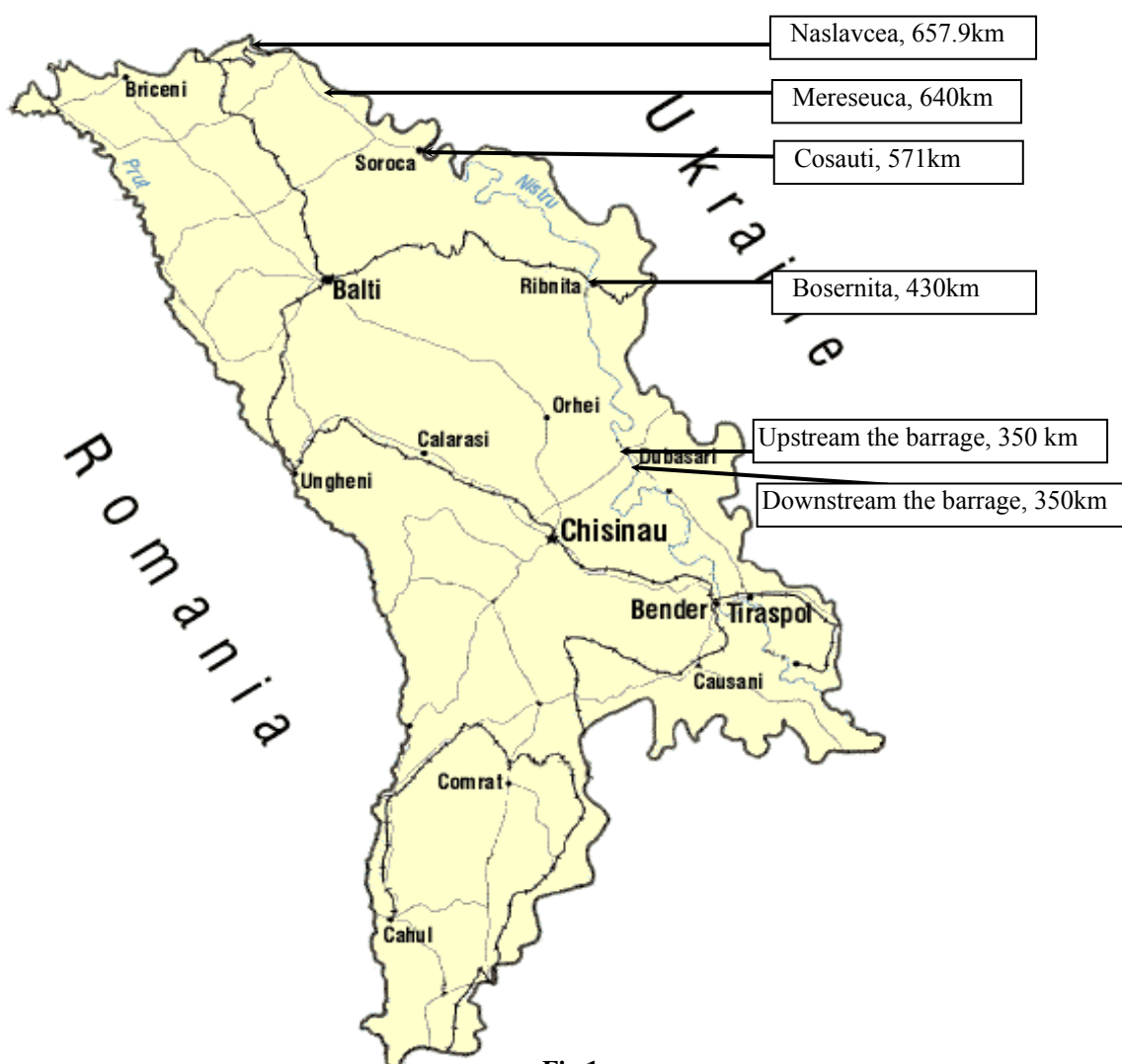
Fig.1
Sections of sample collection

In the framework of another expedition along the Nistru in the segment between the Dubasari dam and the Ciobruciu village (2001) the quality of water was assessed by, alongside with the classical hydrochemical indicators, the rH indicator. For the whole of the river segment including also some of its effluents (Raut, Ichel, Bic, Botna) the rH values pointed at the domination of reductive processes over the oxidative ones, even in the daytime with a maximum

solar radiation. A deterioration of the state of waters along this segment was observed especially after the discharge of some quantity of water from the Dubasari water reservoir [4].

The results of the studies performed in the period of 1987 – 2001 characterize the redox state of the waters and the capacity of inhibition in the segment of the river situated downstream the Dubasari dam. That is why we propose to take as an aim the evaluation of the Nistru water state upstream the dam, especially as northward there is another dam, that of the Novodnestrovsc electric power station and the Naslavcea barrage.

With this purpose in April-October 2003 and September-October 2005 there were carried out expeditions along the segment between the village of Naslavcea and the Dubasari barrage. The water samples were taken in the following sections (fig.1): Naslavcea village (200 m around the Naslavcea barrage), Mereşeuca village, Cosăuţi village, Boşerniţa village, the Dubasari water reservoir upstream the barrage, 100 m downstream the Dubasari barrage.

Short characteristics of the sampling sites:

1. v. Naslavcea – cca 50-100 m downstrean the barrage between Ukraine and Moldova.

2. v. Meresheuca – small amounts of green algae, the water flow is considerable.

3. v. Cosauti – on the Ukrainian side there is situated the Iampoli town, 2 ferries are in function there, there is a presence of green algae, the water flow is considerable circulă.

4. v. Boshernitsa –situated 5-10 km upstream the towns of Rezina and Ribnitsa. From here starts the Dubasari water reservoir, there is a presence of considerable number of algae, the water course is smaller than in the first 3 sampling points.

4. Upstream the Dubasari barrage the sample is are collected directly from the barrage, a big number of algae, the water course very low.

5. Downstream the Dubasari barrage the sample is collected about 50-100 m downstream the barrage, the water course varies, depends on the period of collection.

The water samples were collected from the surface layer (h = 0.5 m). The collected samples were studied for kinetic parameters: the content of hydrofen peroxide and of reductive substances that are oxidized by H_2O_2, the dynamics of H_2O_2 content and the redox state of the natural waters, the content of free OH radicals and the self-purification capacity of the water in the presence of free radicls (the inhibition capacity). The mentioned measurements were done following the methods described in [6]. Besides there were determined the following classical hydrochemical parameters: temperature, pH, Eh, rH, electrical conductivity, the main ions that define the mineralization of water, total hardness, the concentration of dissolved oxygen (DO), biochemical oxygen demand (BOD_5), permanganate value (CCO_{Mn}), chemical oxygen demand (CCO_{Cr}), the concentration of nitrates, nitrites, ammonium nitrogen, phosphates, fluorine, iron, copper, phenols. The measurements were done using a field spectrometer HACH 4010.

Recent data point at the fact that even now there is evidence of variation of the redox state of the Nistru water (tab. 1).

Table 1. The content of hydrogen peroxide and of reductive substances ($[H_2O_2]/[DH_2]$)
in the Nistru water in May-September 2003 and August-December 2005

Locality, km from the firth	$[H_2O_2],M / [DH_2],M$					
	May 2003	July 2003	September 2003	September 2005	October 2005	November 2005
Naslavcea, 657,9 km	$3.5 \cdot 10^7 / 0.0$	$0.0 / 3.1 \cdot 10^7$	$0.0 / 4.1 \cdot 10^7$	$0.0 / 1.1 \cdot 10^7$	$1.2 \cdot 10^6 / 0.0$	$3.2 \cdot 10^7 / 0.0$
Meresheuca, 640 km	$4.0 \cdot 10^7 / 0.0$	$0.0 / 7.2 \cdot 10^7$	$0.0 / 3.6 \cdot 10^7$	$1.2 \cdot 10^6 / 0.0$	$1.1 \cdot 10^6 / 0.0$	$3.5 \cdot 10^7 / 0.0$
Cosautsi, 571 km	$3.1 \cdot 10^7 / 0.0$	$0.0 / 6.2 \cdot 10^7$	$0.0 / 3.8 \cdot 10^7$	$1.8 \cdot 10^6 / 0.0$	$1.9 \cdot 10^6 / 0.0$	$7.0 \cdot 10^7 / 0.0$
Boshernitsa, 430 km	$4.5 \cdot 10^7 / 0.0$	$0.0 / 3.8 \cdot 10^7$	$0.0 / 3.0 \cdot 10^7$	$1.4 \cdot 10^6 / 0.0$	$0.0 / 0.0$	$0.0 / 0.0$
Upstream the Dubasari barrage, 350 km	-	-	$3.2 \cdot 10^7 / 0.0$	$9.5 \cdot 10^6 / 0.0$	$1.5 \cdot 10^6 / 0.0$	$3.3 \cdot 10^7 / 0.0$
Downstrean the Dubasari barrage, 350 km	-	$0.0 / 3.4 \cdot 10^7$	$0.0 / 3.4 \cdot 10^7$	$8.5 \cdot 10^6 / 0.0$	$0.0 / 0.0$	$4.2 \cdot 10^7 / 0.0$

Thus in May 2003 along the mentioned segment the state of waters was characterized as instable oxidative, the samples did not contain reductive substances of peroxide nature, whereas the content of H_2O_2 was lower than the physically required – $(3.5\text{-}4.5) \cdot 10^{-7}$ mol/l. In July and September the same year the collected samples there was no hydrogen peroxide observed, but they showed a content of reductive substances ($3 \cdot 10^{-7}$ - $4 \cdot 10^{-7}$ mol/l) which take oxidation by H_2O_2 more effectively than by molecular oxygen the concentration of which remained within the

admissible limits. The results show that towards the end of July the water is in the reductive state, staying at the same level until September inclusively. Similar analysis, performed in the period of August-November 2005, showed that along almost the whole monitored segment, with some exceptions, the waters were in the oxidative state. In September the sample collected near the village of Naslavcea did not contain H_2O_2, with a concentration of reductants being of the order of $1,1 \cdot 10^{-7}$ mol/l. The reductive state of the waters observed downstream the barrage of Naslavcea may be a result of disequilibrium in the water reservoir upstream the barrage caused by the penetration of big quantities of reductive substances of peroxidase nature. The negative impact of the disequilibrium kept abating along the analized segment because beginning with the collection section v. Meresheuca in the samples there was observed a presence of hydrogen peroxide in the range of values $1,2 \cdot 10^{-6} - 8,5 \cdot 10^{-6}$ mol/l. In October-November the analysis of samples collected near the location of Boshernitsa and downstrean the Dubasari barrage (October) points at the formation of an instable state which is characterized by the absence in the samples of either hydrogen peroxide or reductive substances of peroxidase nature.

The evaluation of waters according to the capacity of inhibition indicator gave the results presented below.

In October 2005 the inhibition capacity values in the Nistru waters pointed at a normal course of free radical self-purification processes ($2,95 \cdot 10^5 - 8,02 \cdot 10^5 \, s^{-1}$), with the exception of the Cosautsi collection site ($1,31 \cdot 10^6 \, s^{-1}$) and downstream the Dubasari barrage ($2,31 \cdot 10^6 \, s^{-1}$). In November there was evidence of the same unfavorable situation in self-purification in the region of the Cosautsi village ($1,24 \cdot 10^6 \, s^{-1}$) and downstream the Dubasari barrage ($1,40 \cdot 10^6 \, s^{-1}$), demonstrating a deviation from the normal course of radical self-purification processes, including the Naslavcea point ($1,30 \cdot 10^6 \, s^{-1}$). Through the obtained inhibition capacity values the waters can be characterized as being in a normal state in the studied segment (order of $10^5 s^{-1}$) with the exception of the v. Naslavcea, v. Cosautsi points and downstream the Dubasari barrage (order of $10^6 s^{-1}$).

Conclusions

The content of waters depends on both the natural climatic conditions and on the regime of operation of various hydrotechnical sites, and respectively on the volume and the composition of the incoming water and that going out downstream the barrage and hydro stations. The Nistru waters that find their way to the territory of Ukraine are polluted with organic substances that disturb the redox components' equilibrium in the section of the village Naslavcea. The deterioration of the Nistru water quality is based on the degree of pollution of the effluents and waste waters discharged from the riverain localities. From the said above results the importance of continuous monitoring of the Nistru water quality, especially through integral kinetic indicators.

The results showed that the Nistru waters remain to be polluted with reductive substances that reduce the content of hydrogen peroxide in the water body and inhibit the autopurification processes with free radicals participation, creating conditions for the formation of the reductive state in water ecosystems – an unfavorable state for aquatic forms.

It is important that the analysis of kinetic parameters and the classical hydrochemical ones did not show any correlation between them. In case of the change of the redox state of the natural waters from oxidative to reductive as well as the identification of unsatisfactory capacity of inhibition, the hydrochemical indicators correspond to those in the normal state of the waters. This is why the *concentration of hydrogen peroxide*, *redox state, the concentration of OH radicals* and *the capacity of inhibition* have to be considered the fundamental indicators in the assessment of the quality of natural waters.

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STUDIES ON THE WATER SOLUBILIZATION PROCESSES OF OENOTANNINS AND THEIR PHISICO-CHEMICAL PROPERTIES

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Abstract: The results of investigation of oenotannins content in the seeds of different grape varieties are presented in the paper. It was demonstrated that the oenotannins content depends on the grape variety as well as on the geographycal zone of grape cultivation. A new procedure for water sollubilization of oenotannins by depolimerization has been elaborated. The mechanism of the oenotannins depolimerization has been reveiled by masss-spectrometric studies. It has been established, that the depolimerization process brings about formation of carboxilic acids and organic peroxides. The presence of the carboxilic and peroxidic groups was detremined on the basis of IR spectral analysis. It was demonstrated that the antioxidant properties of modified tannins are higher then those of initial unmodified ones.

Introduction

Tannins are wide spread in natural sources. They can be found in fruits, fruit shels, in leaves and seeds of different plants. Natural tannins form two large groups: hydrolisable and condensed or catehinic tannins. Tannins from the first group decompose under the action of mineral acids to give a monosacharide, usually D-glucose, and gallic acid or its derivative. Condensed tannins do not contain a sugar component and can be cleaved in simplier fragments only by alkaline melting. The hydrolisable tannins are transformed under dry heating into pyrogalol and the condensed tannins into pyrocatehine [1,2].

The grape seeds represent in the Republic of Moldova the most convenient source of tannins. Depending on grape variety, they contain from 3 to 14% tannins. Tannins obtained from grape seeds are called oenotannins. Most of these are water insoluble. They dissolve only in ethanol, methanol, ethylacetate, acetone and other organic solvents.

Oenotannins represent a complex mixture of catehine and epicatehine oligomers. Their composition varies from monomers to decamers of catehine or epicatehine. The polymeric chain is formed on condensation of functional groups at C4 carbon atom in C-cycle and C8 carbon atom in A-cycle. Polimerization processes of catehine and epicatehine and its mechanism have been studied previously [3].

There have been reported in the literature on the fungicide and antibacterial action of oenotannins [4], but these properties are weak. It is the limited water solubility that makes difficult utilization of these compounds in medicine and agriculture.

We provide in the present paper a new procedure for oenotannins solubilization in water, the possible chemistry of this process, as well as some physico-chemical properties of the modified tannins.

Table 1.

The enotannins content in grape seeds

Grape variety	Geographical zone of cultivation	Tannins content, %
Rcaţeteli	Bulboaca, Anenii Noi	6,4
Sovignion	-,,-	4,0
Feteasca	-,,-	3,1
Cabernet	-,,-	3,7
Rcaţeteli	Căuşeni	5,4
Sovignion	-,,-	5,1
Merlot	-,,-	5,3
Feteasca	-,,-	4,0
Cabernet	-,,-	10,7
Rcaţeteli	Bardar, Ialoveni	6,6
Aligote	-,,-	6,4
Cabernet	-,,-	9,6
Merlot	-,,-	5,9
Fraga neagra	-,,-	14,1

Results and discussions

The enotannins content in different grape varieties is presented in table 1. An examining of the results presented in this table can lead us to the conclusion that the oenotannins content in the grape seeds depends on the grape variety as well as the geographical zone of grape cultivation. The content of oenotannins lies between 3,1 and 14,1%.

Mass-spectrometric data confirm the catehinic nature of compounds from the studied mixture. According to

(1), m/z 271

(2), m/z 180

(3), m/z 162

(4), m/z 166

(5), m/z 198

(6), m/z 182

(7), m/z 60
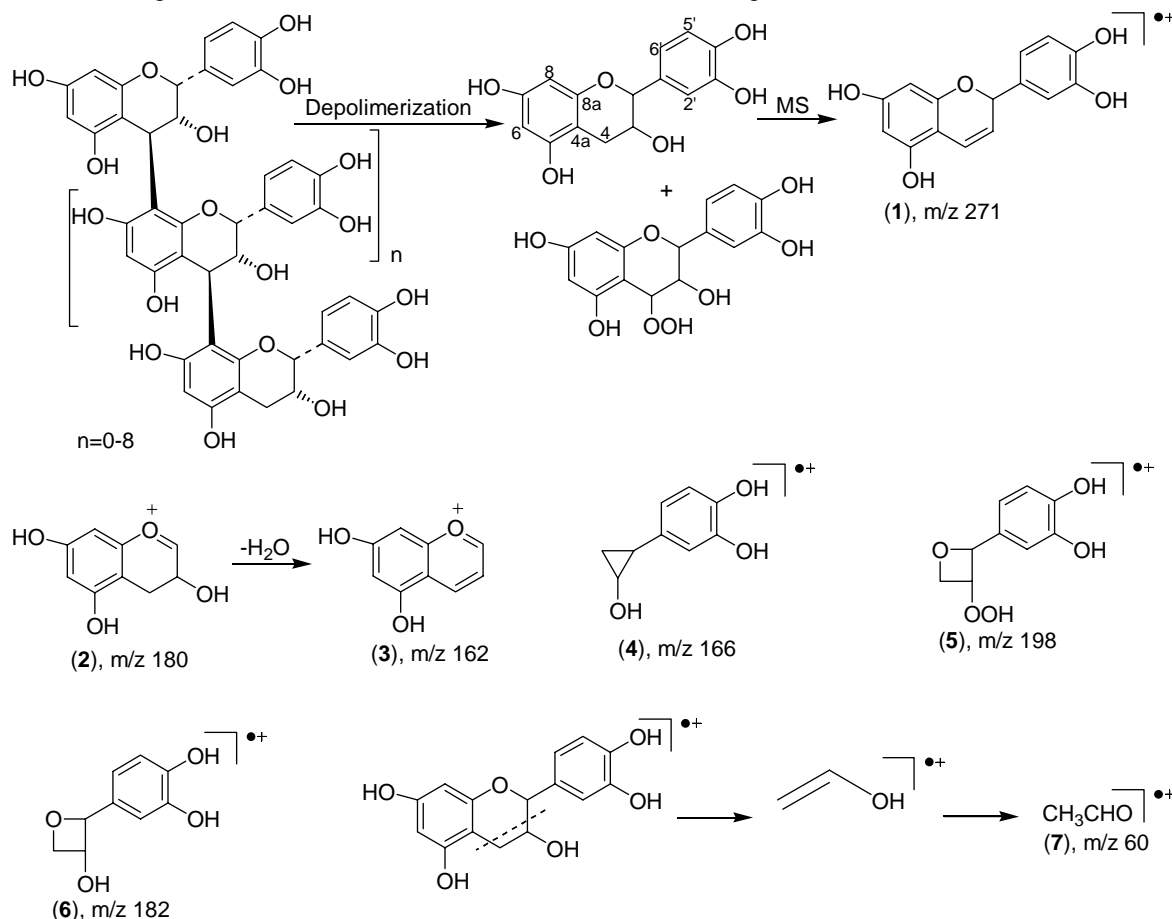
the peaks intensities, the monomeric structures predominate, but there are also dimeric (peaks in the region of m/z 620-670), trimeric (m/z 918) and tetrameric (m/z 1118-1158) structures. There are no peaks with higher m/z value in the spectra. Trimeric and tetrameric compounds are in smaller amounts. The ions with m/z 271 (1), 180 (2), 162 (3), 166 (4), 198 (5), 182 (6) and 60 (7) belong to the catehinic structure.

A series of peaks show the presence in the studied mixture of compounds with hydroperoxidic residues in positions C-3 [ions with m/z 198 (5) and 182 (8)] and C-4 [peaks with m/z 74 or 75, formed by transformation (9)→(10) and m/z 171 (11)] of catehine.

The presence of hydroperoxide groups is confirmed too by the presence of the peak with m/z 17 (OH- group) in one of the spectra.

(8), m/z 182

(11), m/z 171

(9) m/z 321

(10), m/z 74
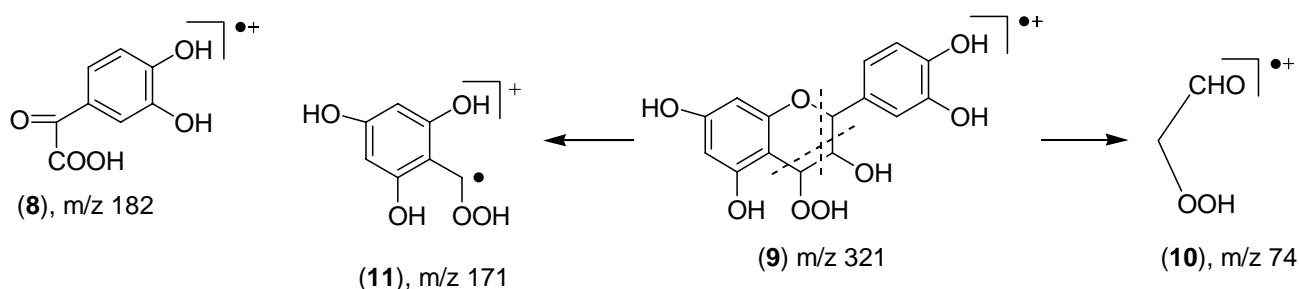
The peaks of ions with m/z 443 (12) and m/z 333 (13) confirm the presence in the mixture of galic acid esters, linked with an esteric group with catehine at C3 position.

Above mentioned data prove that chemical treatment of oenotannin with H_2O_2 brings about depolimerisation of catehine and epi-catehine oligomers to form monomeric derivatives both in the free form and esterified with galic acid at C-3. Most probably, breaking the C4-C8 bond between the catehinic residues leads to introduction of the hydroperoxidic residue at C4 position. There also a possibility of introduction of the hydroperoxidic group at C3 position by nucleophilic substitution.

The possibility of deep oxidative cleavage of cyclies B and C of catehinic skeleton is not excluded too. There is obviously possible that a certain MS peak corresponds to different ions with the same m/z but with different structures and this is characteristic for MS cleavage.

(**12**), m/z 443

(**13**), m/z 333

(**14**), m/z 170

(**15**), m/z 198
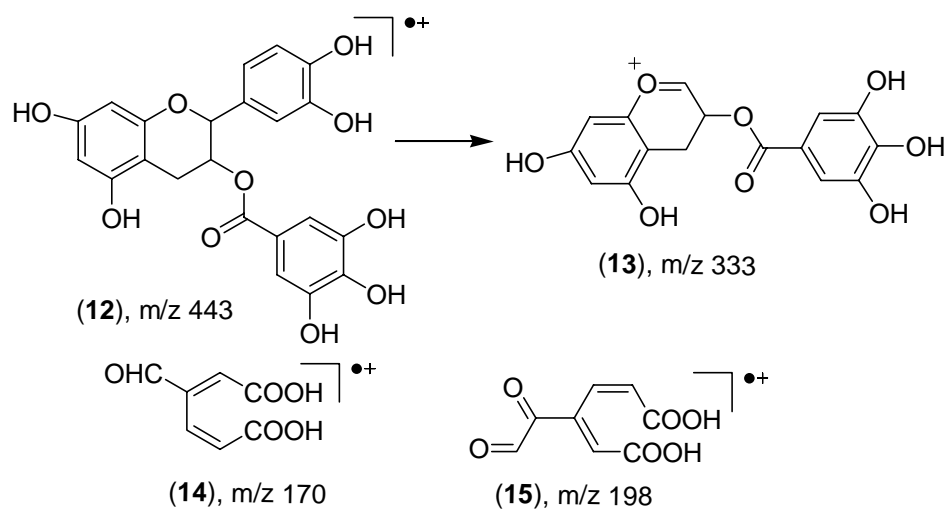
The IR spectra of the original and modified oenotannins are presented in fugures 1 and 2.

Figure 1.

IR spectrum of unmodified oenotannins
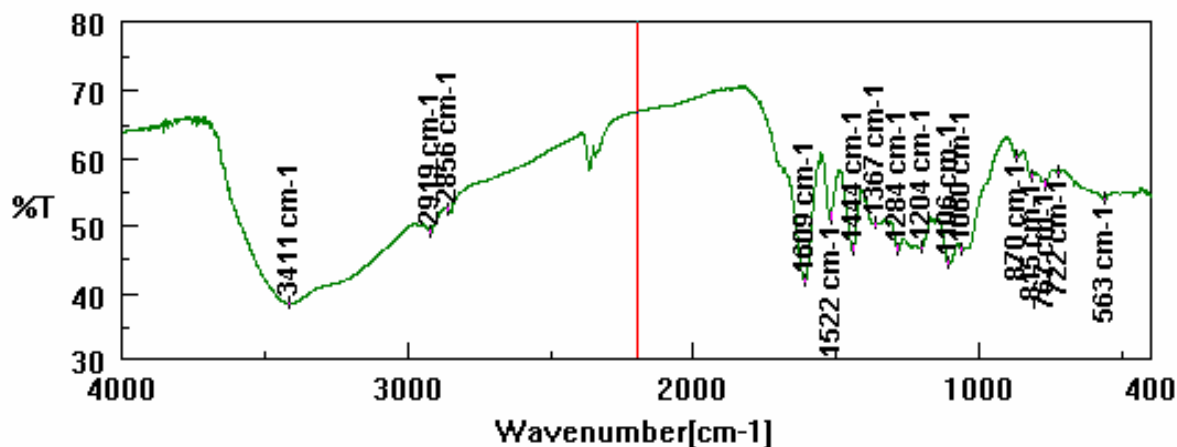
Figure 2.

IR spectrum of modified oenotannins
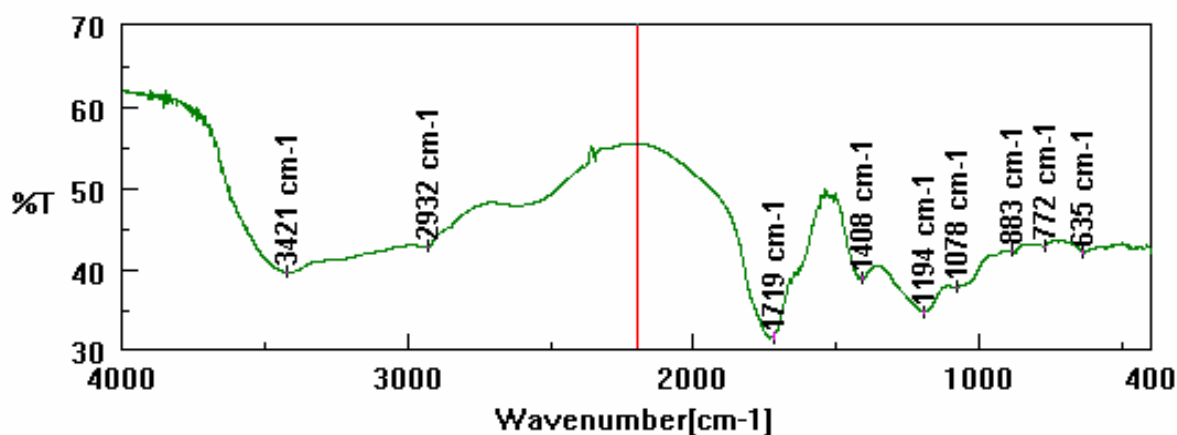
Spectral analysis reveals that in both cases the samples contain strong hydrogen bonds (broad bands at 3411 and 3421 cm⁻¹ respectively). An essential difference between is seen in the region of the digital imprints of original and modified oenotannins spectra. The original unmodified sample shows bands characteristic to aromatic rings with different substitution pattern (bands at 762 cm⁻¹, 815 cm⁻¹, 1,2,3 substitution; 870 cm⁻¹ 1,2,4 substitution; 1060 cm⁻¹ 1,3 substitution; 1444 cm⁻¹ and 1609 cm⁻¹ benzene ring). The most intensive peak in the modified product is detected at 1719 cm⁻¹ that is a characteristic signal of carboxylic acids (dimers). This is the essential difference between the two products, since this band is absent in the original unmodified oenotannin. The spectrum of the modified product shows also a strong band at 1194 cm⁻¹ that is also absent in the original oenotannin. This band can be attributed to the hydroperoxidic group. Its presence was also confirmed by chemical means, making use of the oxido-reductive test with potassium iodide in acidic conditions.

The IR spectrum of modified tannins shows bands characteristic to aromatic compounds (772, 883, 1078 cm^{-1}) but their intensity is much smaller then those of the unmodified product and this can be accounted for a substantial degree of aromatic rings cleavage in the modified product.

The antioxidative activity was determined on both original and modified tannins using the luminol/hydrogen peroxide system (Fig. 3). The antioxidant activity of original oenotannins represents 38,1% and of the modified product − 51,3%.

The obtained results denotes that the modified oenotannins have a more prominent antioxidative activity then the original ones.

Figure 3.

Time evolution of chemiluminiscence signals of oenotannins
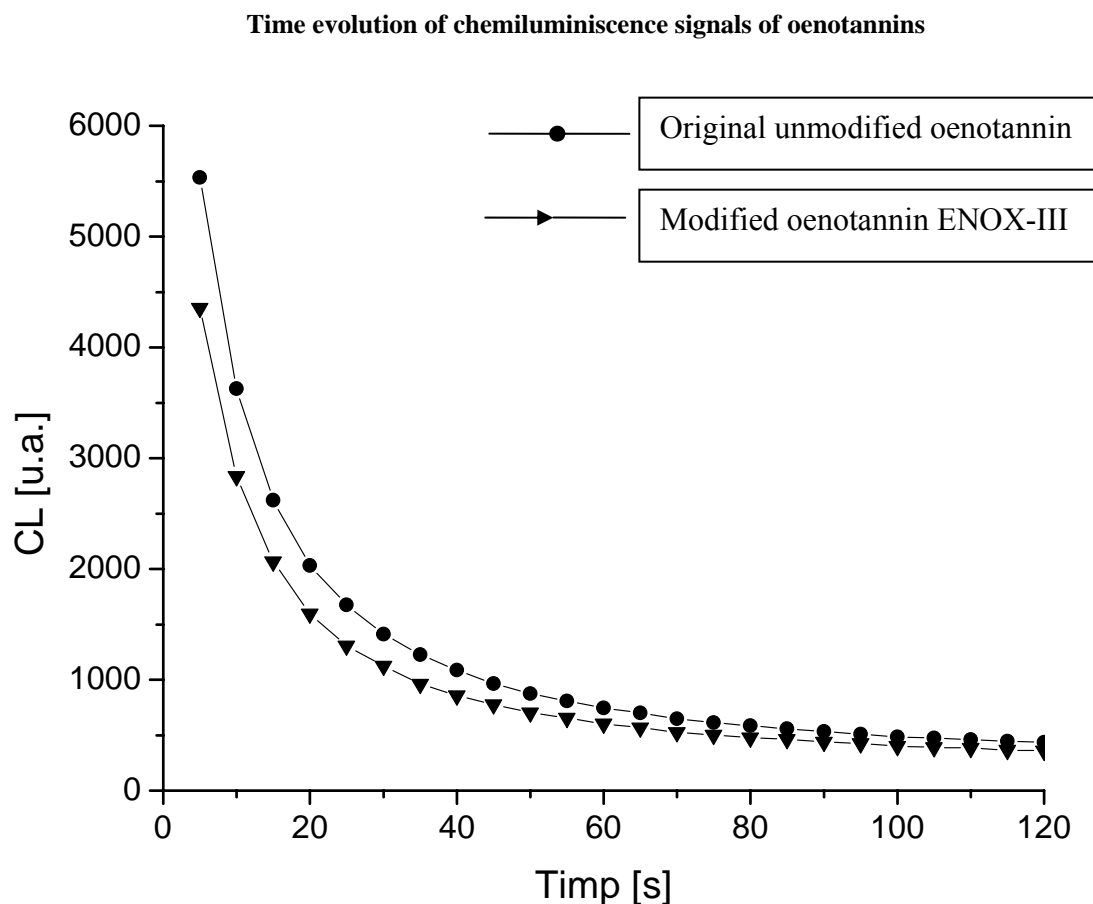
Additional investigations on biological activity of the oxidized oenotannins were performed in the "N. Testemiteanu" Moldova State Medical and Pharmacy University, Institute of Microbiology and Biotechnology and Institute of Genetics and Plant Phisiology, Academy of Sciences of Moldova. These investigations showed that oxidized oenotannins are more water soluble and possess relevant antimicrobial activity.

Experimental part

Oenotannins have been extracted from the grape seeds originated from different grape varieties grown in different geographycal zones of the Republic of Moldova. Extraction has been performed in a glass column with 30 mm i.d. and 500 mm length. The seeds have been crushed in an electrical mill to a fraction not larger then 1 mm in diameter. As extraction solvent ethanol has been used. The solvent was passed in a descending mode through the column with a 10 ml-min rate until oenotannins extraction was complete. The obtained extract was concentrated on a rotary evaporator under vacuum, until the density of the residue reached 1,12 g/cm^3, then dried in an oven at 60°C to a constant mass [5].

Water solubilization of oenotannins was realized by their oxidation with hydrogen peroxide at 70-90°C. The obtained product was dried in an oven at 45-60°C to a constant mass [6]. The mass spectrometric investigation was performed on a Bruker Autoflex II mass spectrometer using laser ionization. The IR spectra have been recorded on a Jasco FT-IR 620 spectrometer. Antioxidative activity of both modified and original oenotannins was measured in the luminol-peroxide system on a Turner Design TD 20/20 chemiluminometer.

Conclusions

1. The oenotannins content in the investigated grape seeds varies from 3,1 to 14,1%. The oenotannins content is higher in black grape varieties.

2. The hydrogen peroxide promote depolymerization of catehine and epicatehine oligomers in oenotannins to provide monomeric derivatives of free and esterified carboxylic acids, as well as peroxidic compounds.
3. The presence of carboxylic and peroxidic functional groups was demonstrated on the basis of IR spectra analysis.
4. The enhanced antioxidant properties of modified tannins was demonstrated by the chemiluminiscence method.

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IODINATION OF VEGETABLE OIL AS A METHOD FOR CORRECTING IODINE DEFICIENCY

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Abstract. The aim of this work is the study made for obtaining iodized oil that would satisfy the requirements in iodine for human body. The sunflower oil is a product with the most important value, thus the production of oil fortified with iodine would be a cheap and accessible option. These studies indicate that lipids present an important vehicle for the fortification with iodine. Eradication of the iodine deficiency may be realized not only by injection of the iodinated oil, but also by its use as an ingredient for the formulation of different food compositions. This method, complementary with the iodinated salt, would allow the increase of the efficiency of the prophylactic undertaken measures, because is based on the use of vegetal material – sunflower oil; it is cost-efficient and does not require substantial investments.

Keywords: iodine deficiency, food fortification, iodinated sunflower oil.

1. INTRODUCTION

THE PROBLEM OF THE IODINE DEFICIENCY IN REPUBLIC OF MOLDOVA AND POSSIBILITY OF ERADICATION

The iodine is an essential microelement necessary for the synthesis of the thyroid hormones [1]. Its importance, particularly for the development period, consists in the fact that the thyroid hormones have a capital role in the processes of growth, differentiation and maturation of the numerous cell tissues, especially for the bony and central nervous system tissue.

A malnutrition contribution in iodine would have as consequences the adulteration of the function of thyroid gland but also a direct impact concerning the physical and mental development of a person. The above pyramid (Figure 1) illustrates the fact that the visible effects of IDD (cretinism) account for only as much as 10% of the ramifications. At least 90% of IDD consequences remain hidden [2].
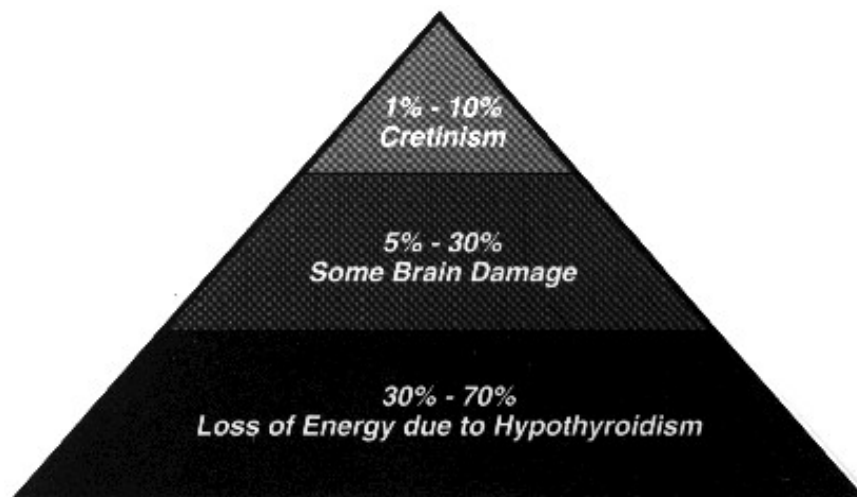
Figure 1. Iodine Deficiency Disorders (IDD) problem pyramid [2]

The normal contribution constitutes 150μg/day for children over 10 years and for adults and for children under 10 years constitutes 40-120μg/day. The supplementation of the ration with 25-50μg/day in the period of pregnancy and lactation is necessary with a view to prevent the endemic cretinism [6,7].

In the last 10-15 years the incidence of iodine deficiency disorders (endemic goiter) increased by 8-10 times [3]. The number of children and teen-agers at which the endemic hyperplasia of the thyroid gland is manifested is 33-47%, and 2,8 -5,7% of them have endemic goiter that is manifested by the appearance of visible knots, while 1,5-4,2% suffers from hyperthyroidism [3,4]. The main cause of this phenomenon consists in the fact that the environment of Republic Moldova is characterized by a reduced values of the iodine content:4,5-5,3mg/kg soil, 40mg/l water and 0,03-0,22mg/kg of vegetation, on a dry content of substances. The content of the urinary iodine for children (7,84μg iodine/100dL) is the lowest from the European countries [5]. In order to eliminate the iodine deficiency disorders, the government of Republic of Moldova adopted a National Program by the year 2004 (decision nr. 46) [8].

However, the situation did not evolve too much in this direction. A recent estimation of the situation in the Republic of Moldova, based on official statistics, the reports of some experts-nutritionists and studies realized by international organs (UNICEF, WHO) pointed out the presence of palpable goiter for ≈ 36,7% children with the age between 8 and 10 years, and for the adult population the endemic goiter prevails at ≈ 40% of women in the period of begetting children [5]. There is an alarming growth of cases of disorders of thyroid gland cancer which is strongly connected with the accident from Chernobyl, according to the estimation of some experts. Only 32% of families consume adequate iodinated salt, because it has a low storage period, after what it loses its curable quality [3, 4, 5]. It is obvious that the nutritional problems affect not only the health of certain groups of population, but also bring enormous harms to the economy of the country and to its socio-human potential, because:

- Iodine deficiency in the prenatal period and for children at early age decreases its Intelligence Quotient (IQ) with 5-13 points [9,10].
- Causes the mental retardation, which affects 9-9,6% of children of 5-12 years old [11,12].
- The combined deficiency in iodine, iron and vitamin A decreases the economical performances of the country with more than 5% [13].

The specific strategies used in the developed countries in order to eliminate the nutritional deficiencies, can be classified in three main groups [14,15,16]:

- The improvement of food practice;
- The supplementation of population groups of risk with tablets that contain necessary micronutrients;
- The fortification of large consumption food with micronutrients.

The application of the strategy of nourishment diversification in Republic Moldova is confronting a lot of problems: the precarious economical situation and the small wages of the majority of families, the high cost of the products that have a big content of hemic iron, iodine, calcium (beef, sea fish, milk products); traditional diets, which includes mainly products of vegetal origin with a high content of antinutrients (phytates, tannins, oxalates) which contribute to unavailability of the micronutrients.

The supplementation of population groups of risk with tablets that contain necessary micronutrients puts the problem of costs and logic. And also, this way represents a passive approach, which can't ensure some steps at national level, but can have only a strict temporary character and limited in time.

There are more opinions that the food fortification with micronutrients is an efficient method for the improvement of the statute in micronutrients of the population on a long term [7].

Once developed, food fortification is an inexpensive and durable method. An effective program of food fortification requires efforts of cooperation between Government, food industry and consumers.

The only way for food fortification, used nowadays in Republic of Moldova is iodination of salt. Iodinated salt constitutes traditionally the most applied method, because of the accessibility and because it is largely consumed by the local population. According to the investigation [5], the contribution of iodine from salt is yet insufficient. This depends on more facts: the consumption of salt varies from 2g/day to 10-12g/day, being lowest for children and elderly persons. The technology of iodination of salt (iodide, iodate); the concentration of iodine (10-15mg/kgsalt), as well the integral and partial utilization of iodinated salt, bring about considerable fluctuations in the contribution of iodine proceeded in this way. A deficiency of this method constitutes also the instability of iodine in salt.

Thus, the elaboration and implementation of some fortification technologies of widely consumed products, which will ensure a sufficient intake and bioavailability of micronutrients is extremely actual. A special role in this field play the technologies based on the use of natural local resources, because these are cost-efficient, there is no need to modify the structure of the traditional products and does not require considerable capital investments.

THE PROPHYLAXIS AND TREATMENT OF THE IODINE DEFICIENCY

Individually, the long term administration of iodine or thyroid hormones seams to be very efficient for the reduction the incidence of the iodine deficiency related diseases. For severe cases chirurgical treatment may be applied. But these interventions are expensive and may not be applied for all individuals. The most recommended way is the prophylaxis through the optimization of the iodine intake. This is recommended in the case when the urinary iodine excretion is less then 10 μg/day, or when the incidence of the endemic goiter is higher than 10%. Iodine may be administered either as iodinated salt or as iodinated oil.

In the salt the iodine is usually added as potassium or sodium iodide or iodate. Iodate is less stable, and is recommended for the regions with high humidity. In practice, this way of prophylaxis raises many important issues. First, it is about the variability of the iodine content, which may be between 4.3 – 14.1 mg/kg for the same product depending on the method and shelf life.

Another major problem is the iodination of the salt meant for home consumption, while the salt used in food industry it is not iodinated. Finally, the contribution of the salt is about 6-10 g/day for women and 10-12 g/day for men. Considering these values, it was set that a contribution of 15 mg iodine/kg salt is not sufficient to ensure an intake of 150 μg iodine/day. In fact, the iodinated salt intake is estimated to be 2.2 g/day for adults, part of it being evaporated during cooking process. Thus, the real intake of iodinated salt is estimated to be 1.6 g/day. However, this is not accepted by any legislation of any country.

Finally, a series of other problems, such as quality, cost, preservation regularity diminishes considerably the food iodine intake. From this point of view, in the regions with moderate and severe iodine deficiency the iodine prophylaxis is made by administration of the iodinated oil, usually injectable. The injection of the iodinated oil, which contains 475 mg iodine/ml provides a high amount of iodine which is slowly absorbed, depending on the human body's requirements. For 0-6 old children 0.2-0.4 ml can be administered, and for 6-45 years old persons 1-2ml (475-950 mg iodine), which would cover the human body requirements for about 3-5 years. These strategies are indicated especially for women during fertile period to prevent neonatal hypothyroid.

However, these drastic strategies may not be applied without a legal insurance which is essential. Over intake of the iodinated salt may lead to the administration of an excess of sodium ions, which is extremely inauspicious. Increased iodine intake, accomplished through the injection of the iodinated oil increases the incidence of the thyreotoxicoses, especially for individuals over 45 years old and for individuals with knotted endemic goiter.

The severances of the consequences of the iodine deficiency, as well as above mentioned factors makes this pathology very specific. The prophylaxis of the iodine deficiency, despite of the relatively simple strategies suggested, does not achieve proposed goals.

Thus, the decrease of the consequences related to an insufficient iodine intake may be achieved not solely through one method applied for all population, but through the application of a fortification strategy of different foodstuffs consumed by different population categories. These should be complementary with the iodinated salt, thus total intake should not overtake the daily recommended amount, so that this will not lead to any hyperthyroid status, which is manifested by anxiety and weight loss. In fact, the tolerance limit of the human body to the iodine excess is significant – 1g/ day (actually this value is the base of the administration of the injectable iodinated oil), but an overdose that should be taken into account is over 250 μg/day.

Iodine, being a liposoluble element, its administration in products with a lipid origins represents a remarkable interest. First, this would allow the easy incorporation of the iodine in the food products. Secondly, the daily intake of lipids being limited, would allow an easy regulation of the iodine consumption, this being complementary with that from the iodinated salt and other products.

The problem is the establishment of some iodination principles of the lipids and of the incorporation of these ones into the food products. Therefore, the aim of the present work is to evaluate ways of incorporation of the iodine in its molecular state in the vegetal lipids – sunflower oil, and the study of the physico-chemical properties of the iodinated oil during storage and the technological transformation which might take place.

Sunflower oil being a widely consumed product for the population from Republic of Moldova, the fortification with iodine would be a considerable supplement (40-50 μg/day), which associated with the iodine intake from the iodinated salt, would eradicate the iodine deficiency.

2.   RESULTS AND DISCUSSIONS

The physico-chemical properties of the lipids, which have a enormous importance for the food technology are determined by the chemical composition and their structure. The sunflower oil is part of the vegetal oils group and has a high content of mono- and poliunsaturated fatty acids [20] and is characterized by a high unsaturation degree, which means by a high number of sites capable to fix molecular iodine. Therefore, saturated fatty acids constitute just 11.3-11.6%, iodine indices of the oil varying from 119 to 135. Generally, unsaturated fatty acids from the vegetal oils are situated in the position 2 of the glycerin molecule. Linoleic acid, which is most abundant in this oil is mainly situated in this position. Oleic acid is situated in position 1, and saturated fatty acids in position 3 (fig. 2):

Position 1

Position 2
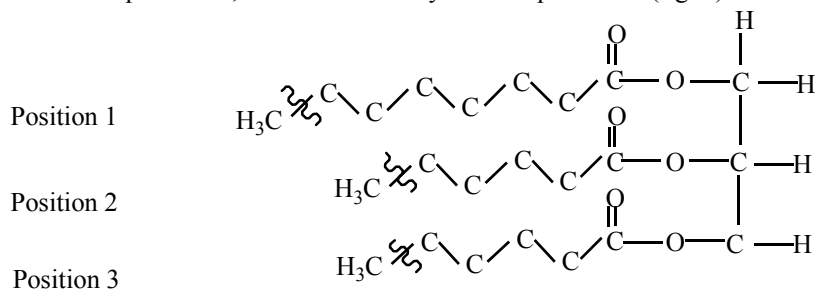
Position 3

Figure 2. Fatty acids positioning in the trigliceride molecule

This positioning, as well as the „fourchette" shape specific for triglicerides facilitates the molecular iodine attack and its clamping in the position 2, mostly occupied by the linoleic acid (fig. 3).
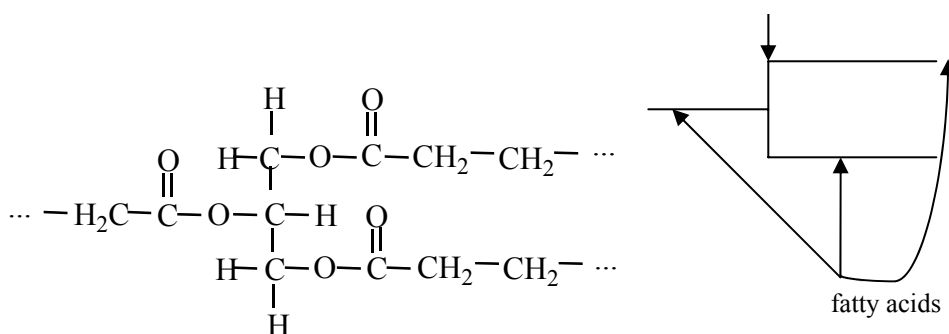
Figure 3. Shape « fourchette » of a trigliceride molecule

Lipids are susceptible to different degradation reactions, which may lead to the premature spoilage of the food products. These are:

- Hydrolytic oxidation;
- Oxidative oxidation.

During hydrolytic rancidity, triglicerides degraded and an liberation of fatty acids take place, thus the acidity of the lipid increases. During oxidative rancidity the spoilage take place as a result of the attack on the double bonds by the O_2 from the air. The reaction is accelerated by light and temperature, the presence of the metallic and enzymatic catalyses.

These processes may be evaluated using different quality indices for lipids, which characterize the status of the lipid.

The study of the composition and quality indices of the iodinated sunflower oil

In order the evaluate the influence of the administration of iodine in the sunflower oil, main quality indices of the oil were studied, which were compared with the standards for the product.

It was found out, that the iodine indices does not varies greatly; even for the sample with the highest iodine amount (1000 μg/ml) its value does not overtake the highest allowable amount. This proves that the administrated iodine does not bind to the double bond through covalent bonds.

Refraction indices varies insignificantly, which disputes the presence of the free iodine in the samples with that contain 1-100 μg/ml iodine. Only for the samples with 1000 μg/ml iodine the presence of the free iodine could be certified.

Physico-chemical indices of the iodinated oil are indicated in table 1.

Table 1. Physical-chemical properties of the iodinated oil

Physico-chemical indices	Reference sample	Iodinated oil, $\mu g / ml$				Maximum allowed
		1	10	100	1000	
Iodine indice	134 ± 1	131 ± 1	130 ± 2	129 ± 1	127 ± 2	119-135
Refraction indice (20°C)	1,474 ± 0,001	1,475 ± 0,002	1,476 ± 0,001	1,476 ± 0,001	1,479 ± 0,002	1,472 – 1,476
Saponification indice, mg KOH/g oil	193 ± 3	191 ± 2	195 ± 2	196 ± 1	198 ± 2	181 - 198
Free fatty acids content, % oleic acid	0,245 ± 0,005	0,245 ± 0,004	0,275 ± 0,003	0,285 ± 0,003	0,360 ± 0,005	Maximum 0,4
Peroxid indice, méq/kg,	10,0 ± 0,2	8,9 ± 0,1	9,8 ± 0,2	10,9 ± 0,1	23,0 ± 0,3	Maximum 12
Humidity and the volatile substance %, maximum	0,100 ± 0,005	0,055 ± 0,005	0,068 ± 0,005	0,100 ± 0,005	0,098 ± 0,005	0,100

It is well known that halogens are capable to saturate double bonds present in the unsaturated lipids. For active halogens, such us fluoride and chloride, the addition to the double bonds takes place according to the mechanism that involves the formation of an ion type halonium as a result of the nucleophile bimolecular substitution [20]:
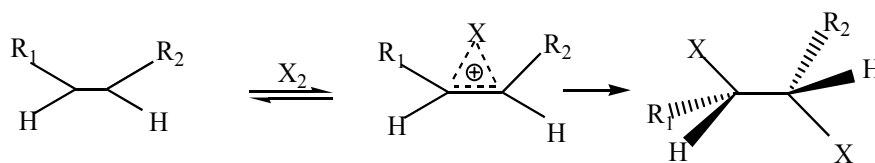
The iodine addition through this mechanism does not take place, because the energy necessary to activate the reaction is very high. However, the electrophile attack of the iodine is frequently used for the mixed halogens. Thus, the measurement of the iodine indice is realized through the reactive Wijs – ICl. The addition of the iodine chloride takes place rapidly and constitutes an effective way to establish the unsaturation degree of the triglicerides.

As well, the value of the iodine indice considerably depends on the position of the double bond comparing with the carboyile group –COO-. Thus, experimental values of the iodine indice, obtained depending on the positioning of the double bond in the oleic acid molecule vary considerably depending on the distance between the double bond and carboxyle group (table 2):

Table 2. Experimental values of the iodine indices obtained for different oleic acid isomers*

Double bond positioning	Theoretical values	Experimental values
-2=3-	89,7	9,04
-3=4-	89,7	16,27
-4=5-	89,7	26,96
-6=7-	89,7	89,7

* [20]

It was established that, while the number of the carbon atoms between the carboxyl group –COO- and the double bond increases, the probability that the addition of the halogen reaction will take place decraeses [20]. Since fatty acids, present in the sunflower oil have double bonds situated in the position -9=10- and -11=12- (linoleic acid), the probability that the iodine addition in these conditions will take place is very low.

It is obvious that, during iodination of the sunflower oil the iodine addition cannot take place. The activity of the double bonds is weaker more they are away from the carboxyl group. The growth of the carbon atoms in the acid chain decreases the activity of the double bonds and reduces the saturation speed.

The amount of the saturated fatty acids, monounsaturated and poliunsatured in the reference sample and after the iodination of the oil was determined by gaz chromatography with a flame ionization detector. These analyses were anticipated by the esterification of the samples (methanolize).

Therefore, it was certainly established that the amount of main fatty acids in the sunflower oil (oleic and linoleic acid) does not vary significantly. As well the amount of the respective saturated acids does not vary greatly (table 3). Only the concentration of the monounsaturated acids vary, which are present in inessential amounts: palmitoleic acid (C 16:1) and gatoleic acid (C 20:1).

Table 3. The amount (%)of the fatty acids in the iodinated sunflower oil

No.	Sample	Iodine concentr. $\mu g / ml$	Concentration , %				
			$C_{16:0}$ (Palmitic)	$C_{18:0}$ (Stearic)	$C_{18:1}$ (Oleic)	$C_{18:2}$ (Linoleic)	$C_{20:0}$ (Arahidic)
1	Reference	-	$6,46 \pm 0,03$	$3,37 \pm 0,03$	$22,37 \pm 0,05$	$66,40 \pm 0,18$	$0,46 \pm 0,05$
2	1:1000	1	$6,42 \pm 0,02$	$3,38 \pm 0,05$	$22,37 \pm 0,05$	$66,70 \pm 0,20$	$0,56 \pm 0,03$
3	1:100	10	$6,42 \pm 0,02$	$3,37 \pm 0,04$	$22,29 \pm 0,05$	$66,57 \pm 0,15$	$0,75 \pm 0,05$
4	1:10	100	$6,42 \pm 0,02$	$3,37 \pm 0,05$	$22,23 \pm 0,04$	$66,61 \pm 0,18$	$0,63 \pm 0,06$
5	1:1	1000	$6,41 \pm 0,03$	$3,33 \pm 0,05$	$22,29 \pm 0,03$	$66,77 \pm 0,22$	$0,67 \pm 0,07$

According to the data obtained during the experiments, following was established:

- Incorporation of the molecular iodine in the sunflower oil does not lead to the bursting of the double bond and the addition of the iodine according to the nucleophile bimolecular substitution mechanism that is characteristic to other halogens. This was established certainly by the estimation of the composition of fatty acids in the triglicerides from the oil for the iodine concentration ranging from 1 to 1000μg/ml. As well verification of the unsaturation degree of the product (iodine indices) confirms the invariability of the number of double bonds from the trigliceride molecule.

- In the infrared region of the electromagnetic field the lipid absorbs radiant energy at 2 specific waveleghts in the middle infrared – λ_{max} = 3.45 μm and 5.73μm; and 2 specific wavelengths in the near infrared – 1724 cm^{-1} and 1230 cm^{-1}. The vibration of the characteristic groups of the lipids for these wavelengths causes an important variation of the optical density, which is correlative directly with the lipid amount having these groups.

In order to evaluate the influence of the administration of the molecular iodine in the sunflower oil the infrared field of the iodinated sunflower has been analyzed (IR) in comparison with the non iodinated sunflower oil.

For the non iodinated oil as well as for the iodinated one (1 to 1000μg/ml) the spectrum in both specific wavelengths for lipids was analyzed: 1724 cm^{-1} for the carbonyl group C=O of the unsaturated acids and 1230cm^{-1} (resonance strip) with two harmonious strips at 1110 cm^{-1} and 1163 cm^{-1} specific for the C-O group. It was established, that the intensity of the absorption strips of the light for these specific wavelengths does not vary as a matter of fact regardless to the iodine concentration and correspond to the literature data for the sunflower oil.

- The presence of the molecular free iodine was certified just for the high concentrations – at 1000μg/ml, and for concentrations 1-100μg/ml free iodine is absent in the solution. This is also confirmed by the evolution of the peroxide indices, which remains constant for iodine concentrations 1-100μg/ml.

Iodine occupies a special place and is different from the other halogens due to its capacity to form complex compounds while delocalizing the electronic density, such as:

$$I^- + I_2 \rightarrow [I_3]^-$$
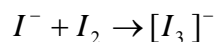
In the case of the iodinated oil the fixation of the molecular iodine takes place to the double bond with the formation of clathrate type compounds, without breaking the double bond from the unsaturated acids molecules:
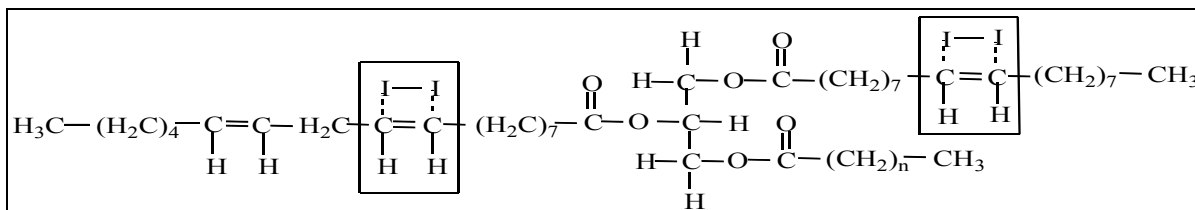
This fact was established by expansion of absorption maximums corresponding to fatty acids double bonds (figure 4).
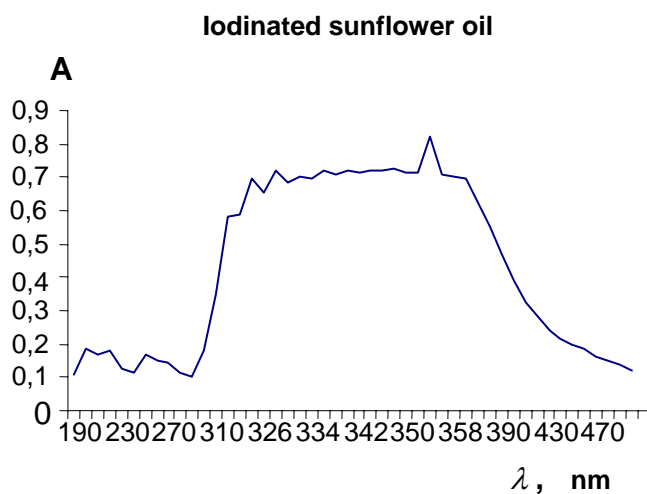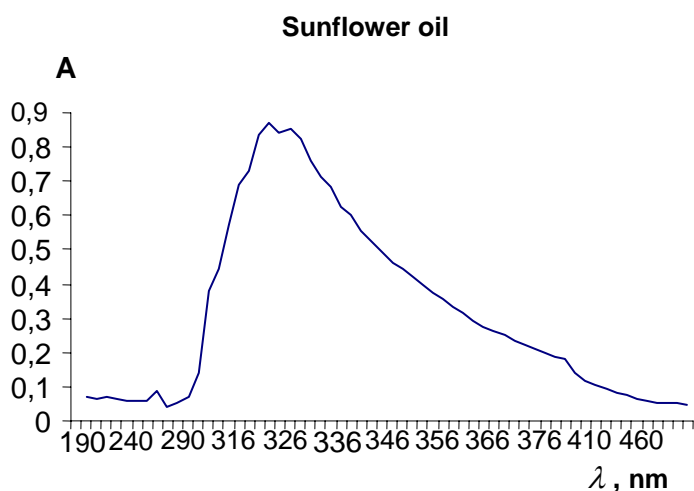
Figure 4. The sunflower and iodinated sunflower oil's absorption spectrum

In the compounds which form the delocalization of the double bond takes place with the displacement of the electronic density to the iodine molecule, this being more electronegative, which ensures the stability of the formed cycle.

3. CONCLUSIONS

It was established that the iodination of the sunflower oil may be considered as a admissible method, which allows the incorporation of a considerable amount of iodine (1-100μg/ml) without modifying the physical-chemical properties of the product. Physical-chemical indices of the iodinated oil are within the admissible standards for the above-mentioned product.

In the case of the iodination of the oil the addition of the iodine does not take place, but the fixation of molecular iodine to the double bond is performed with the formation of the clathrate type compounds, without the breakage of the double bond from the unsaturated fatty acids molecules. In the formed compounds, the delocalization of the double bond is performed with the displacement of the electronic density to the iodine molecule, this being more electronegative, which ensures the stability of the formed cycle. This allows the efficient incorporation of the molecular iodine in a large range of concentrations (1-100μg/ml) without a sensible modification of the physical-chemical properties of the product.

These studies indicate that lipids present an important vehicle for the fortification with iodine. Eradication of the iodine deficiency may be realized not only by injection of the iodinated oil, but also by its use as an ingredient for the formulation of different food compositions. This method, complementary with the iodinated salt, would allow the increase of the efficiency of the prophylactic undertaken measures, because is based on the use of vegetal material – sunflower oil; it is cost-efficient and does not require substantial investments.

4. EXPERIMENTAL

In this study, double rafinated and deodorized oil was used (purchased from local stores), STAS – 18848-73. To obtain the iodinated oil, in one liter of oil 1g of chemically pure, crystalline iodine (I_2) was administrated, STAS – 4159- 79 [17]. The iodinated oil had a deep brown color, due to the presence of the free iodine. The oil with the total iodine content 1000μg/ml, was diluted (1:100), obtaining a product with a the iodine content of 10μg/ml. Diluting (1:10) the oil sample with 1μg/ml was obtained. After the establishment of the equilibrium, iodinated oils were used as samples for the present study.

All the measurements were made according to the standard methods and standards STAS – 1129-93 [7,8]. Iodinated oil was analyzed dynamically for three months. The quality indices for oils were determined (physico-chemical indices) [18,19]:
- Refraction indices (n_d^{40}) – allows the determination of the unsaturation degree of the oil;
- Iodine indices(II) – allows the determination of the global unsaturation of the lipids;
- Saponification indices (IS) – indicates the average molecular mass of the fatty acids;
- Titrable acidity (TA) – and free fatty acids (FFA) – indicates the hydrolytic oxidation degree;
- Peroxide indices (PI) – indicates the degree of the oxidation.

The analysis of the fatty acids in the samples with iodinated oil was performed by gas chromatography with flame ionization detector, using gas chromatograph (helium) HPCHEM 1 FID1 A, equipped with a database and a auto sampler. Fatty acids were separated depending on the length of the chain and depending on the nonsaturation degree. Parameters: start temperature 55 ºC; temperature at the loop of the column and the transfer line 110ºC; ventilation 10sec; injection 1.0min, 1μl. The temperature of the injector – 180ºC and the components of the eluent were detected using a flame ionization detector at 250ºC. The concentrations were determined from the area of the pick using the standard curve of the authentic oil and the database.

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HOMO- AND HETERONUCLEAR COMPLEXES OF COPPER (II) WITH SCHIFF BASE OBTAINED ON THE BASE OF 2-HYDROXY-3-CARBOXYNAPHTALDEHYDE

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Abstract: The complexes of general formula $Cu(H_2L)$ **(II)**; $[CuLn(L)(NO_3)(H_2O)_n]$ (where $H_4L=N,N^I$-bis[2-hydroxy(3-carboxynaphtalidene)]ethylenediamine; Ln: Nd, n=6 **(III)**; Eu, n=4 **(IV)**; Gd, n=6 **(V)** have been synthesized and investigated by different methods (IR spectroscopy, TG analysis and magnetochemistry). The coordination set of complex generators are $Cu(N_2O_2)$ and $Ln(O_{8-9})$. The effective magnetic moment values, $\mu_{eff,}$ at 300 K are: 1.78 **(II)**, 3.22 **(III)**, 6.44 **(V)** B.M. The temperature dependence (300-2 K) of magnetic susceptibility of $[CuNd(L)(NO_3)(H_2O)_6]$ indicates the antiferromagnetic interaction between metal ions.

Keywords: copper (2+); d-f complexes; Schiff base; magnetic properties

Introduction

In the last time homo- and heteropolynuclear coordination compounds attract an increasing interest due to their unusual physicochemical properties caused by the character of a metal-metal exchange magnetic interaction [1-8]. One of the methods of synthesis of polynuclear compounds is the usage of polydentate ligands, which, using the donor atoms, have the ability to carry out stage coordination of two or several metal ions in dependence on their nature (d, f) and mutual arrangement in the molecules of these polydentate ligands [9-17]. The Schiff bases can serve an attractive example of such multifunctional ligands.

The purpose of the present investigation is the synthesis of new polidentate Schiff base to study an opportunity of stage synthesis of heteronuclear (d, f) coordination compounds and characterization of their physicochemical properties. In the present paper the results of synthesis and study of new azomethyne ligand (H_4L) **(I)** obtained by the condensation of 2-hydroxy-3-carboxynapthaldehyde [18] with ethylene diamine, and the complex compounds on its base are presented.
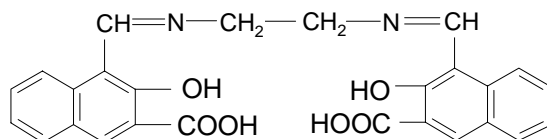
Also it is necessary to mention, that interest to this class of compounds is explained by its biological activity (antimicrobial, antitumor etc.) too [5, 19-21].

Results and discussion

Reaction of condensation of 2-hydroxy-3-carboxynapthaldehyde with ethylene diamine in the ratio 2:1 yielded a new polydentate Schiff base, N,N'-bis(2-hydroxy-3-carboxynaphtalidene)ethylenediamine (H_4L) . The interaction of a synthesized ligand with the Cu^{2+} ions resulted the compound CuH_2L **(II)** of green color, which composition has been confirmed by the data of the elemental analysis.

The mode of ligand coordination in **II** was determined from the IR spectroscopy data. In the IR spectrum of H_4L the basic characteristic frequencies are presented at 3340, 1707, 1533 cm^{-1} and correspond to the stretching vibrations of hydroxy $\nu(OH)$, carboxy $\nu(COOH)$, and azomethine (C=N) groups [22]. They characterize the formation of the Schiff base. The comparison of the IR-spectra of the ligand and complex exhibits some essential differences: the stretching vibration band of azomethine fragment is shifted from 1533 to 1507 cm^{-1}; the relative intensity of hydroxy band is decreased. At the same time the position of $\nu(CO)(COOH)$ band (1707 cm^{-1}) practically doesn't change. These facts indicate the coordination of copper ion to oxygen of phenyl group and nitrogen of azomethine fragment with the formation of the more probable coordination set CuO_2N_2 [17, 22]. The availability of non-coordinated carboxylic group in the synthesized CuH_2L compound affords a possibility of its use as a "ligand - complex" in the reaction with salts of homo- and heterometals.

By the reaction of CuH_2L compound with the lanthanide (Nd, Eu, Sm) nitrate at the presence of LiOH results the heteronuclear coordination compounds of the composition $[CuLn(L)(NO_3)(H_2O)n]$, where Ln: Nd, n=6 **(III)**; Eu, n=4, **(IV)**; Sm, n= 6 **(V)**.

In the IR spectra of copper – lanthanide complexes **(III-V)** the absorption band in the region 1707 cm^{-1} is absent and the new bands in the range of 3626-3380, 1620, 1400, and 1308-1312 cm^{-1} are presented. The absence of 1707 cm^{-1} absorption band indicates that the coordination of lanthanide ions to the deprotonated of carboxylic groups is realized. The absorption bands in the field of 1620 and 1400 cm^{-1} are characteristic for asymmetric and symmetric vibrations of carboxylic group, $\nu_{as,s}(COO)$. The occurrence of a broad absorption band in the range 3626-3380 cm^{-1}, typical for $\nu_{as,s}(OH)$, confirms the presence of water molecules in the composition of heterometallic complexes, which complete the coordination number of lanthanide ions up to 8-9.

Table 1.

Data of the thermal analysis of the complexes with composition
[CuLn(L)(NO₃)(H₂O)n], where Ln: Nd, n=6 (III), Eu, n=4 (IV);Gd, n= 6 (V).

Compound	Number of effects	Effect	Temperature of decomposition, °C			Loss of mass, %; (corresponds)
			T_{init}	T_{max}	T_{fin}	
III	1	endo	20	80	180	13(13) (-6H₂O)
	2	exo	180		340	23(36)
	3	exo	340		640	38(74)
IV	1	endo	20	70	140	8(8) (-4H₂O)
	2	exo	140	190	320	25(33)
	3	exo	320	-	570	44(77)
V	1	endo	25	70	170	11(11) (5-6H₂O)
	2	exo	170	290	330	26(33)
	3	exo	330	-	590	45(78)

The data of the element analysis for compounds **III-V** specify the availability of no more than one nitrate-group in the complexes necessary for the neutralization of a charge (+3) of a lanthanide ion. According to the literary data [10, 22], bidentate nitrate-group is usually characterized by four absorption bands: 1450-1500, 1300, 1030, and 815 cm⁻¹. Due to the overlap of different bands in the IR spectra of copper–lanthanide compounds in this region, only one new band was found in the range 1308-1312 cm⁻¹, which was assigned to the coordination of nitrate anion, entering in the inner coordination sphere of the complex. This effect probably explains the low solubility of these compounds. The observed identity of the IR spectra of heterocomplexes **III-V** specifies their isostructural character.

The thermal stability of the heteronuclear compounds **III-V** was determined by TGA method. The derivatograms of heterocomplexes have the similar shape that testifies the analogy in a composition and structure of the studied compounds (**III-V**). The thermal decomposition of investigated compounds proceeds in several stages (tab. 1). In the temperature region of 20 - 180°C for all the compounds the endothermic effect is observed, which corresponds to the loss of crystallization as well as coordinated water molecules. In the 180 – 640 °C temperature region two exothermic effects are observed, which correspond to the gradual combustion of the ligand and complete decomposition of the complexes. The decomposition residues in the form of mixed oxides constitute 25-29 % of the full mass. The data of the thermogravimetric analysis are in according to the elemental analysis data.

Magnetic susceptibility studies. Room and variable-temperature of magnetic succeptibility (χ_m) study have been performed on powdered samples of synthesized (**II, III,V**) complexes. The effective magnetic moment $\mu_{эф}$ of **II** at room temperature is found to be equal to 1.78 M.B. i.e. the monomeric structure of complex is realized. The values of effective magnetic moments for heterocomplexes **III, V** (T=300 K) are equal to 3.31 and 6.64 M.B., respectively, and specify the availability of lanthanide ions in the structure of these complexes [2]. Temperature dependence of the magnetic susceptibility of {Cu(L)Nd(H₂O)₆(NO₃)}, is shown in fig. 1. At 300 K the $\chi_M T$ is equal 1.273 cm³·K·mol⁻¹. With decrease of temperature the $\chi_M T$ value is diminished up to 0.527 cm³·K·mol⁻¹ at 1.7 K, that indicates the predominant antiferromagnetic interaction between the copper(II) and neodymium(III) ions.

In conclusion, the synthesized ligand forms the homonuclear copper(2+) compounds, which can be used as ligand for synthesis of new heteronuclear complexes with f- or d-elements. In the synthesized heterocomplexes the copper (II) and lanthanide (III) ions are bound at the inside (N₂O₂) and the outside (O₄) coordination site of synthesized ligand respectively.

Figure 1.Dependence $\chi_M T$ (T) for compound [Cu(L)Nd(H₂O)₆](NO₃)

Experimental

General. The carbon and hydrogen content was determined by standard micro-methods in the microanalytical group of the Institute of Chemistry of the Academy of Sciences of Moldova. The copper(II) was determined by trilonometric method using the murexid as indicator [23]. The atomic absorption spectroscopy method at the Automation and Metrology Centre of the Academy of Science of Moldova was used to determine the Ln(III) and

copper(II) content simultaneously. IR spectra of polycrystalline samples were recorded (4000- 400 cm^{-1}) as oil mulls on a Specord M-75 spectrophotometer. TG studies were performed on a Paulik-Paulik-Erdey derivatograph in air, with platinum crucible, Al_2O_3 as calibration standard and at a speed of heating equal to 5 ^oC/min. DTG - 1/5; DTA - 1/10; TG - 100/100. T_{max} =1000 ^oC. Magnetic measurements of **II**, **III**, **V** at 300 K were performed using Guy method. Variable temperature susceptibility of **III** was measured with an Oxford Instruments Vibrating Sample Magnetometer (VSM) working between 0 and 12 T and in the 1.5–350.0 K temperature range.The diamagnetic Pascal's constants were used to correct the magnetic values [2]. To determine the value of μ_{eff} the relation $(\mu_{eff})_M = \sqrt{8\chi_M T}$ (B.M.) was used.

  Synthesis. All manipulations were performed under aerobic conditions with the initial substances commercially obtained and used without any further purification.

  The synthesis of Schiff base (H_4L) was carried out by the addition of ethylene diamine to methanol solution of 2-hydroxy-3-carboxynapthaldehyde in a molar ratio of 1:2. 2-hydroxy-3-carboxynaphtaldehyde was synthesized according to [18]. A precipitate of the ligand, separated on the glass filter, was washed out consequently by alcohol and ether and dried above an anhydrous calcium chloride up to a constant mass. M. p. of a new synthesized ligand, N,N'-bis(2-hydroxy-3-carboxynaphtalidene)ethylenediamine is ~ 310 ^oC. Found, %: C, 67.52; H, 4.22; N, 5.85. Calc. for $C_{26}H_{20}N_2O_6$, %: C, 68.43; H, 4.38; N, 6.14. The basic IR frequencies, (nujol oil, cm^{-1}): 3340mb, 1707s, 1653m, 1627s, 1613s, 1587m, 1547m, 1533m, 1413m, 1200ssh, 1027m, 853m, 800m, 741m, 640m, 480m.

*Cu(H$_2$L)(**II**)*. $CuCl_2 \cdot 2H_2O$ (0.17g, 1mmol) was dissolved in 10 ml of ethanol and added to a suspension of H_4L ligand (0.45g, 1mmol) in 20 ml of ethanol. The solution was heated on the water bath (~70 ^oC) with permanent stirring on the magnetic stirrer till the green homogeneous precipitate was formed. A final product was filtered off on the glass filter, washed by ethanol and ether and dried above anhydrous $CaCl_2$ up to a constant mass. The yield was 0.32 g (61%). Found, % C, 60.37; H, 4.20; N, 5.78; Cu, 12.10. Calc. for $C_{26}H_{18}N_2O_6Cu$, %: C, 60.30; H, 3.47; N, 5.41; Cu, 12.27. IR spectrum (nujol oil, cm^{-1}): 1707s, 1640m, 1627s, 1616s, 1587m, 1547m, 1507m, 1413s, 1200m, 1160m, 1093w, 1027w, 853w, 800m, 733m, 653w, 602w, 533vw, 467w.

*Cu(L)Nd(NO$_3$)(H$_2$O)$_6$ (**III**)*. To a suspension of copper complex, CuH_2L (0.52 g, 1mmol) in 30 ml of ethanol the alcohol solution of $LiOH \cdot H_2O$ (2,5 mmol) was slowly added. The obtained intermediate complex was separated on the filter, washed out and was further added to (0.44 g, 1 mmol) of neodymium nitrate in 10 ml of EtOH. The reaction product of light green color was filtered off, washed out by several portions of alcohol and ether. Yield: 0.43g (56% relative to). Found, %: C, 38.18; H, 3.05; N, 4.54; Cu, 8.00; Nd, 18.00. Calc. for $(C_{26}H_{28}N_3O_{15}CuNd)$, %: C, 37.62; H, 3.37; N, 5.06; Cu, 7.65; Nd, 17.38. IR-spectrum (nujol oil, cm^{-1}): 3620mb, 3413mb, 1640m, 1627s, 1600s, 1547m, 1507m, 1400s, 1308m, 1200msh, 1160w, 1100w, 1030w, 880w, 800m, 747m, 653w, 613w, 587w, 533w, 453w.

*Cu(L)Eu(NO$_3$)(H$_2$O)$_4$ (**IV**)* was synthesized following the similar procedure by the interaction of CuH_2L (0.52g, 1mmol) with $Eu(NO_3)_3 \cdot 6H_2O$ (1 mmol) in the presence of LiOH. Yield: 0.46 g (58%). Found, %: C, 38.45; H, 3.57; N, 3.68; Cu,~9.17; Eu, ~ 14-18. Calc. for $(C_{26}H_{24}N_3O_{13}CuEu)$, %: C, 38.94; H, 2.99; N, 5.24; Cu, 7.92; Eu, 18.95. IR-spectrum (nujol oil, cm^{-1},): 3626mb, 3386mb, 1650m, 1627s, 1600m, 1547 **s**, 1507m, 1400s, 1312m, 1200m, 1160w, 1107w, 1027w, 880w, 800m, 747m, 653w, 619w, 587w, 534w, 453w.

*Cu(L)Gd(NO$_3$)(H$_2$O)$_6$ (**V**)* was synthesized following the similar procedure applying $Gd(NO_3)_3$ $6H_2O$ as a lanthanide salt (1 mmol). Yield: 0.44g (~52%). Found, %: C, 36.65; H, 3.22; N, 5.33; Cu, 8.17; Gd, 14-18. Calc. for $(C_{26}H_{28}N_3O_{15}$ CuGd), %: C, 37.04; H, 3.32; N, 4.98; Cu, 7.53; Gd, 18.65. IR-spectrum (nujol oil, cm^{-1}): 3600mb, 3410mb, 1650m, 1627s, 1600s, 1547m, 1507m, 1400m, 1308m, 1200m, 1160w, 1105w, 1027w, 880w, 800m, 747m, 654w, 613w, 587w, 533w, 453w.

  The synthesized heteronuclear complexes of the composition {Cu(L)Ln(NO$_3$)(H$_2$O)$_n$} (**III-V**) are of light green color, stable in air, soluble in dimethylformamide and in dimethylsulfoxide, insoluble in water and in majority of the widespread used organic solvents. Because of weak solubility it was not possible to receive monocrystals for an confirmation of final structure of complexes.

Conclusions

The interaction of a new ligand (N,N$'$-bis (2-hydroxy-3-carboxynaphtalidene(ethilenediamine)) (H$_4$L) with the Cu^{2+} ions results the compound CuH$_2$L. The copper(2+) ions coordinate to an interior chromophore (N$_2$O$_2$) of synthesized ligand, the carboxylic groups remaining free . The presence of free carboxylic groups in the CuH$_2$L compound affords a possibility of its use in reaction with salts of homo- and heterometals. The heterocomplexes with composition [CuLn(L)(NO$_3$)(H$_2$O)$_n$] were synthesized. Coordination of lanthanide ion (Nd^{3+} , Eu^{3+}, Gd^{3+}) is supposed to an carboxylate oxygen atoms of ligand. In heterocomplexes the antiferomagnetic exchange for pair Cu-Nd is present.

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THE SYNTHESIS AND STUDY OF TETRANUCLEAR CLUSTER $[Fe_4O_2(CCl_3COO)_8(THF)_2(DMF)(H_2O)]\cdot THF$

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Abstract: The novel bis(μ_3-oxo) tetranuclear trichloracetate cluster, $[Fe_4O_2(CCl_3COO)_8(THF)_2(DMF)(H_2O)]\cdot THF$ **(1)**, has been synthesised and subsequently characterised by X-ray structure analysis, magnetic measurements and infra red (IR). The structure of cluster is "butterfly" type. The Fe···Fe separation has the value of 2.883(1) - 3.441(7) Å. The coordination number of iron (III) is 6. Magnetic studies reveal the presence of an antiferromagnetic exchange in the parallelogram skeletons of the tetranuclear species. Using the spin Hamiltonian $H = -2J_{wb}(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_4 + \hat{S}_4\hat{S}_1) - 2J_{bb}\hat{S}_2\hat{S}_{4v} + g\mu_\beta(\hat{S}_{1z} + \hat{S}_{2z} + \hat{S}_{3z} + \hat{S}_{4z})B$, the fitting parameters $J_{bb} = -14.3$ cm^{-1}, $J_{wb} = -32.1$ cm^{-1}, g = 2.07, $\rho_{param. impur.} = 4.2$ %, $\Theta_{Curie-Weiss const.} = -0.5$ K and R = 6.8·10^{-5} were obtained.

Keywords: $\{Fe_4O_2\}$ core; Homotetranuclear carboxylate; Crystal structure; Antiferromagnetic exchange.

1. Introduction

For a long time the permanent interest of the investigators to oxo- carboxylate complexes of transition metals was due to their usefulness in resolving the problems of theory of magnetism of coordination compounds [1-5] and practical problems connected with the specific catalysis [6] and biological active substances [7].

In the last few years this class of substances has become the focus of much attention by the development of the new scientific direction concerning the best way to obtain single molecule magnet (SMM) [8-10]. At the same time the oxo iron carboxylate complexes are good model compounds for the active centers of a number of metalloproteins such as: hemerythrin (Hr) [11, 12], ribonucleotide reductase (RR) [11, 12], purple acid phosphatases (PAPs) [11-14]; ferreascidin (Fasc) [15, 16], and ferritin (Fn) [17,18]. Hr, RR, PAPs contain dinuclear iron sites, Fasc – supposedly - three nuclear sites, and Fn – a large polynuclear iron oxide core. After the first publication of the synthesis and study the tetranuclear iron(III) trifluoroacetate [19-21] the large number of complexes of this series was synthesized and investigated by different methods [22-26].

In attempt to continue the previous studying and obtaining the model of the active centers of polyiron enzymes we report herein the synthesis of tetranuclear iron(III) complex with trichloracetic acid.

2. Results and discussion

Up to date various polynuclear complexes with chloro containing acetic acids have been synthesized and structurally characterized [27–31]. Most of these complexes were synthesized through step concerning treatment of basic acetates of d - elements with corresponding acids in aqueous solutions. It is worth mentioning that complex **1** was prepared by the procedure concerning the extract of the barium ion in heterotrinuclear complex by sulphate anion in "water-THF-toluene" mixture.

2.1. Structure

The crystal **1** has a molecular structure build from neutral tetranuclear $[Fe_4O_2(CCl_3COO)_8(THF)_2(DMF)(H_2O)]$ complexes and THF solvate molecules in 1:1 ratio. The X-ray study revealed that tetranuclear entity could be described as a typical "butterfly" type structure, as depicted in figure 1. The four metal atoms are linked through two μ_3-oxo centers and six bidentate-bridged carboxylate ligands coordinated in *syn-syn* fashion. Other two carboxylate anions behave as monodentate ligands being coordinated to Fe(3) and Fe(4) atoms. The Fe···Fe separation within the $Fe_4(\mu_3-O)_2$ core exhibit the following values: Fe(1)-Fe(4) 3.441(7); Fe(1)-Fe(3) 3.372(6); Fe(1)-Fe(2) 2.883(5); Fe(2)-Fe(4) 3.373(7); Fe(2)-Fe(3) 3.437(6) Å (Tabl.2). In contrast to Fe(3) and Fe(4), Fe(1) and Fe(2) atoms coordinate as a monodentate ligand one DMF molecule (Fe(1)-O(19) = 2.03(2) Å) and one water molecule (Fe(2)-O(1w) = 2.02(2) Å), respectively. The coordinated water molecule O(1w) forms two H-bonds, one with the oxygen atoms of solvate THF and another with the monodentate carboxylate ligands with the distances O(1w)···O(18) 2.81(4), O(1w)H···O(18) 1.97, O(1w)···O(22) 2.74(3), O(1w)H···O(18) 1.99 (Å) and angles O(1w)HO(18) 155.1, O(1w)HO(22) 140.2 (º). The $Fe_4(\mu_3-O)_2$ core is essentially non-planar. The dihedral angle between two $Fe_3(\mu_3-O)$ fragments is equal to 33.0(1)°. The deviation of μ_3-oxigen atoms from the respective plane is different: 0.35(1) Å for O(1) and 0.24(2) Å for O(2). Each iron ions has an O_6 slightly distorted octahedron coordination, but their environment is different. In particular, the

coordination site of the Fe(3) and Fe(4), which comprises only one μ_3-O bridging atom, are similar and differ from that for Fe(1) and Fe(2) atoms, which include only two μ_3-O bridging atoms (Fig. 1).
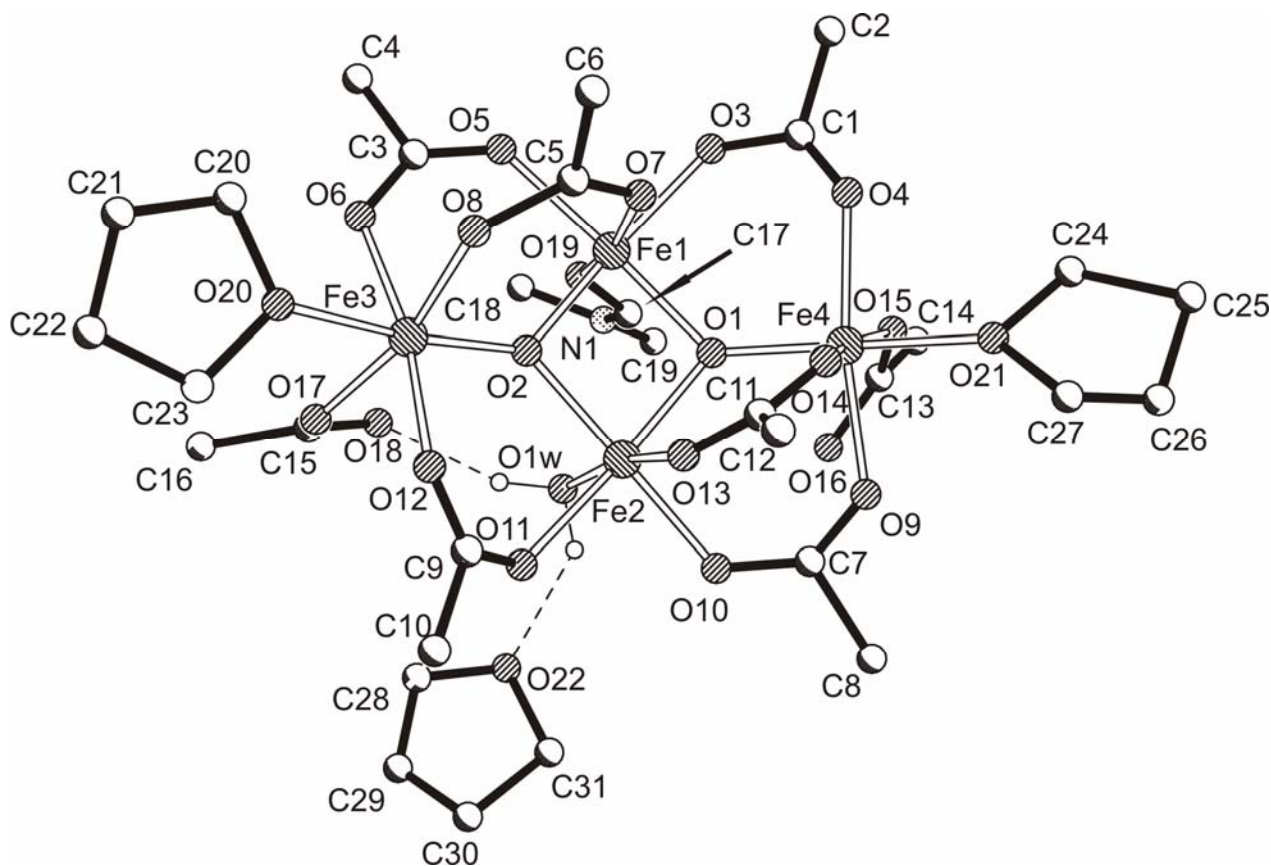
Figure 1. View of the unsymmetrical unit in crystal structure of [Fe$_4$O$_2$(CCl$_3$COO)$_8$(THF)$_2$(DMF)(H$_2$O)]·THF (1). The chloride atoms and the H atoms bonded to carbon are omitted for clarity.

At the same time, the coordination site of the last pair is also different as the coordination of Fe(1) atoms is completed by DMF molecule (Fe(1)–O(19) = 2.03(2) Å), while the coordination of Fe(2) – by one water molecule (Fe(2)–O(1w) = 2.02(2) Å).

Table 1. Selected bond lengths (Å) and angles (deg) for [Fe$_4$O$_2$(CCl$_3$COO)$_8$(THF)$_2$(DMF)(H$_2$O)]·THF.

O(1)-Fe(1)	1.942(18)	O(1)-Fe(2)	1.978(17)
O(2)-Fe(3)	1.85(2)	O(2)-Fe(1)	1.882(18)
O(2)-Fe(2)	1.946(19)	O(1W)-Fe(2)	2.01(2)
O(3)-Fe(1)	1.954(18)	O(4)-Fe(4)	2.05(2)
O(5)-Fe(1)	2.02(2)	O(1)-Fe(4)	1.85(2)
O(7)-Fe(1)	2.05(2)	O(6)-Fe(3)	2.074(16)
O(9)-Fe(4)	2.04(2)	O(8)-Fe(3)	2.03(2)
O(11)-Fe(2)	2.09(2)	O(10)-Fe(2)	2.03(2)
O(13)-Fe(2)	2.084(19)	O(12)-Fe(3)	2.073(15)
O(15)-Fe(4)	1.946(18)	O(14)-Fe(4)	2.051(19)
O(19)-Fe(1)	2.03(2)	O(17)-Fe(3)	2.00(2)
O(21)-Fe(4)	2.09(3)	O(20)-Fe(3)	2.091(18)
C(1)-O(4)	1.295(19)	C(1)-O(3)	1.298(19)
C(1)-C(2)	1.54(4)	C(3)-O(5)	1.14(4)
C(3)-O(6)	1.42(3)	C(3)-C(4)	1.53(5)
C(5)-O(7)	1.40(2)	C(5)-O(8)	1.41(2)
C(5)-C(6)	1.34(4)	C(7)-O(9)	1.25(2)
C(7)-O(10)	1.25(2)	C(7)-C(8)	1.64(4)
C(9)-O(11)	1.257(16)	C(9)-O(12)	1.257(16)
C(11)-O(14)	1.209(18)	C(9)-C(10)	1.53(3)

C(11)-C(12)	1.56(4)	C(11)-O(13)	1.209(18)
C(13)-O(16)	1.28(5)	C(13)-O(15)	1.20(4)
C(15)-O(17)	1.27(4)	C(13)-C(14)	1.53(4)
C(15)-C(16)	1.64(6)	C(15)-O(18)	1.32(4)
C(17)-N(1)	1.366(19)	C(17)-O(19)	1.25(4)
C(18)-N(1)	1.38(6)	C(19)-N(1)	1.42(4)
C(20)-O(20)	1.45(2)	C(20)-C(21)	1.48(2)
C(21)-C(22)	1.48(2)	C(22)-C(23)	1.48(2)
C(23)-O(20)	1.45(2)	C(24)-O(21)	1.45(2)
C(24)-C(25)	1.48(2)	C(25)-C(26)	1.48(2)
C(26)-C(27)	1.48(2)	C(27)-O(21)	1.45(2)
C(28)-O(22)	1.45(2)	C(28)-C(29)	1.47(2)
C(29)-C(30)	1.48(2)	C(30)-C(31)	1.48(2)
C(31)-O(22)	1.45(2)		

O(2)-Fe(1)-O(1)	84.7(8)	O(2)-Fe(1)-O(19)	96.4(9)
O(1)-Fe(1)-O(19)	94.3(8)	O(2)-Fe(1)-O(3)	174.1(9)
O(1)-Fe(1)-O(3)	95.0(9)	O(19)-Fe(1)-O(3)	89.5(8)
O(2)-Fe(1)-O(5)	95.2(9)	O(1)-Fe(1)-O(5)	177.9(8)
O(19)-Fe(1)-O(5)	83.7(9)	O(3)-Fe(1)-O(5)	85.2(9)
O(2)-Fe(1)-O(7)	90.3(8)	O(1)-Fe(1)-O(7)	94.5(7)
O(19)-Fe(1)-O(7)	169.4(7)	O(3)-Fe(1)-O(7)	83.8(8)
O(5)-Fe(1)-O(7)	87.6(8)	O(2)-Fe(1)-Fe(2)	41.9(6)
O(1)-Fe(1)-Fe(2)	43.1(5)	O(19)-Fe(1)-Fe(2)	93.7(5)
O(3)-Fe(1)-Fe(2)	138.0(7)	O(5)-Fe(1)-Fe(2)	136.7(7)
O(7)-Fe(1)-Fe(2)	96.8(5)	O(2)-Fe(2)-O(1)	82.2(8)
O(2)-Fe(2)-O(1W)	88.2(9)	O(1)-Fe(2)-O(1W)	101.1(7)
O(2)-Fe(2)-O(10)	170.4(8)	O(1)-Fe(2)-O(10)	94.8(8)
O(1W)-Fe(2)-O(10)	83.3(9)	O(2)-Fe(2)-O(13)	98.5(8)
O(1)-Fe(2)-O(13)	88.1(7)	O(1W)-Fe(2)-O(13)	169.3(7)
O(10)-Fe(2)-O(13)	90.5(8)	O(2)-Fe(2)-O(11)	93.1(8)
O(1)-Fe(2)-O(11)	169.3(8)	O(1W)-Fe(2)-O(11)	88.3(8)
O(10)-Fe(2)-O(11)	91.3(8)	O(13)-Fe(2)-O(11)	83.1(8)
O(2)-Fe(2)-Fe(1)	40.3(6)	O(1)-Fe(2)-Fe(1)	42.1(5)
O(1W)-Fe(2)-Fe(1)	92.7(5)	O(13)-Fe(2)-Fe(1)	97.9(4)
O(10)-Fe(2)-Fe(1)	135.3(6)	O(11)-Fe(2)-Fe(1))	133.2(6
O(2)-Fe(3)-O(17)	101.4(9)	O(2)-Fe(3)-O(8)	90.1(9)
O(17)-Fe(3)-O(8)	167.0(9)	O(2)-Fe(3)-O(6)	94.4(7)
O(17)-Fe(3)-O(6)	85.4(7)	O(8)-Fe(3)-O(6)	87.7(7)
O(2)-Fe(3)-O(12)	97.0(7)	O(17)-Fe(3)-O(12)	89.4(7)
O(8)-Fe(3)-O(12)	95.3(7)	O(6)-Fe(3)-O(12)	168.2(8)
O(2)-Fe(3)-O(20)	171.3(9)	O(17)-Fe(3)-O(20)	87.3(8)
O(8)-Fe(3)-O(20)	81.2(8)	O(6)-Fe(3)-O(20)	85.2(7)
O(12)-Fe(3)-O(20)	84.0(7)	O(1)-Fe(4)-O(15)	99.4(9)
O(1)-Fe(4)-O(9)	95.3(9)	O(15)-Fe(4)-O(9)	91.7(9)
O(1)-Fe(4)-O(4)	94.5(9)	O(15)-Fe(4)-O(4)	88.3(9)
O(9)-Fe(4)-O(4)	170.1(11)	O(1)-Fe(4)-O(14)	93.5(9)
O(15)-Fe(4)-O(14)	167.1(12)	O(9)-Fe(4)-O(14)	86.8(8)
O(4)-Fe(4)-O(14)	91.1(8)	O(1)-Fe(4)-O(21)	175.6(8)
O(15)-Fe(4)-O(21)	85.0(10)	O(9)-Fe(4)-O(21)	85.0(10)
O(4)-Fe(4)-O(21)	85.1(9)	O(14)-Fe(4)-O(21)	82.1(10)

2.2. Infrared spectra

The solid state IR spectra of **1** indicate the presence of carboxylate, THF, H_2O and $\{Fe_4O_2\}$ groups. The characteristic vibration frequencies for THF groups appear at ~3450-3600 and 2800–3000 cm^{-1}. At the same time it is possible to appreciate the presence of a double pair of carboxylate stretching vibrations ν_{as} (COO) and ν_s (COO) at 1645 and 1670 cm^{-1}, and 1380 cm^{-1} respectively i.e. two types of carboxylate group in their crystal structures are present which is in according with X-ray data. These bands are shifted to lower energy by 45–75 cm^{-1} relative to the trinuclear basic acetates [32] due to the replacement of the CH_3 radical by the much more powerfully electron-accepting CCl_3

moieties which weaken the M - O_{carb} force constant. The ν_{as} (C-Cl) (A″, A′) vibration frequencies for CCl_3 groups are present at 832 (s) and 826 (s) cm^{-1} [33].

2.3. Magnetic properties

The magnetic properties of compound **1** have been measured in the 300 – 1.8 K range of temperature. At 300 K the value of $\chi_M \cdot T$ is 3.91 $cm^3 \cdot K \cdot mol^{-1}$. Lowering the temperature this value is diminished gradually and at 1.8 K is equal 0.10 $cm^3 \cdot K \cdot mol^{-1}$ thus indicating on antiferromagnetic interaction between ions of iron (III). In order to describe the magnetic properties of the investigated complex with the geometry, which is presented in scheme 1, the spin Hamiltonian (equation 1) model was used [4, 5].

$$\hat{H}_{total} = \hat{H}_z + \hat{H}_{HDvV} , \qquad (1)$$

where the isotropic (Heisenberg) exchange coupling term is described by

$$\hat{H}_{HDvV} = -2J_{wb}(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_4 + \hat{S}_4\hat{S}_1) - 2J_{bb}\hat{S}_2\hat{S}_4 \quad (2)$$

and Zeeman interaction of the Fe(III) spins with the applied magnetic field B, assumed in the z direction, is given by

$$\hat{H}_z = g\mu_B(\hat{S}_{1z} + \hat{S}_{2z} + \hat{S}_{3z} + \hat{S}_{4z}) \qquad (3)$$
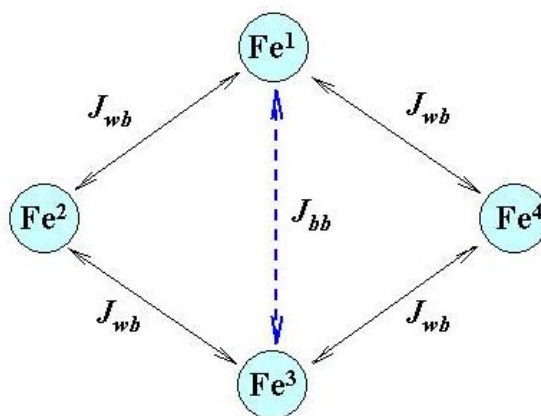
Scheme 1.

where $\hat{S}_i$ is the spin operator on the i_{th} Fe(III) ion; J is the exchange integral couplings Fe(III) ions; (The sign of J is positive for parallel and negative for antiparallel spin coupling); g is the electronic gyromagnetic ratio; μ_B is the Bohr magneton and B – magnetic field strength.

The original least-squares fitting computer program FDHM [34] with a Full Diagonalisation of Hamiltonian Matrix approach was employed to fit $(\chi T)_{exp.}$ vs. T, in order to obtain the exchange couplings constants. By use of the spin product basis set of spin wave functions $\psi = | m_{S_1} m_{S_2} m_{S_3} m_{S_4} >$ a total of 1296 ($= \prod_{i=1}^{4}(2S_i + 1)$) spin wave functions are obtained. The action of the spin Hamiltonian (1) on these wave function yields energy levels distributed with coupled spin quantum numbers, $0 \leq S_t \leq 10$.

The energy levels were determined by diagonalising the matrix

$$H_{ij}(H_{ij} = <\psi_i | \hat{H}_{total} | \psi_j >) \qquad (4)$$

The diagonalisation was simplified by block-factoring the matrix into M_{S_t} ($= \sum_{i=1}^{4} m_{S_i}$) submatrices, with the corresponding dimensions   1, 4, 10, 20, 35, 56, 80, 104, 125, 140, 146.

The magnetic susceptibilities of the compound were calculated from the spin-coupled wave function by using a simplified form of the Van Vleck equation [2]

$$\chi_{mol} = \frac{N_A}{kT} \frac{\sum_{i=1,n} |<\psi_i | \hat{\mu} | \psi_i >|^2 \exp(-E_i / kT)}{\sum_{i=1,n} \exp(-E_i / kT)} \qquad (5)$$

$$\chi_{mol} = (1-\rho) \frac{N_A}{kT} \frac{\sum_{i=1,n} |<\psi_i | \hat{\mu} | \psi_i >|^2 \exp(-E_i / kT)}{\sum_{i=1,n} \exp(-E_i / kT)} +$$

$$\rho \frac{1}{3} \frac{N_A \mu_B^2}{k} \bar{g}^2 \frac{S_{Fe(III)}(S_{Fe(III)}+1)}{1 - \dfrac{\theta_{Curie\_Weis}}{T}}$$

where E_i is the energy level with wave function ψ_i and $\hat{\mu}$ is the moment operator given by $\hat{\mu} = g\mu_B \sum_{i=1,4} \hat{S}_{z_i}$.

The results of a least-squares fit of the magnetic data are illustrated in Fig. 2 as plots of the $(\chi T)_{obs.}$ and $(\chi T)_{calc.}$ vs. T.
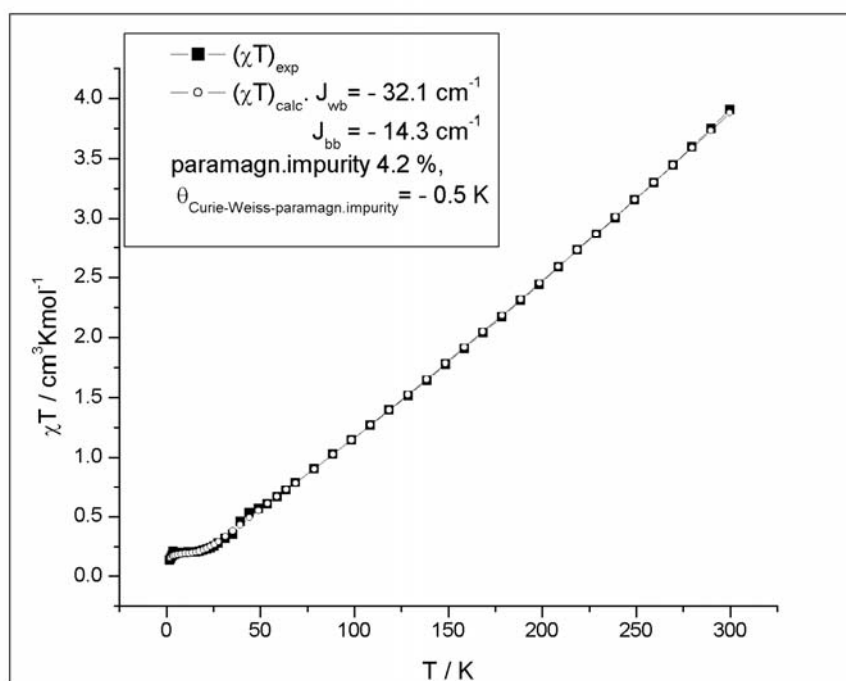
Figure 2. Temperature dependence of the magnetic susceptibility (χT vs. T) of the 1 and best fit curve obtained with parameters reported in the text.

The calculated curve drawn through the experimental points represents the best fit of the model using the fitted parameters: $J_{wb} = -32.1$ cm^{-1}, $J_{bb} = -14.3$ cm^{-1}, $\bar{g} = 2.07$, $\rho_{par.\ imp.} = 4.2$ %, $\Theta_{Curie-Weiss\ const.} = -0.5$ K, $R = 6.8 \cdot 10^{-5}$, where

$$R \equiv \sum [(\chi T)_{obs.} - (\chi T)_{calc.}]^2 / \sum (\chi T)^2_{obs})$$

- the reliability factor.

From the acquired data it is obvious that the absolute value of magnetic exchange parameter is very close to literature data [20, 22-26].

3. Conclusion

The novel bis(μ_3-oxo) tetranuclear trichloracetate cluster, $[Fe_4O_2(CCl_3COO)_8(THF)_2(DMF)(H_2O)]\cdot THF$ **(1)**, has been synthesised and subsequently characterised by X-ray structure analysis, magnetic measurements and infra red (IR). The structure of cluster is "butterfly" type and is typical for such class of clusters. Magnetic studies reveal the presence of an antiferromagnetic exchange in the parallelogram skeletons of the tetranuclear species with next fitting parameters: $J_{bb} = -14.3$ cm^{-1}, $J_{wb} = -32.1$ cm^{-1}, $g = 2.07$, $\rho_{param.\ impur.} = 4.2$ %, $\Theta_{Curie-Weiss\ const.} = -0.5$ K and R = $6.8 \cdot 10^{-5}$. It is necessary to mention that the antiferomagnetic interaction between Fe1 and F3 is unexpected but according [35] the

value and sign of this parameter doesn't have any importance in fitting process of experimental and theoretical data. This fact needs the new conception in interpretation.

4. Experimental

General: The carbon and hydrogen content of complex was determined by standard micro-methods in the group of microanalysis of the Institute of Chemistry of the Academy of Sciences of Moldova.

IR spectrum of polycrystalline sample was recorded as vaseline mulls on a Specord M-75 spectrophotometer.

Synthesis of $[Fe_4O_2(CCl_3COO)_8(THF)_2(DMF)(H_2O)]\cdot THF$ (**1**). The red tetrahydrofuran solution (THF, 20 mL) of $[Fe_2BaO(CCl_3COO)_6(THF)_6]\cdot 0{,}5H_2O\cdot 0{,}5THF$ (2.15 g, 1.286 mmol) [36] and aqueous solution (20 mL) of $La_2(SO_4)_3\cdot 9H_2O$ (0.62 g, 0.849 mmol) were added to toluene (40 mL) and the mixture stirred for 2 h after which "toluene-THF" orange layer was carefully removed out and kept at room temperature until all solvent was evaporated. The obtained orange powder was re-dissolved in DMF/THF/heptane (1:9:2) mixture (12 mL). After three days light orange single crystals of 1 grew that were suitable for X-ray analysis. Yield: 0.17 g (14 % based on Fe). Elemental analysis (%): Found: C, 20.86; H, 1.75; Fe, 12.12 %. Calcd. for $(C_{31}H_{33}Cl_{24}NO_{23}Fe_4)$: C, 20,00; H, 1.78; Fe, 12.00.

IR data show (vaseline mulls, cm^{-1}): 3650m, 3470mb, 1700m, 1673msh, 1645s; 1593s; 1590m; 1380s, 1340s; 1010w; 940w; 748 sh; 720m; 675m; 670s; 469m; 440m.

Magnetic measurements. Variable temperature susceptibility of **1** was measured with an Oxford Instruments Vibrating Sample Magnetometer (VSM) working between 0 and 12 T and in the 1.8–300.0 K temperature range. The diamagnetic Pascal's constants were used to correct the magnetic values [4, 5].

Crystallographic data. X-ray diffraction experimental data for **1** were collected at 100 K on a Kuma KM4CCD diffractometer (monochromated MoK$_\alpha$ radiation). The crystal was positioned at the distance of 70 mm from the CCD chamber. Reflections of 142 frames in one set were collected with ω angle between the frames 0.5°. Intensity data were corrected for the Lorentz and polarization effects. The structure was solved by direct methods [37] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms [38]. The CH_2 hydrogen atoms of THF moieties were located on ΔF map and their distances to C atoms have been standardized to 0.96 Å with the isotropic displacement parameters fixed at $1.2 \times U_{eq}$ of the relevant carbon atom. Positional parameters of H-atoms of coordinated water molecules were verified by the geometric parameters of the corresponding hydrogen bonds. The structural parameters together with details of data collection and refinement for **1** are given in Table 2, while selected bond lengths and angles – in Table 1.

Table 2. Summary of Crystal Data and refinement details for $[Fe_4O_2(CCl_3COO)_8(THF)_2(DMF)(H_2O)]$ THF (1).

Empirical formula	$C_{31}H_{33}Cl_{24}Fe_4NO_{23}$
M	1861.78
Wavelength, Å	0.71073
Crystal system, Space group	Monoclinic, P2$_1$/n
a, Å	14.215(3)
b, Å	37.018(7)
c, Å	14.341(3)
β, deg	109.11(3)
V, Å^3	7131(3)
Z	4
$\rho_{(calcd.)}$, Mg/m^3	1.734
μ_{Mo}, mm^{-1}	1.760
Crystal size, mm	$0.3 \times 0.25 \times 0.20$
θ range, deg	3.43 to 23.26
Number of reflections:	
Measured	7374
Unique	5296 [R$_{int}$ = 0.1012]
Number of refined parameters	258
GOOF for F^2	1.042
$^a R$	0.1402
$^b wR$	0.3865
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, eÅ^3	1.035 and -0.923

$^a R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^b wR = [\Sigma w(|F_o^2|-|F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$

5. Acknowledgements

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SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF HETEROMETALLIC NITRILOTRIACETATES OF CHROMIUM(III) WITH SOME *3d* METALS

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Abstract: Heterometallic complexes of chromium (III) with some *3d* metals have been synthesized based on nitrilotriacetic acid (H_3nta), like $M(bpy)_2Cr_2(OH)_2(nta)_2 \cdot nH_2O$, where $M = Mn^{2+}$, Co^{2+}, Ni^{2+} and Zn^{2+}; $bpy = \alpha,\alpha'$-bipyridine; n = 8 or 9. Their chemical composition has been determined from the results of the elemental analysis and thermogravimetric study. The coordination modes of the nta^{3-} ligand and the type of chemical bonds have been proposed basing on IR spectra.

Keywords: heterometallic, nitrilotriacetates, chromium(III), *3d* metals, bipyridine.

Introduction

The scientific and technological interest for new materials by means of complex combinations is explained suggestively having as objective the obtaining of new materials with useful properties. Complex compounds are perspective precursors for the synthesis of materials with catalytic [1-3], electric [4-6] and magnetic [7-9] properties. In this sense chromium (III) compounds came to be promising in the design of magnetic materials [10-17]. Thus, depending on basic ligands, the bridging and contraions ones from outer sphere, compounds with ferro- and antiferromagnetic [7-23] properties are obtained.

Taking into consideration the high interest for this type of compounds systemic investigations have been proposed to be carried out that will allow the enlarging of the knowledge about heterometallic combinations of chromium (III) with some elements from 3d blocs based on nitrilotriacetic acid (H_3nta).

Results and Discussions

Heterometallic complexes of chromium (III) with some *3d* metals have been synthesized based on nitrilotriacetic acid (H_3nta), like $M(bpy)_2Cr_2(OH)_2(nta)_2 \cdot nH_2O$, where $M = Mn^{2+}$ [**1**], Co^{2+}[**2**], Ni^{2+} [**3**], and Zn^{2+}[**4**], $bpy = \alpha,\alpha'$-bipyridine; n = 8 or 9 were prepared by exchange reaction between the complex salt $Ba[Cr_2(\mu\text{-}OH)_2(nta)_2] \cdot 5H_2O$ [24] and the respective sulfates on the basis of α,α'-bipyridine. The reactions proceed in aqueous solutions.

The composition of compounds **1-4** was determined from the elemental, thermogravimetric analysis (table 1), IR(table 2) and UV-Vis spectroscopy.

The electronic absorption spectra recorded for the aqueous solutions of compounds **1-4** show 3 bands. Together with the two bands, $v_1(^4A_{2g} \rightarrow {}^4T_{2g}) = 17422$ cm^{-1} ($\varepsilon = 147.5$ $1 \cdot mol^{-1} \cdot cm^{-1}$) and $v_2(^4A_{2g} \rightarrow {}^4T_{1g}) = 24876$ cm^{-1} ($\varepsilon = 165$ $1 \cdot mol^{-1} \cdot cm^{-1}$) characteristic for $\{NO_5\}$ octahedral coordination for Cr(III) with nta^{3-} ligand, which are also present in the spectra of the complexes $MCr_2(OH)_2(nta)_2 \cdot nH_2O$ described in [25], appears one more signal at $v_3(\pi \rightarrow \pi^*) = 31847$ cm^{-1} ($\varepsilon = 900$ $1 \cdot mol^{-1} \cdot cm^{-1}$).These parameters confirm the idea that the complexes **1-4** dissociate in solutions but keep the anionic structure unchanged [25, 26].

The analysis of the IR spectra showed that the spectra of the compounds **1-4** are identical having unimportant vibrations of the signals shift. The spectrum of the compound **1** is a little different (table 2).

In the spectrum of the compound **1** a very intense signal appears at 1606 cm^{-1} with a shoulder at 1627 cm^{-1} and three signals appear at 1386, 1344 and 1312 cm^{-1} related to $v_s(COO^-)$. The differences $\Delta v = v_{as}(COO^-) - v_s(COO^-)$ are equal to 220, 262 and 294 cm^{-1} (for the first signal) and 241, 283 and 315 cm^{-1} (shoulder signal). According to [27-29] Δv differences higher than 250 cm^{-1} indicate that COO^- groups are monodentate, but differences lower than 250 cm^{-1} indicate that these groups are bidentate; but if $\Delta v > 225$ cm^{-1} the bonds are predominantly covalent and if $\Delta v < 225$ cm^{-1} the bonds are predominantly ionic. Taking into consideration these data two coordination modes of the COO^- groups are realized in compound **1**: two are monodentate having predominantly covalent $M-O(COO^-)$ bonds and a COO^- group is bidentate having intermediary covalent-weak ionic $M-O(COO^-)$ bond [29]. In the spectra of compounds **2-4** $v_{as}(COO^-)$ signals appear at *ca* 1605 (**2**), 1606 (**3**) and 1605 cm^{-1} (**4**), but $v_a(COO^-)$ signals appear at 1384 (with shoulder), 1318 cm^{-1} (**2**), 1384, 1342, 1318 cm^{-1} (**3**) and 1384 (with shoulder), 1319 cm^{-1} (**4**). Differences $\Delta v = 221, 287$ cm^{-1} (**2**), 221, 264, 288 cm^{-1} (**3**) and 221, 286 cm^{-1} (**4**). These Δv values are the result of the similar COO^- groups coordination of these compounds (**2-4**) by forming predominantly covalent bonds of the $M-O(COO^-)$ bonds and of some weak-ionic bonds of the $M-O(COO^-)$ bonds. It could be supposed that the appearance of such low values $\Delta v \sim 221$ cm^{-1} find the explanation in the existence of $H \ldots O(COO^-)$ bonds, values that cause the diminution of the order of $M-O(COO^-)$ bonds from covalent to weak-ionic. Hydrogen bonds (intermolecular, three-dimensional) appear in the IR spectra as strong absorption bands with maximum at 3217 cm^{-1} (**1**) and 3318 cm^{-1} (**2-4**).

The IR spectra of compounds **2-4** showed three bands $\delta_{(O\text{-}C\text{-}O)}$, $\rho_{\omega(O\text{-}C\text{-}O)}$ and $\pi_{(O\text{-}C\text{-}O)}$. This phenomenon is due to the fact that the donor carboxylic groups contribute to the formation of M−O(COO⁻) groups. The fact that a COO⁻ group of the nta^{3-} ligand is fixed between two coordination centers leads to the lack of a $\rho_{\omega(O\text{-}C\text{-}O)}$ signal in the spectra of compound **1** unlike the series **2-4**.

Absorption band $\delta_{(Cr\text{-}O\text{-}H)}$ appeared in the IR spectra at 913 (**1**), 910 (**2**), 909 (**3**) and 910 (**4**) cm⁻¹ as a very intense signal. The thermogravimetric analyses of compounds **2-4** showed that these compounds are subdued to some thermal transformation while heating (table 1). Dehydration and deaquation processes proceeded over the range 20-180°C in two steps with maximum for the first step *ca* 70-100°C and for the second step at *ca* 120-180°C. Dehydration of **1** occurred in one step with the maximum at 100°C. This different behavior can be explained in the following way: the heating determines the system energy to grow, on the other hand the non-coordinated bipyridine molecules become in such conditions disposed to coordination and substitute the water molecules from the coordination sphere of the Mn atom.

At temperatures over 180-500°C thermal decomposition of the organic parts took place. These processes occurred in one step resulting finely in inorganic residues.

Experimental Section

Synthesis

[(α,α′-bipyridyl)-triaqua-manganese(II)-{di-μ-hydroxy-bis-(nitrilotriacetato)dichromium(III)}]-(α,α′-bipyridylate)-pentahydrate, [Mn(H₂O)₃(*bpy*)Cr₂(OH)₂(*nta*)₂]·(*bpy*)·5H₂O (**1**)

0,246g (1mmol) MnSO₄·7H₂O and 0,32g (2mmol) α,α-bipyridine were dissolved in 30ml of hot water. A pale yellow solution was obtained. 0,742g (1mmol) crystalline BaCr₂(*nta*)₂(OH)₂·5H₂O, prepared according the source [24], was then added. The mixture was then heated and stirred for an hour at a temperature of 40-50°C. All this gave an intense green-bluish solution, which was filtered and concentrated by evaporation at a temperature of 40-50°C to a 20ml volume. Within 24 hours a green-bluish crystalline substance precipitated from the solution, which was then filtered, washed with cold water, alcohol and then with acetone and dried at room temperature. Yield 75%. *Anal.* Found %: Cr 10.20; C 37.39; H 4.65; N 8.05. Calc. for MnCr₂C₃₂H₄₆N₆O₂₂ (**1025.67**) %: Cr 10.14; C 37.47; H 4.52; N 8.19.

[Di-(α,α′-bipyridyl)-diaqua-cobalt(II)][di-μ-hydroxy-bis-(nitrilotriacetato)dichromate(III)] heptahydrate, [Co(*bpy*)₂(H₂O)₂][Cr₂(OH)₂(*nta*)₂]·7H₂O (**2**)

Compound **2** was prepared according to synthesis **1**, but the procedure took place in CO₂ and N₂ environment. After 48h a crystalline blue-violet substance crystallized from the solution, which was then filtered, washed with cold water, alcohol and then with diethyl ether and dried at room temperature. Yield 60%. *Anal.* Found %: Cr 10.00; C 36.52; H 4.50; N 7,90. Calc. for CoCr₂C₃₂H₄₈N₆O₂₃ (**1047.68**) %: Cr 9.93; C 36.69; H 4.62; N 8.02.

[Di-(α,α′-bipyridyl)-diaqua-nickel(II)][di-μ-hydroxy-bis-(nitrilotriacetato)dichromate(III)] heptahydrate, [Ni(*bpy*)₂(H₂O)₂][Cr₂(OH)₂(*nta*)₂]·7H₂O (**3**)

Compound **3** was prepared according to synthesis **1**. A crystalline blue-violet substance was obtained. Yield 68%. *Anal.* Found %: Cr 9.98; C 36.57; H 4.52; N 8.00. Calc. for NiCr₂C₃₂H₄₈N₆O₂₃ (**1047.44**) %: Cr 9.93; C 36.69; H 4.62; N 8.02.

[Di-(α,α′-bipyridyl)-diaqua-zinc(II)][di-μ-hydroxy-bis-(nitrilotriacetato)dichromate(III)] heptahydrate, [Zn(*bpy*)₂(H₂O)₂][Cr₂(OH)₂(*nta*)₂]·7H₂O (**4**)

Compound **4** was prepared according to synthesis **1**. A crystalline blue-violet substance was obtained. Yield 62%. *Anal.* Found %: Cr 9.70; C 36.65; H 4.47; N 7.95. Calc. for ZnCr₂C₃₂H₄₈N₆O₂₃ (**1054.14**) %: Cr 9.87; C 36.46; H 4.59; N 7.97.

Compounds **1-4** are soluble in water, especially at heating; DMSO, DMF soluble; insoluble in methanol, ethanol, acetone and diethyl ether.

Table 1. Thermogravimetric analysis

Nr	Complex	Dehydration and deaquation processes, °C						Thermal decomposition, °C	
		-nH₂O	Δexp.	Δcalc.	Start	Max.	Fin.	Start	Fin.
1	Mn(*bpy*)₂Cr₂(*nta*)₂(OH)₂·8H₂O	8	14.5	14.05	50	100	120	220	470
2	Co(*bpy*)₂Cr₂(*nta*)₂(OH)₂·9H₂O	4	6.5	6.88	50	100	120	240	460
		5	9.0	8.60	120	150	180		
3	Ni(*bpy*)₂Cr₂(*nta*)₂(OH)₂·9H₂O	4	6.5	6.88	40	80	100	180	470
		5	9.0	8.60	100	140	180		
4	Zn(*bpy*)₂Cr₂(*nta*)₂(OH)₂·9H₂O	5	8.5	8.54	20	70	100	180	430
		4	7.0	6.84	100	120	180		

Chemical and Physicochemical analyses

The chemical composition was determined from the general methods of Cr, C, H and N chemical analysis. The water was determined from thermal analysis (table 1).

The thermogravimetric analysis was performed on a Paulik-Paulik-Erday M-102 derivatograph, under air atmosphere, over the temperature range t_{room} – 800°C, at 2,5°C/min or 5°C/min speed of tests heating. Compounds **1-4** were

analyzed by IR spectroscopy, using tests of tablets form in KBr. IR spectra were recorded on a Perkin Elmer FTIR 1650 spectrometer in the range 4000-400 cm^{-1} at the Institute of Biology and Molecular Chemistry of Lausanne, Switzerland. Data of IR spectra are given in table 2.

Table 2. IR spectra of the compounds 1-4

Complex			1	2	3	4
λ, cm^{-1}						
H$_2$O	ν	H…OH	3217 broad, intense	3318 broad, intense	3318 broad, intense	3318 broad, intense
OH	δ	Cr–O–H	913 intense	910 intense	909 intense	910 intense
COO$^-$	ν_{as}	C–O	1627 (shoulder), 1606 very intense, shoulder	1605 very intense	1606 very intense, shoulder	1605 very intense
	ν_s	C–O	1386 intense, 1344, medium, 1312 medium, split	1384 with two peaks, intense, shoulder, 1318 medium	1384 with two peaks, intense, shoulder, 1318 medium	1384 intense, shoulder; 1319 medium
	$\Delta\nu = \nu_{as} - \nu_s$		220, 241, 262, 283, 294, 315	221, 287	222, 264, 288	221, 286
	δ	O–C–O	776, 745, 736 intensely split	748, 736 intense	747, 735 split, two shoulders, intense	736, two shoulders, intense
	ρ_ω	O–C–O	619 shoulder, intense	613 shoulder, intense	613 intense	613 intense
	π	O–C–O	528, 514 split, intense	551 intense, 522, 512 split, intense	551 intense, 510, 503 shoulder, very intense	550 intense, 522, 513 very intense
CN	ν	C–N	1107, 1096 split, weak, 1007 shoulder, medium	1094 with two peaks, medium, 1022 medium	1105 with two peaks, medium, 1025 medium	1105 weakly split, 1022 medium
CH$_2$	ν	C–H	- weak	2978 weak	- weak	- weak
	δ	H–C–H	1461, 1426 medium split	-	-	-
	ρ_ω	CH$_2$	1271, 1226 medium	1265, split, medium, 1212 medium	1264, split, medium, 1212 medium	1265, split, medium, 1212, medium
	ρ_r	CH$_2$ (gosh)	971 medium	-	-	-
CC (*nta*$^{3-}$)	ν	C-C	943 medium	947 split, shoulder, medium	947 split, shoulder, medium	947 two shoulders, medium
CC (*bpy*)	ν	C=C	1492 weak, 1474 medium, 1441 split, medium	1493 medium, 1443 medium, shoulder	1494 medium, 1474 medium, 1444 medium	1493 medium, 1475 medium, 1443 medium, shoulder

Conclusions

1. Four complexes M(*bpy*)$_2$Cr$_2$(OH)$_2$(*nta*)$_2$·nH$_2$O, where M = Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}; *bpy* = α,α′-bipyridine; n = 8, or 9 have been synthesized. Their chemical composition has been determined from the results of the elemental analysis and thermogravimetric study.

2. According to the data of UV-Vis spectra it has been supposed that complexes **1-4** dissociate in solution but keep the anionic [Cr$_2$(OH)$_2$(*nta*)$_2$]$^{2-}$ structure unchanged.

3. According to the data of the IR spectra two coordination modes of the COO$^-$ groups are realized in complex **1**: two are monodentate having predominantly covalent M–O(COO$^-$) bonds and one COO$^-$ group is bidentate having intermediary covalent-weak ionic M–O(COO$^-$) bond. IR spectra of the complexes **2-4** show that the coordination mode of the *nta*$^{3-}$ ligand is identical, M–O(COO$^-$) bonds have predominantly covalent character and one weak-ionic character of the M–O(COO$^-$). The latter is the result of the existence of H…O(COO$^-$) bonds.

4. Thermal analysis of the complexes **1-4** show that at temperatures over 180°C they loose the hydration and coordination water molecules, but at temperatures over 180-500°C the thermal decomposition of the organic parts takes place.

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[Cr$_3$O(CH$_3$COO)$_6$(H$_2$O)$_3$]NO$_3$·HNO$_3$·H$_2$O, TRIAQUA-HEXAKIS(μ-ACETATO)-μ$_3$-OXO-TRICHROMIUM(III) NITRATE NITRIC ACID SOLVATE MONOHYDRATE

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Abstract: Reaction in methanol solution of the trinuclear 'basic' chromium(III) acetate with Pr(NO$_3$)$_3$·5H$_2$O and further extraction by chloroform-acetone mixture led to the formation of novel unusual [Cr$_3$O(CH$_3$COO)$_6$(H$_2$O)$_3$]NO$_3$·HNO$_3$·H$_2$O (**1**) cluster with one "free" molecule of nitric acid. Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with, at room temperature, a = 13.624(2), b = 15.032(2), c = 15.180(2) Å, β = 112.98(3) °, Z = 4, and V = 2862.09 Å^3. The obtained crystalline compound has been synthesized and characterized by IR and UV/Vis methods.

Keywords: Chromium carboxylate, Polynuclear complex, UV-Vis

1. Introduction

Oxo-centered triangular complexes of the general type [M$_3$O(OOCR)$_6$L$_3$]$^{n+}$ are particularly valuable as frameworks for a systematic study of metal-metal interactions in clusters. They have been characterized for a wide variety of first-row and heavier transition metals, with mixed-metal combinations and with mixed-valence combinations [1]. 'Basic' chromium carboxylates is a general name for a family of chromium(III) complexes in which only RCOO$^-$ and oxo/hydroxo/aquo ligands are present. For many years, the only representative of this group was the classical oxo-centered trinuclear complex [Cr$_3$O(CH$_3$COO)$_6$(H$_2$O)$_3$]$^+$, whose structure was reported almost four decades ago by Figgis and Robertson [2].

Chromium(III) carboxylates have been used extensively for various applications as polymerization and oxidation catalysts [3], suitable building block of zeotype polyoxometalate-macrocations for shape-selective adsorption of water [4], materials in processing of fir bark extract for air fresheners [5], possible DNA-cleaving agents and nutritional supplements [6] and for many other uses [7-10]. Ever since the discovery of chromium as an essential human nutrient, Cr(III) acetates containing [Cr$_3$O(CH$_3$COO)$_6$(H$_2$O)$_3$]$^+$ cation have been administered to animals in biological intake experiments [11], to produce DNA strand breaks in peripheral lymphocytes [12] and in phosphate ester cleavage reactions [13].

Here, we report the crystal structural determination of a new cationic trinuclear Cr(III) complex, which represents a new type of 'basic' chromium carboxylate.

2. Results and discussion

It needs to be mentioned that this synthetic route for the title compound can be realized only in the presence of Pr(NO$_3$)$_3$·5H$_2$O. Using other lanthanide nitrates (Ln = La, Eu) clusters with other structures have been obtained. The reasons for this behavior and the nature of these different products are being investigated.

On the basis of the results of elemental analysis, in the first step of our research it has been assumed that the obtained product is a new 'Cr(III,III,IV)-acetate' cluster. But the absence of splitted components A$_1$ and B$_2$ of E´ [1] in the region 700-500 cm^{-1} of IR spectrum (Fig.1) and typical profile of the electronic absorption spectra (Fig.2) for such trichromium(III) complexes [1] confirm that a member of the investigated class of substances of symmetrical complexes with "Cr$^{III}_3$O"-core has been obtained. Other IR bands are definitely assigned to vibrations of CH$_3$COO$^-$, NO$_3^-$ and H$_2$O groups, but do not represent essential interest for the discussion in the present communication.
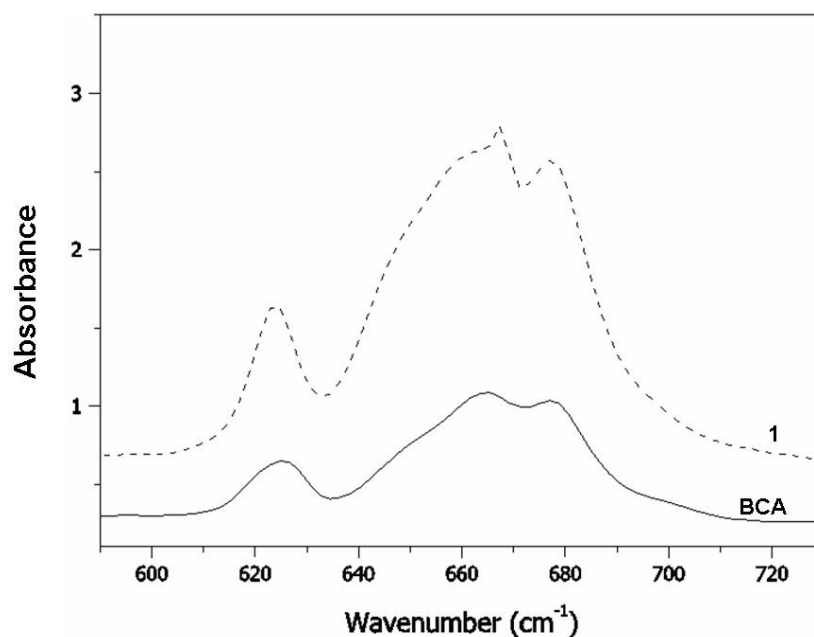
Figure 1. The $\nu_{as}(Cr_3O)$ band of complexes $[Cr_3O(Ac)_6(H_2O)_3]NO_3 \cdot HNO_3 \cdot H_2O$ (1) and $[Cr_3O(CH_3COO)_6(H_2O)_3] \cdot CH_3COO$ (BCA)

The electronic spectrum of **1** in acetone solution shows the familiar two peaks in the visible (Fig.2, bands I and II), corresponding to the $^4A_{2g} \rightarrow ^4T_{2g}$ and $^4A_{2g} \rightarrow ^4T_{1g}$ transitions of Cr(III) in octahedral symmetry.
No spectral features relative to other oxidation states of chromium are present in the UV-Vis-NIR absorption spectra.
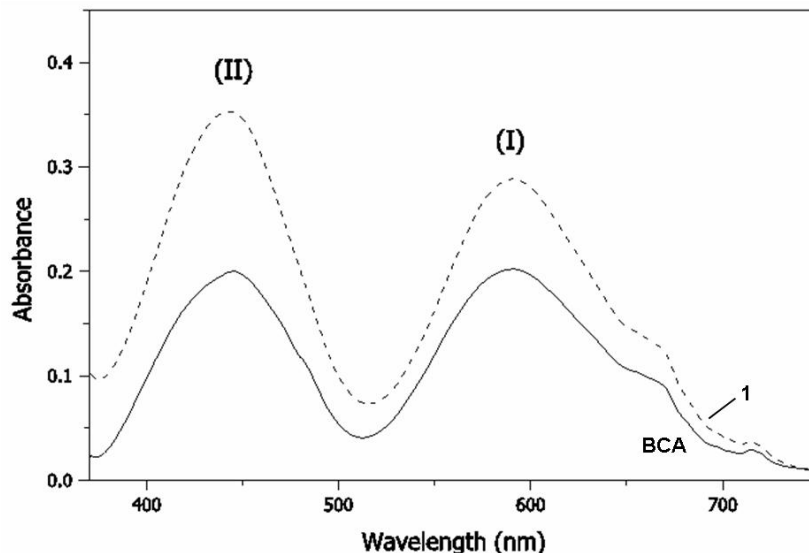
Figure 2. Electronic spectra of $[Cr_3O(Ac)_6(H_2O)_3]NO_3 \cdot HNO_3 \cdot H_2O$ (1) and $[Cr_3O(CH_3COO)_6(H_2O)_3] \cdot CH_3COO$ (BCA), in acetone solution.

X-ray study of **1** showed that the structure consists of three chromium atoms connected together by an oxygen atom. In addition two acetate groups connect the three chromium atoms to each other. So every chromium atom adopts a tetrahedral conformation with four atoms of four different acetate groups as base and the common oxygen and a water molecule in apex positions (Fig.3). Bond distances and angles do not deviate significantly from the normal range. The atomic coordinates of the heavy atoms are in Table 2 and their anisotropic thermal parameters are in Table 4. Table 3 reports the coordinates of H atoms with isotropic thermal parameters. The geometrical parameters are in Table 5. A projection of the complex with the labeling scheme is in Fig. 3.

Table 2. Atomic fractional coordinates (x10^4) and Ueq (x10^4 Å^2)

	x/a		y/b		z/c		Ueq	
CR1	8440	(1)	914	(1)	7170	(1)	314	(2)
CR2	6347	(1)	1475	(1)	7614	(1)	306	(2)
CR3	8661	(1)	2401	(1)	8825	(1)	305	(2)
O1W	9099	(3)	202	(2)	6412	(2)	511	(13)
O2W	4776	(2)	1360	(2)	7367	(3)	483	(12)
O3W	9515	(3)	3299	(2)	9866	(2)	484	(13)
O1	7817	(2)	1597	(1)	7869	(2)	299	(8)
C1A	5610	(5)	1155	(5)	4624	(3)	708	(23)
C2A	6305	(3)	1220	(3)	5670	(2)	394	(14)
O3A	7269	(2)	1096	(2)	5916	(2)	488	(11)
O4A	5847	(2)	1392	(2)	6221	(2)	508	(10)
C1B	6208	(4)	4334	(3)	7510	(4)	529	(20)
C2B	6679	(3)	3427	(2)	7792	(3)	363	(14)
O3B	6084	(2)	2770	(2)	7477	(2)	471	(11)
O4B	7641	(2)	3388	(2)	8336	(2)	475	(11)
C1C	6802	(5)	-1346	(3)	7642	(5)	572	(22)
C2C	7017	(3)	-386	(2)	7558	(2)	371	(13)
O3C	7778	(2)	-202	(2)	7340	(2)	486	(12)
O4C	6414	(2)	167	(2)	7709	(2)	524	(12)
C1D	10205	(4)	3229	(4)	6982	(4)	558	(19)
C2D	9568	(3)	2634	(2)	7342	(3)	362	(13)
O3D	9407	(2)	2896	(2)	8065	(2)	456	(11)
O4D	9224	(2)	1919	(2)	6910	(2)	429	(10)
C1E	11108	(5)	419	(5)	9825	(5)	643	(21)
C2E	10149	(3)	895	(3)	9133	(3)	379	(13)
O3E	9725	(2)	591	(2)	8310	(2)	460	(11)
O4E	9841	(2)	1561	(2)	9445	(2)	473	(10)
C1F	7110	(5)	1508	(4)	10634	(4)	531	(19)
C2F	7256	(3)	1695	(2)	9725	(2)	364	(15)
O3F	8112	(2)	2040	(2)	9790	(2)	478	(11)
O4F	6516	(2)	1491	(2)	8958	(2)	536	(11)
N1G	2252	(3)	1273	(3)	5554	(3)	693	(19)
O1G	3120	(4)	1094	(4)	5549	(4)	1362	(27)
O2G	1455	(3)	1141	(4)	4918	(4)	1483	(29)
O3G	2220	(5)	1516	(5)	6284	(4)	1682	(36)
N1H	3592	(6)	1562	(5)	9199	(5)	1263	(38)
O1H	3885	(7)	1524	(10)	10241	(6)	3135	(91)
O2H	4182	(6)	1507	(7)	8841	(5)	2292	(56)
O3H	2419	(8)	1762	(9)	8569	(8)	2838	(76)
O4W	11146	(5)	-5	(4)	6885	(7)	1076	(35)

Table 3 . Atomic fractional coordinates (x10⁴) and Uiso (x10⁴ Å²).

	x/a		y/b		z/c		Uiso	
H1A	568	(6)	63	(5)	425	(6)	1341	(289)
H2A	491	(7)	113	(5)	444	(5)	1209	(262)
H3A	568	(5)	170	(4)	437	(4)	899	(209)
H1B	560	(6)	437	(4)	735	(5)	1018	(229)
H2B	654	(6)	466	(5)	802	(6)	1345	(288)
H3B	635	(5)	455	(5)	711	(5)	1051	(245)
H1C	615	(5)	-147	(3)	762	(3)	663	(143)
H2C	729	(4)	-163	(3)	801	(3)	586	(149)
H3C	676	(6)	-160	(5)	712	(5)	1257	(274)
H1D	999	(7)	350	(6)	646	(6)	1415	(300)
H2D	1058	(6)	345	(5)	739	(5)	1118	(276)
H3D	1047	(6)	295	(6)	656	(6)	1247	(271)
H1E	1158	(5)	58	(5)	984	(5)	888	(269)
H2E	1119	(6)	43	(5)	1050	(6)	1289	(264)
H3E	1105	(5)	-14	(5)	969	(4)	1085	(241)
H1F	761	(6)	120	(4)	1104	(5)	960	(210)
H2F	709	(5)	202	(5)	1095	(5)	951	(217)
H3F	663	(6)	135	(5)	1051	(5)	1007	(286)
H1W1	886	(4)	-10	(3)	605	(4)	558	(164)
H2W1	982	(5)	9	(4)	663	(4)	778	(172)
H1W2	439	(5)	121	(5)	693	(5)	1021	(249)
H2W2	455	(4)	145	(3)	780	(4)	693	(162)
H1W3	934	(4)	341	(4)	1030	(4)	715	(178)
H2W3	1011	(5)	333	(4)	994	(4)	690	(180)
H1W4	1111	(8)	-37	(7)	636	(7)	1638	(360)
H2W4	1133	(4)	-21	(4)	704	(4)	164	(130)
H1NH	4491	(5)	802	(4)	9221	(4)	1386	(133)

Table 4. Anisotropic thermal parameters (x10⁴ Å²).

	U_{11}		U_{22}		U_{33}		U_{23}		U_{13}		U_{12}	
CR1	294	(3)	314	(3)	353	(3)	-33	(2)	149	(2)	-21	(2)
CR2	251	(3)	337	(3)	326	(3)	-34	(2)	108	(2)	-25	(2)
CR3	271	(3)	315	(3)	316	(3)	-36	(2)	100	(2)	-35	(2)
O1W	448	(17)	553	(19)	583	(18)	-225	(16)	256	(15)	-37	(15)
O2W	298	(14)	658	(20)	479	(17)	-80	(15)	137	(14)	-56	(13)
O3W	395	(16)	562	(19)	488	(17)	-168	(13)	163	(14)	-120	(14)
O1	271	(11)	292	(12)	327	(11)	-37	(9)	110	(9)	-36	(9)
C1A	562	(31)	1127	(52)	337	(22)	-23	(27)	70	(21)	23	(32)
C2A	398	(20)	415	(21)	334	(18)	-17	(15)	104	(16)	-37	(16)
O3A	384	(15)	720	(19)	345	(13)	-85	(12)	126	(11)	-11	(13)
O4A	313	(13)	850	(22)	322	(13)	-96	(13)	79	(11)	1	(13)
C1B	479	(26)	402	(25)	721	(33)	63	(23)	252	(26)	107	(20)
C2B	398	(19)	342	(19)	415	(19)	1	(15)	229	(17)	21	(15)
O3B	306	(13)	368	(15)	687	(17)	-29	(13)	136	(12)	14	(11)
O4B	382	(14)	316	(14)	613	(16)	-84	(12)	69	(13)	19	(11)
C1C	499	(28)	351	(24)	860	(37)	47	(25)	259	(27)	-40	(21)
C2C	353	(18)	331	(19)	393	(18)	24	(15)	107	(15)	-16	(15)
O3C	547	(16)	312	(14)	740	(18)	-71	(12)	405	(15)	-43	(12)
O4C	425	(15)	352	(14)	874	(21)	-15	(14)	338	(15)	-55	(12)
C1D	578	(28)	627	(31)	514	(27)	-32	(24)	263	(25)	-240	(24)

C2D	277	(16)	384	(20)	389	(18)	69	(16)	92	(15)	-18	(14)
O3D	503	(16)	468	(16)	446	(14)	-78	(12)	237	(12)	-183	(12)
O4D	443	(14)	411	(16)	490	(14)	-28	(12)	243	(12)	-87	(12)
C1E	394	(26)	654	(37)	720	(36)	157	(28)	42	(24)	75	(25)
C2E	273	(16)	415	(21)	426	(20)	60	(16)	109	(15)	-1	(15)
O3E	399	(14)	502	(16)	449	(14)	-6	(12)	134	(12)	136	(12)
O4E	391	(14)	492	(16)	410	(14)	-28	(12)	21	(12)	64	(12)
C1F	485	(28)	726	(37)	444	(25)	25	(23)	248	(23)	-72	(26)
C2F	403	(20)	365	(19)	362	(18)	-9	(14)	189	(16)	24	(15)
O3F	453	(15)	650	(18)	369	(13)	-123	(12)	201	(12)	-198	(14)
O4F	354	(14)	912	(23)	359	(14)	-35	(14)	158	(12)	-137	(14)
N1G	422	(22)	895	(32)	639	(25)	-205	(22)	74	(20)	13	(21)
O1G	589	(27)	2204	(65)	1182	(38)	-188	(39)	225	(25)	200	(33)
O2G	523	(24)	1932	(54)	1467	(43)	-1080	(41)	-184	(26)	313	(29)
O3G	1198	(46)	2471	(82)	1271	(46)	-947	(49)	367	(37)	-59	(46)
N1H	1254	(55)	1720	(66)	1077	(46)	-325	(43)	738	(45)	-512	(47)
O1H	1759	(82)	6318	(239)	1226	(59)	-561	(89)	471	(55)	-1211	(108)
O2H	1294	(52)	4826	(154)	1151	(44)	-642	(63)	905	(42)	-176	(67)
O3H	1668	(85)	3735	(148)	2688	(111)	1487	(103)	391	(76)	-254	(90)
O4W	673	(32)	644	(35)	1995	(69)	-137	(36)	611	(37)	142	(24)

Table 5. Bond distances (Å) and angles (°).

CR1	-	O1W	2.021	(4)		C1B	-	C2B	1.496	(6)
CR1	-	O1	1.898	(3)		C2B	-	O3B	1.249	(4)
CR1	-	O3A	1.968	(2)		C2B	-	O4B	1.248	(4)
CR1	-	O3C	1.969	(3)		C1C	-	C2C	1.487	(6)
CR1	-	O4D	1.977	(3)		C2C	-	O3C	1.237	(5)
CR1	-	O3E	1.982	(2)		C2C	-	O4C	1.252	(5)
CR2	-	O2W	2.030	(3)		C1D	-	C2D	1.490	(8)
CR2	-	O1	1.894	(2)		C2D	-	O3D	1.262	(5)
CR2	-	O4A	1.956	(3)		C2D	-	O4D	1.251	(4)
CR2	-	O3B	1.975	(3)		C1E	-	C2E	1.500	(7)
CR2	-	O4C	1.970	(3)		C2E	-	O3E	1.242	(4)
CR2	-	O4F	1.960	(3)		C2E	-	O4E	1.247	(5)
CR3	-	O3W	2.058	(3)		C1F	-	C2F	1.496	(8)
CR3	-	O1	1.894	(2)		C2F	-	O3F	1.244	(5)
CR3	-	O4B	1.968	(3)		C2F	-	O4F	1.245	(4)
CR3	-	O3D	1.958	(3)		N1G	-	O1G	1.216	(7)
CR3	-	O4E	1.971	(3)		N1G	-	O2G	1.155	(6)
CR3	-	O3F	1.963	(3)		N1G	-	O3G	1.183	(9)
C1A	-	C2A	1.502	(5)		N1H	-	O1H	1.474	(11)
C2A	-	O3A	1.231	(5)		N1H	-	O2H	1.135	(13)
C2A	-	O4A	1.250	(5)		N1H	-	O3H	1.538	(12)

O4D	-	CR1	-	O3E	90.0	(1)		O3W	-	CR3	-	O3D	86.3	(1)
O3C	-	CR1	-	O3E	88.3	(1)		O3W	-	CR3	-	O4B	84.3	(1)
O3C	-	CR1	-	O4D	171.2	(1)		O3W	-	CR3	-	O1	177.4	(1)
O3A	-	CR1	-	O3E	169.9	(1)		CR2	-	O1	-	CR3	119.7	(1)
O3A	-	CR1	-	O4D	89.8	(1)		CR1	-	O1	-	CR3	120.2	(1)
O3A	-	CR1	-	O3C	90.3	(1)		CR1	-	O1	-	CR2	120.1	(1)
O1	-	CR1	-	O3E	94.6	(1)		C1A	-	C2A	-	O4A	116.6	(3)
O1	-	CR1	-	O4D	95.3	(1)		C1A	-	C2A	-	O3A	117.9	(3)
O1	-	CR1	-	O3C	93.5	(1)		O3A	-	C2A	-	O4A	125.5	(3)

O1	-	CR1	-	O3A	95.4	(1)	CR1	-	O3A	-	C2A	132.9	(2)
O1W	-	CR1	-	O3E	86.0	(1)	CR2	-	O4A	-	C2A	133.0	(2)
O1W	-	CR1	-	O4D	84.0	(1)	C1B	-	C2B	-	O4B	117.0	(3)
O1W	-	CR1	-	O3C	87.2	(1)	C1B	-	C2B	-	O3B	118.0	(3)
O1W	-	CR1	-	O3A	84.0	(1)	O3B	-	C2B	-	O4B	125.0	(3)
O1W	-	CR1	-	O1	179.1	(1)	CR2	-	O3B	-	C2B	132.4	(2)
O4C	-	CR2	-	O4F	87.3	(1)	CR3	-	O4B	-	C2B	133.6	(2)
O3B	-	CR2	-	O4F	92.3	(1)	C1C	-	C2C	-	O4C	117.7	(4)
O3B	-	CR2	-	O4C	172.8	(1)	C1C	-	C2C	-	O3C	117.0	(3)
O4A	-	CR2	-	O4F	167.1	(1)	O3C	-	C2C	-	O4C	125.3	(3)
O4A	-	CR2	-	O4C	90.1	(1)	CR1	-	O3C	-	C2C	134.4	(2)
O4A	-	CR2	-	O3B	88.7	(1)	CR2	-	O4C	-	C2C	131.7	(2)
O1	-	CR2	-	O4F	95.8	(1)	C1D	-	C2D	-	O4D	118.4	(3)
O1	-	CR2	-	O4C	93.8	(1)	C1D	-	C2D	-	O3D	117.1	(3)
O1	-	CR2	-	O3B	93.4	(1)	O3D	-	C2D	-	O4D	124.5	(3)
O1	-	CR2	-	O4A	96.9	(1)	CR3	-	O3D	-	C2D	134.4	(2)
O2W	-	CR2	-	O4F	83.2	(1)	CR1	-	O4D	-	C2D	132.3	(2)
O2W	-	CR2	-	O4C	86.8	(1)	C1E	-	C2E	-	O4E	116.5	(3)
O2W	-	CR2	-	O3B	86.0	(1)	C1E	-	C2E	-	O3E	117.7	(4)
O2W	-	CR2	-	O4A	84.1	(1)	O3E	-	C2E	-	O4E	125.8	(3)
O2W	-	CR2	-	O1	178.8	(1)	CR1	-	O3E	-	C2E	133.9	(2)
O4E	-	CR3	-	O3F	86.8	(1)	CR3	-	O4E	-	C2E	131.7	(2)
O3D	-	CR3	-	O3F	168.9	(1)	C1F	-	C2F	-	O4F	117.8	(4)
O3D	-	CR3	-	O4E	90.6	(1)	C1F	-	C2F	-	O3F	117.6	(3)
O4B	-	CR3	-	O3F	94.1	(1)	O3F	-	C2F	-	O4F	124.7	(3)
O4B	-	CR3	-	O4E	170.7	(1)	CR3	-	O3F	-	C2F	132.4	(2)
O4B	-	CR3	-	O3D	86.8	(1)	CR2	-	O4F	-	C2F	134.3	(2)
O1	-	CR3	-	O3F	95.8	(1)	O2G	-	N1G	-	O3G	117.9	(6)
O1	-	CR3	-	O4E	95.4	(1)	O1G	-	N1G	-	O3G	117.8	(5)
O1	-	CR3	-	O3D	95.2	(1)	O1G	-	N1G	-	O2G	123.8	(5)
O1	-	CR3	-	O4B	93.7	(1)	O2H	-	N1H	-	O3H	118.3	(7)
O3W	-	CR3	-	O3F	82.8	(1)	O1H	-	N1H	-	O3H	117.1	(7)
O3W	-	CR3	-	O4E	86.7	(1)	O1H	-	N1H	-	O2H	124.4	(7)

Table 6. Possible H bonds and contcts <2.5 (D= donor, A = acceptor)

D-H (Å)		D...A (Å)		H...A (Å)		D-H...A (°)	
O1W-H2W1	0.91(7)	O1W...O4W	2.612(8)	H2W1...O4W	1.71(7)	O1W-H2W1...O4W	171(5)
O2W-H1W2	0.70(6)	O2W...O1G	2.828(5)	H1W2...O1G	2.14(6)	O2W-H1W2...O1G	167(7)
O2W-H2W2	0.83(7)	O2W...O2H	2.670(9)	H2W2...O2H	1.85(7)	O2W-H2W2...O2H	171(5)
O1W-H1W1	0.69(5)	O1W...O2Gi	2.745(7)	H1W1...O2Gi	2.07(5)	O1W-H1W1...O2Gi	164(6)
O3W-H2W3	0.76(7)	O3W...O2Gii	2.746(6)	H2W3...O2Gii	2.02(7)	O3W-H2W3...O2Gii	158(11)

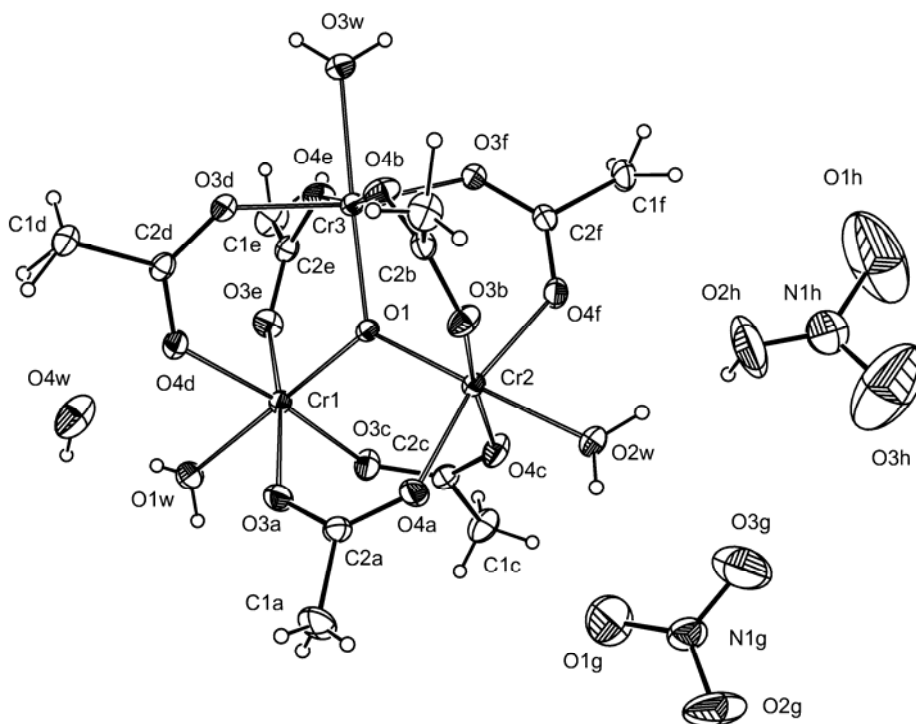Equivalent positions: i = -x+1,-y,-z+1; ii = x+1,-y+1/2,z+1/2

Figure 3. Projection of the complex with arbitrary numbering. The ellipsoids are at 20% probability level.
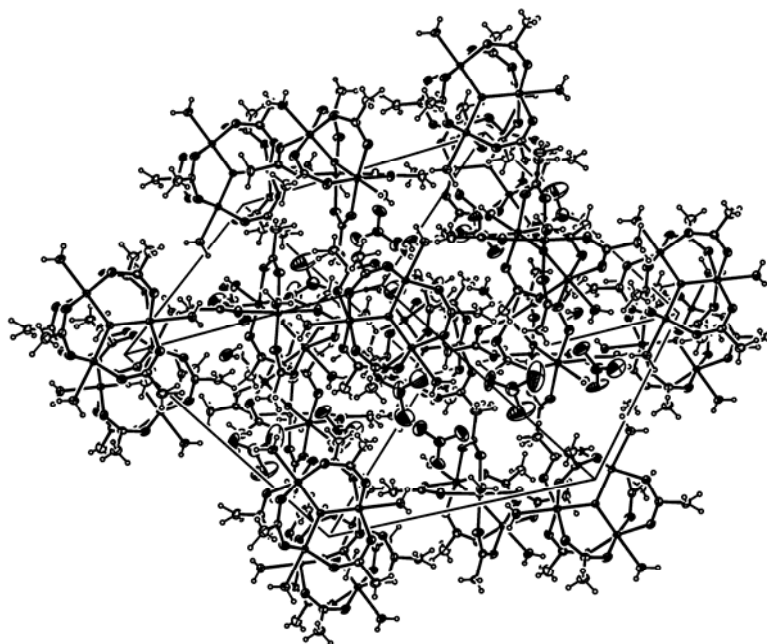

Fig. 4. Packing of the complex 1.

The single acetate groups are planar and the dihedral angles formed by the couples which connect Cr1 with Cr2, Cr1 with Cr3 and Cr2 with Cr3 are 88.1(3), 93.5(2) and 103.8(2)°, respectively.

In the solid state the molecules are connected by intermolecular and intramolecular H-bonds (Fig.4).

3. Conclusion

In summary, new basic chromium acetate has been isolated and characterised by spectroscopic techniques. This novel compound contains the well-known $[Cr_3O(CH_3COO)_6(H_2O)_3]^+$ triangular cation, but is characterised by the unusual presence of a "free" HNO_3 molecule. This could give rise to differences in the interaction of this compound with biological molecules, with respect to other basic chromium carboxylates.

Supporting information available: IR data, listing crystallographic parameters in CIF format, atomic coordinates, bond distances and angles, thermal parameters and hydrogen atom positions for the title complex. This material is available free of charge from the authors.

4. Experimental

General: All chemicals and solvents were used as received. All preparations and manipulations were performed under aerobic conditions. [Cr$_3$O(CH$_3$COO)$_6$(H$_2$O)$_3$]·CH$_3$COO was prepared as previously described [14].

The *UV-Visible absorption spectra* were measured with a conventional double beam UVIKON 941 plus spectrophotometer using a resolution of 1 nm. The solvent (acetone) was used as a reference.

The *diffuse reflectance* spectra in the medium infrared region (4000-400 cm^{-1}) were measured using a Nicolet Magna 740 FTIR spectrometer. The powders of the samples under investigation were dispersed in KBr in a 1:100 mass ratio and the spectra were measured using KBr as a reference. All the spectroscopic measurements were performed at room temperature.

Synthesis of [Cr$_3$O(Ac)$_6$(H$_2$O)$_3$]NO$_3$·HNO$_3$·H$_2$O **(1)**. Solutions of [Cr$_3$O(CH$_3$COO)$_6$(H$_2$O)$_3$]·CH$_3$COO ('basic' chromium acetate, 0.8176 g, 1.279 mmol) and Pr(NO$_3$)$_3$·5H$_2$O (1.6001 g, 3.836 mmol) in methanol (ca. 10 mL) were added with continuous stirring (30-45 min.) to 40 mL of acetonitrile – toluene (1 : 3). After 4-5 days the obtained dark green viscous mass was dissolved in part in a chloroform-acetone mixture (2:1, ca. 25 mL) and filtered off. During the first 3 days the transparent solution of dark green color was separated constantly until the first crystals have appeared. A microcrystalline product was obtained, which was recrystallized from a mixture of acetone and toluene (4:1, ca. 15 mL). After 1 week the resultant dark green crystals were collected by filtration, washed with toluene, and dried in vacuum. Yield: ~30% (270 mg) Calc. for C$_{12}$H$_{27}$N$_2$Cr$_3$O$_{23}$: C, 19.93; H, 3.76; N, 3.87%. Found: C, 19.99; H, 3.42; N, 3.78%.

Crystallographic data: The structure was solved by direct methods with SIR97 [15]. The refinement was carried out with SHELX97 [16]. After some full-matrix anisotropic cycles all H atoms were found in a ΔF map and all refined isotropically. The ORTEP drawings were performed with ORTEP-3 program [17]. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC reference number 612714. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk]. The crystal data and pertinent details of the experimental conditions are summarized in Table 1.

Table 1. Experimental and crystallographic information for 1.

Formula	(CH$_3$COO)$_6$·O·NO$_3$·HNO$_3$·(H$_2$O)$_3$·Cr$_3$·(H$_2$O)
Formula weight	723.36
Crystal: color	dark green
shape	prismatic
dimensions (mm)	0.19x0.23x0.34
Crystal system	Monoclinic
Space Group	P21/c
Cell Constants: a (Å)	13.624(2)
b (Å)	15.032(2)
c (Å)	15.180(2)
β (º)	112.98(3)
Cell volume (Å^3)	2862.09
Formula units	4
Temperature	room
Diffractometer	Bruker AXS
Radiation, wavelength (Å)	MoKα, 0.71069
Reflections measured	27926
Unique reflections, R$_{int}$	6461, 0.055
Reflections. observed [I>2σ(I)]	4547
2θ max (º)	56.7
Indices range: h, k, l	-18/17, -19/19, -19/19
No. of refined parameters	465
R	0.048
R$_w$	0.14
Weights	w=1/[(σ^{2}Fo+0.099P^2+0.22P)]
GOF	0.84
Δρ$_{min/max}$(e/ Å^3)	-0.57/0.50

5. Acknowledgements

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MAGNETIC INVESTIGATION OF AN UNUSUAL DISSYMMETRIC BINUCLEAR MANGANESE CARBOXYLATE COMPLEX

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Abstract: The magnetic susceptibility (χT) of an unusual dissymmetric binuclear manganese corboxylate complex has been measured from 2 to 300K. The magnetic data which have been fitted with help of the Heisenberg Dirac Van Vleck HDVV spin-exchange Hamiltonian $\vec{H} = -J\vec{S}_1\vec{S}_2$, indicate that an antiferromagnetic interaction equal to J = -0.90(1) cm^{-1} is present. A correlation between J values and Mn-H$_2$O-Mn angles has been tempted.

Keywords: manganese(II) carboxylates; magnetic properties

Introduction

The most important role in nature for manganese (Mn) is its involvement in water oxidation/oxygen evolution centre (WOC) within the photosynthetic apparatus of green plants and cyanobacteria.[1] A large variety of studies have shown manganese to be the site of binding and oxidation substrate (eq.1).

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \tag{1}$$

Nowadays special attention is focused on studying the cooperative action of binuclear or multinuclear Mn(II) compounds. Indeed, binuclear dimanganese(II) metal centers are present in several enzymes, including arginase, catalase, thiosulfate-oxidizing enzyme and glycohydrolase.[2]

Due to these facts, carboxylate-bridged di- or poly-manganese centers have attracted growing interest in both systematic modeling and physical characterization.

Results and discussion

We previously described the synthesis and X-ray analysis of an unexpected dissymmetric manganese (μ -aqua) dimer compound obtained with use of trichlorocetic acid and that corresponds to the following formula: [Mn$_2$(μ-H$_2$O)(μ-CCl$_3$COO)$_2$(CCl$_3$COO)$_2$(H$_2$O)$_4$]H$_2$O (**I**).[3] The present paper reports on the magnetic investigation of this compound. A view of the X-ray structural determination is presented in Figure 1.
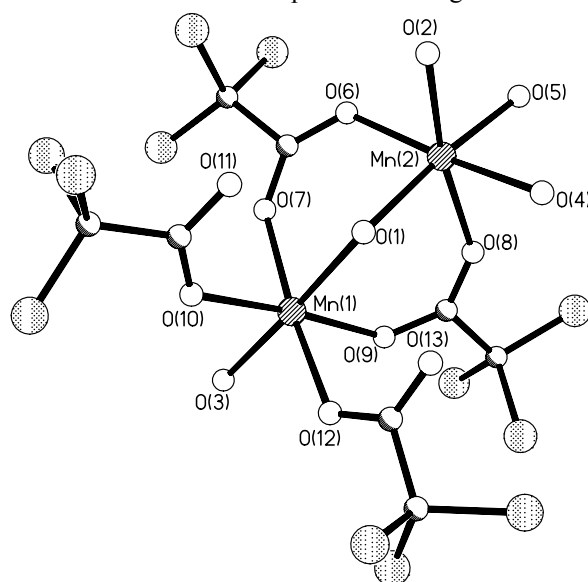

Figure 1. Structure of [Mn$_2$(μ-H$_2$O)(μ-CCl$_3$COO)$_2$(CCl$_3$COO)$_2$(H$_2$O)$_4$]H$_2$O.

The magnetic susceptibility (χT) of powdered samples has been measured from 2 to 300K with use of a SQUID magnetometer. At 297.8 K, the magnetic moment is equal to 8.39 BM, value that corresponds to two uncoupled high spin (S = 5/2) manganese(II) ions.[4a,b] (Fig. 2). The μ_{eff} value continuously decreases upon cooling and reaches

5.15 BM at 1.97 K, a value which is characteristic of an antiferromagnetic interaction between the two metal atoms through the double carboxylate and the water bridging molecule (Fig. 1). In order to evaluate the magnitude of the spin-exchange interaction, the magnetic data were fitted with help of the Heisenberg Dirac Van Vleck HDVV spin-exchange Hamiltonian [4c] (eqs. (2) and (3)).

$$\overline{H} = -J\vec{S}_1\vec{S}_2 \tag{2}$$

$$\chi = \frac{2Ng^2\beta^2}{k(T-\theta)} \cdot \frac{e^{J/kT} + 5e^{3J/kT} + 14e^{6J/kT} + 30e^{10J/kT} + 55e^{15J/kT}}{1 + 3e^{J/kT} + 5e^{3J/kT} + 7e^{6J/kT} + 9e^{10J/kT} + 11e^{15J/kT}} + N_\alpha \tag{3}$$

The coupling between the two paramagnetic $S=5/2$ spins generates states S having the following energies E: $S(E) = 0(0)$, $1(-J)$, $2(-3J)$, $3(-6J)$, $4(-10J)$, $5(-15J)$. The least-squares fit of the experimental data gives the following set of parameters: $g = 2.002(1)$, $\theta = -1.28(2)$K $N_\alpha = 0.002(6)$ $J = -0.90(1)$ cm^{-1} The agreement factor $\sum(\chi T_{calc} - \chi T_{obs})^2 / \sum(\chi T_{obs})^2$ is then equal to $1.2 \cdot 10^{-4}$. The θ value has been obtained from the Curie-Weiss law (Fig. 3) (C = 2.49(2) cm^3·K·mol^{-1} $\theta = -1.28(2)$ K) and suggests the presence of second-order effects (such as intermolecular interactions, etc.).
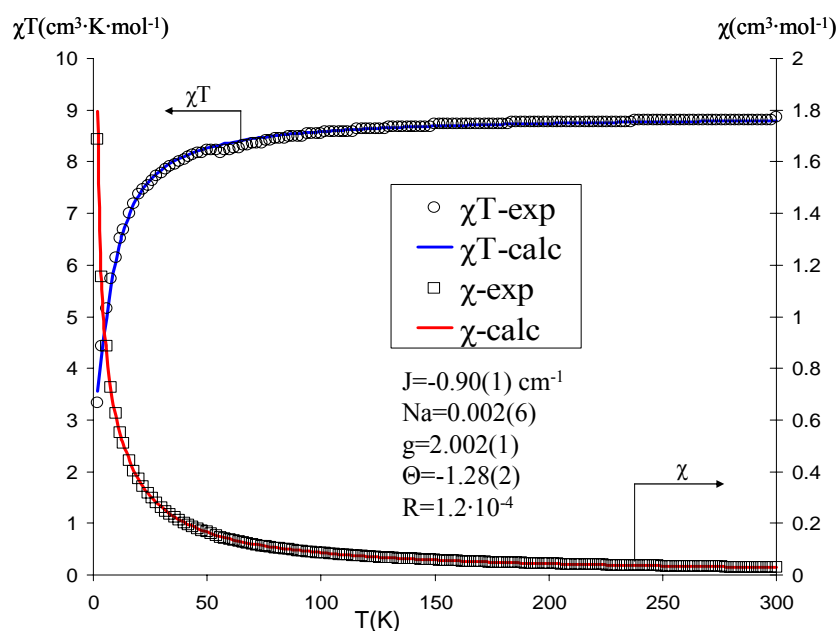

Figure 2. Temperature dependence of χ and χT for **I**. The solid line is the best fit for a pair of exchange-coupled $S = 5/2$ spins (eq. 3).
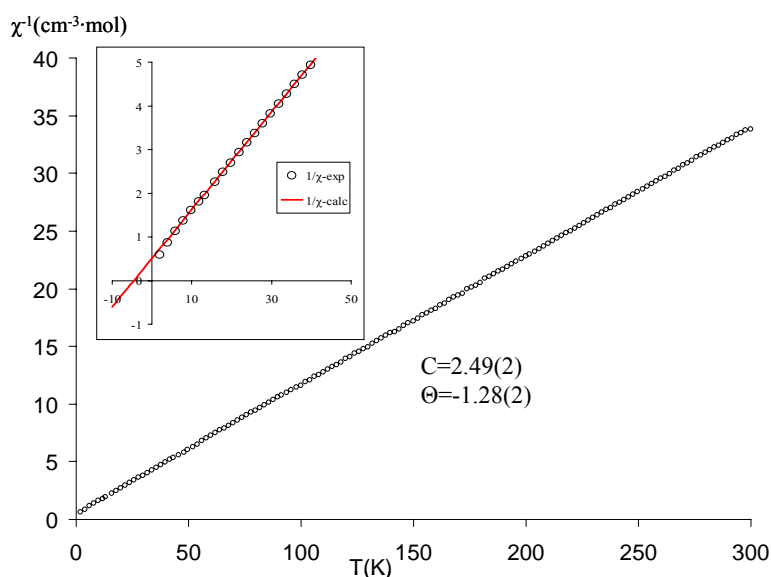

Figure 3. χ^{-1} versus temperature plot for **I** with the best fit plot according to the Curie-Weiss law.

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The obtained J value, similar to the ones given in earlier published works, confirms the existence of an antiferromagnetic interaction (Table 1).[5] The bridging ligands control the metal-metal separations and provide an orbital overlapping through these ligand orbitals. Unfortunately the J value corresponds to the global behaviour, so that we are not able to differentiate the contributions from the carboxylate bridges and from the water bridge, as in the previously published results (Table 1). In order to compare our value with the literature data obtained with a different Hamiltonian ($H = -2JS_1S_2$), we have to take into account two factors. As the variations of the Mn-H_2O-Mn angles and of the Mn-Mn distances are very small, a correlation between these parameters and the J values is inappropriate. It is clear that these parameters are not the good ones to attempt a correlation. A comparison with the previously published symmetrical complexes indicates that the non symmetry of our complex could be considered as a factor responsible for the weakening of the antiferromagnetic interaction. Eventually, our data do confirm that the magnetic interaction through the μ-H_2O bridge is weak.

Table 1.
Structural and magnetic data for μ-aqua bridged manganese(II) carboxylate dimers.

Compound	Mn-Mn(Å)	Mn-H_2O-Mn(deg)	J(cm^{-1})	Ref
$Mn_2(\mu$-$H_2O)(H_2O)_4(Cl_3CCO_2)_4$	3.79	113.4	-0.9	This work
$Mn_2(\mu$-$H_2O)(imd)_4(OAc)_4$	3.777	114.4	-1.26	[5a]
$Mn_2(\mu$-$H_2O)(L)_2(C_2F_5CO_2)_4$	3.739	114.6	-1.65	[5b]
$Mn_2(\mu$-$H_2O)(Me_2bpy)_2(Piv)_4$	3.595	110.2	-2.73	[5c]
$Mn_2(\mu$-$H_2O)(tmeda)_2(OAc)_4$	3.621	110.0	-2.95	[5c]
Imd=imidazole; L=2-ethyl-4,4,5,5-tetramethyl-3-oxo-4,5-hydro-1H-imidazolyl-1-oxyl; tmeda=N,N,N',N'-tetramethylethylenediamine; Me$_2$bpy=4,4' dimethylbipyridil; OAc=acetato ion, piv=pivalato ion				

Experimental

Magnetic susceptibility data (2-300K) were collected on powdered samples with a Quantum Design MPMS SQUID susceptometer working in a 0.1T applied magnetic field. All data were corrected for diamagnetism of the ligands estimated from Pascal's constants.[6] The synthesis of the title compound was described before [3].

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THREE SPIROSTANOL GLYCOSIDES FROM THE SEEDS OF HYOSCYAMUS NIGER L.

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Abstract: Three steroidal glycosides of spirostane series have been isolated from the seeds of *Hyoscyamus niger L.* (Solanaceae). Their structures were determined on the basis of chemical evidence and extensive spectroscopic methods including one-dimensional, two-dimensional NMR and MS analysis. In the genus Hyoscyamus the given compounds have been found out for the first time.

Keywords: steroidal glycoside, NMR analysis, Hyoscyamus.

Introduction

Hyocyamus niger L., commonly known as Black herbane, is widely distributed in Europa and Asia [1]. The chief constituent of Henbane leaves is the alkaloid Hyoscyamine, together with smaller quantities of Atropine and Hyoscine, also known as Scopolamine [2,3]. Other constituents of Henbane are a glucosidal bitter principle called hyoscytricin, choline, mucilage, albumin, calcium oxalate and potassium nitrate. On incineration, the leaves yield about 12 per cent of ash. By destructive distillation, the leaves yield a very poisonous empyreumatic oil. The basic component of the seeds is about 0.5 to 0.6 per cent of alkaloid, consisting of Hyoscyamine, with a small proportion of Hyoscine. The seeds also contain about 20 per cent of fixed oil [4].

Constituents of Henbane are generally used in various pharmaceutical preparations, which possess anti-spasmodic, sedative and analgesic properties [5]. All parts of the plant are very toxic. Symptoms of poisoning include impaired vision, convulsions, coma and death from heart or respiratory failure. H. niger has also shown the presence of tyramine derivative [6], withanolides [7], lignanamides [8] and flavonoids [9].Our interest in the chemical constituents elaborated by plants of Solanaceae family prompted us to take up the phytochemical investigation of the seeds of H. niger and report the isolation and structural elucidation of steroidal glycosides.

Results and Discussion

The ^{1}H NMR spectrum of **1** showed signals for four steroidal methyl groups at δ0.89 (3H, s, Me-19), 0.84 (3H, s, Me-18), 1.02 (3H, d, H-21), 0.98 (3H, d, Me-27), two methine proton signals at δ 3.68 (1H, m, H-3) and 4.39 (1H, m, H-16) indicative of secondary alcoholic functions, two methylene proton signals at δ3.41 (1H, m, H-26a) and 3.29 (1H, m, H-26b), ascribable to a primary alcoholic function, and signals for two anomeric protons at δ 4.52 (1H, d, J = 7.5 Hz) and 5.21(1H, d, J = 7.5 Hz). On the basis of the HSQC and HMBC correlations, the aglycone moiety of compound **1** was identified as (25R)- 5α-spirostan-3β, 26-diol - tigogenin. The C-25 configuration was deduced to be R based on the difference of chemical shifts ($\Delta_{ab} = \delta_a - \delta_b$) of the geminal protons at H$_2$-26 (Δ_{ab} = 0.12 ppm). It has been described that Δ_{ab} is usually > 0.57 ppm in 25S compounds and < 0.48 in 25R compounds [10]. 5α configuration was deduced by HMBC correlation between the methyl signal at δ 0.89 (Me-19) and carbon resonances at δ 55.7 (C-9), 46.0 (C-5) and 37.9 (C-1). Using a combination of 1D-TOCSY and DQF-COSY spectral analysis, the sugar moiety have been identified as glucose and rhamnose. A glycosidation shift was observed for C-2$_{glc}$ (δ 79.3). The HMBC spectrum showed key correlation peaks between the proton signal at δ 4.52 (H-1$_{glc}$) and the carbon resonance at δ 78.3 (C-3 of the aglycon), the proton signal at δ 5.21 (H-1$_{rha}$) and the carbon resonance at δ 79.3 (C-2$_{glc}$). Thus, the structure of compound **1** was deduced as (25R) - 5α - spirostan - 3β, 26-diol - 3-O-[α-L-rhamnopyranosyl-(1→2) - β - D-glucopyranoside].

Compound **2**, in the positive ESIMS, showed a major ion peak at m/z 723[M + Na]$^+$ and significant fragments at m/z 579 [M + Na - 146]$^+$ attributable to the loss of a pentose or a rhamnose unit. The molecular formula of **2** was unequivocally established to be $C_{39}H_{62}O_{12}$ by HR-MALDI-MS (m/z 725.392 [M + Na]$^+$). The ^{1}H NMR spectrum of **2** showed signals for four steroidal methyl groups at δ 0.79 (s, 3H-18), 0.79(d, 3H-27), 0.79(d, 3H-21) and 1.03(s, 3H-19), two methine proton signals at δ 3.38 (t, H-26a) and 3.47 (dd, H-26b) ascribable to a primary alcoholic functions, two methylene proton signals at δ 3.49 (1H-3) and 4.41 (1H-16) indicative of secondary alcoholic function and one double bond δ 5.35 (broad d, 1H-6). On the basis of the HSQC and HMBC correlations, the aglycon moiety was identified as (25R)–spirost-5-ene-3β, 26-diol – diosgenin. The NMR data of sugar moiety was identical of compound **1.** The structure of compound **2** was assigned as (25R)-spirost 5-ene-3β,26-diol 3-O-[α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyde]. Compound **1** and **2** have been previously reported in literature [11].

Table 1. ^{13}C NMR spectral data (600MHz, CD$_3$OD) of saponins (1-3) compounds carbon

| carbon	1	2	3
1	38.0	38.3	37.9
2	30.6	32.6	30.4
3	78.3	79.4	79.0
4	34.9	40.9	34.9
5	46.2	141.8	45.8
6	32.9	122.8	32.9
7	40.8	32.6	34.6
8	36.6	31.2	36.0
9	55.6	51.6	55.2
10	36.8	37.8	36.5
11	21.6	21.4	31.0
12	40.9	40.7	40.5
13	41.2	41.4	41.8
14	57.7	57.6	57.5
15	32.4	32.5	32.3
16	82.0	82.3	82.1
17	63.7	63.4	63.7
18	16.6	16.9	16.7
19	12.8	14.7	12.5
20	43.1	42.8	42.6
21	14.3	18.0	14.2
22	110.5	110.7	110.5
23	32.5	32.5	32.2
24	29.5	29.7	29.1
25	31.1	31.1	31.2
26	67.7	67.8	67.7
27	16.6	19.8	16.7
1'	100.2	100.2	102.4
2'	79.3	79.3	72.9
3'	78.9	78.9	75.2
4'	71.4	71.4	80.3
5'	77.4	77.4	79.1
6'	62.6	62.6	60.6
1"	101.8	101.8	104.8
2"	71.9	71.9	84.8
3"	72.2	72.2	78.0
4"	73.5	73.5	77.9
5"	69.5	69.5	71.6
6"	18.8	18.8	63.0
1'''	106.1		106.1
2'''	76.1		76.1
3'''	75.2		75.2
4'''	73.5		73.5
5'''	70.5		70.5
6'''	61.4		61.4

The ^{1}H NMR spectrum of **3** showed signals for four steroidal methyl groups at δ 0.89 (3H, s, Me-19), 0.82 (3H, s, Me-18), 1.00 (3H, d, H-21), 1.12 (3H, d, Me-27). The HMBC correlation of methyl groups clearly showed that the aglycon moiety was similar of compound **1** was identified as (25*R*)- 5α - spirostan-3β, 26-diol. One primary alcoholic function at δ 67.7 (C-26), suggesting the occurrence of a glycoside spirostanol skeleton. The ^{1}H NMR spectrum showed signals for three anomeric protons at δ 4.39 (1H, d, *J* = 7.5 Hz), 4.56 (1H, d, *J* = 7.5 Hz), and 4.69 (1H, d, *J* = 7.5 Hz). It was evident from the ^{1}H and ^{13}C NMR data that the sugar chain at C-3 of **3** consisted of three sugar units. The chemical shifts of all the individual protons of the three sugar units were ascertained from a combination of 1D-TOCSY and DQF-COSY spectral analysis, and the ^{13}C chemical shifts of their relative attached carbons could be assigned unambiguously from the HSQC spectrum. These data showed the presence of one β-galactopyranosyl unit (δ 4.40) and two β-glucopyranosyl unit (δ 4.56 and 4.69). A glycosidation shifts were observed for C-4$_{gal}$ (δ 80.3) and for C-2$_{glc}$(δ 85.9). The HMBC spectrum showed key correlation peaks between the proton signal at δ 4.40 (H-1$_{gal}$) and the

carbon resonance at δ 79.2 (C-3 of the aglycon), the proton signal at δ 4.56 (H-1$_{glc}$) and the carbon resonance at δ 80.3 (C-4$_{gal}$), the proton signal at δ 4.69 (H-1$_{glcI}$) and the carbon resonance at δ 85.9 (C-2$_{glc}$). The proton signal at δ 4.26 (H-1$_{glcII}$) and the carbon resonance at δ 75.9 (C-26 of the aglycon). Thus, the structure of compound **3** was deduced as (25*R*) - 5α- spirostan - 3β, 26-diol 3-*O*-[β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl -(1→4)-*O*-β-D-galactopyranoside], which has been previously isolated from Solanum plants [12].
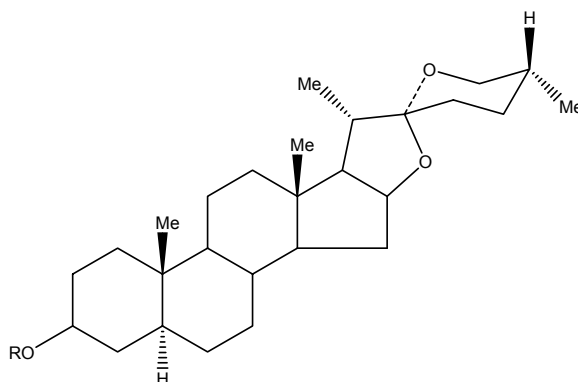
1: R=Rha(1-2)Glc

3: R=Glc(1-2)Glc(1-4)Gal
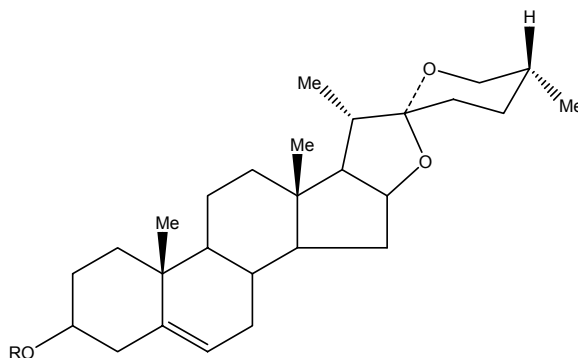
2: R=Rha(1-2)Glc

Conclusion

Three steroidal glycosides of spirostane series have been isolated for the first time from the seeds of *Hyoscyamus niger L*. During the investigation their structures have been determined as (25*R*) - 5α - spirostan - 3β, 26-diol - 3-*O*-[α-L-rhamnopyranosyl-(1→2) - β - D-glucopyranoside] for compound **1**, (25*R*)-spirost 5-ene-3β,26-diol 3-*O*-[α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyde] for compound **2**, and (25*R*) - 5α- spirostan - 3β, 26-diol 3-*O*-[β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl -(1→4)-*O*-β-D-galactopyranoside] for compound **3**. The given compounds have been earlier described in the literature.

Experimental

Plant Material has been collected in the scientific research field of the Institute of Scientific Researches and Technological Constructions for Tobacco and Tobacco Products of Moldova in November 2001 year. The voucher specimen has been deposited in the Laboratory of Selection

500 g of dry seeds were extracted three times in 50°C with n-buthanol saturated with water. After evaporation of n-butanol water extract was purified with chloroform and finally was crystallised in acetone. The residue was dried in vacuum at 40°C and the sum of steroidal saponins has been obtained in yellow powder in the yield 3,7%. 5g of extract has been chromatographied on silica gel column (30-500mm, 60-100μm, Merck). The column was washed with system chloroform-methanol-water (8:2:0→20:10:1) and 4-4ml fractions were collected. Fractions showing identical characteristics [TLC, silica gel, chloroform-methanol (4:1)] were combined. Obtained fractions were further separated on a C$_{18}$ column (7,8x300mm, LiChroprep RP18, 25-40μm, X Terra Waters) using a MeOH/H$_2$O (60-80% MeOH) gradient. Three single compounds were obtained.

1. HRMS, *m/z* 725.321 [calculated for C$_{39}$H$_{64}$O$_{12}$ (M)$^+$]; 579.7 [M-146]$^+$; ^{1}H NMR (aglycon) δ 4.41 (1H, m, H-16), 3.77 (1H, m, H-3), 3.47 (1H, m, H-26a), 3.34 (1H, m, H-26b), 0.88 (3H, s, Me-19), 0.82 (3H, s, Me-18), 1.00 (3H, d, H-21), 1.12 (3H, d, Me-27). (sugars) 4.52 (d, *J*=7.5 Hz, H-1Glc), 3.48 (dd, *J*=7.5 and 9.0 Hz, H-2Glc), 3.37 (dd, *J*=9.0 and

9.0 Hz, H-3Glc), 3.29 (dd, J=9.0 and 9.0 Hz, H-4Glc), 3.27 (ddd, J=2.5, 4.5 and 9.0 Hz, H-5Glc), 3.67 (dd, J=4.5 and 11.5 Hz, H-6aGlc), 3.88 (dd, J=2.5 and 11.5 Hz, H-6bGlc). 5.21 (d, H-1Rha), 3.95 (dd, H-2Rha), 3.67 (dd, H-3Rha), 3.42 (dd, H-4Rha), 4.16 (m, H-5Rha), 1.26 (d, H-6Rha). For ^{13}C NMR see Table 1.

2. HRMS, m/z 723.547 [calculated for $C_{39}H_{62}O_{12}$ (M)$^+$]; 577.5 [M-146]$^+$; ^{1}H NMR (aglycon) δ 4.41 (1H, m, H-16), 3.93 (1H, m, H-3), 3.47 (1H, m, H-26a), 3.34 (1H, m, H-26b), 1.02 (3H, s, Me-19), 0.84 (3H, s, Me-18), 0.82 (3H, d, H-21), 1.02 (3H, d, Me-27). (sugars) 4.52 (d, J=7.5 Hz, H-1Glc), 3.48 (dd, J=7.5 and 9.0 Hz, H-2Glc), 3.37 (dd, J=9.0 and 9.0 Hz, H-3Glc), 3.29 (dd, J=9.0 and 9.0 Hz, H-4Glc), 3.27 (ddd, J=2.5, 4.5 and 9.0 Hz, H-5Glc), 3.67 (dd, J=4.5 and 11.5 Hz, H-6aGlc), 3.88 (dd, J=2.5 and 11.5 Hz, H-6bGlc). 5.21 (d, H-1Rha), 3.95 (dd, H-2Rha), 3.67 (dd, H-3Rha), 3.42 (dd, H-4Rha), 4.16 (m, H-5Rha), 1.26 (d, H-6Rha). For ^{13}C NMR see Table 1.

3. HRMS, m/z 903.443 [calculated for $C_{45}H_{74}O_{18}$ (M)$^+$]; 741.6 [M-162]$^+$; 579 [M-2x162]$^+$; ^{1}H NMR (aglycon) δ 4.40 (1H, m, H-16), 3.69 (1H, m, H-3), 3.47 (1H, m, H-26a), 3.34 (1H, m, H-26b), 0.89 (3H, s, Me-19), 0.82 (3H, s, Me-18), 0.99 (3H, d, H-21), 1.27(3H, d, Me-27). (sugars) δ4.39 (d, J=7.4 Hz, H-1Gal), 3.60 (dd, J=7.4 and 9.0 Hz, H-2Gal), 3.53 (dd, J=4.0 and 9.0 Hz, H-3Gal), 4.02 (dd, J=2.5 and 4.0 Hz, H-4Gal), 3.69 (ddd, J=2.5, 2.5 and 4.5 Hz, H-5Gal), 3.62 (dd, J=4.5 and 12.0 Hz, H-6aGal), 3.95 (dd, J=2.5 and 12.0 Hz, H-6bGal), 4.56 (d, J=7.5 Hz, H-1Glc), 3.55 (dd, J=7.5 and 9.0 Hz, H-2Glc), 3.60 (dd, J=9.0 and 9.0 Hz, H-3Glc), 3.35 (dd, J=9.0 and 9.0 Hz, H-4Glc), 3.25 (ddd, J=2.5, 4.5 and 9.0 Hz, H-5Glc), 3.60 (dd, J=4.5 and 11.5 Hz, H-6aGlc), 3.93 (dd, J=2.5 and 11.5 Hz, H-6bGlc), 4.69 (d, J=7.5 Hz, H-1GlcI), 3.29 (dd, J=7.5 and 9.0 Hz, H-2GlcI), 3.36 (dd, J=9.0 and 9.0 Hz, H-3GlcI), 3.40 (dd, J=9.0 and 9.0 Hz, H-4GlcI), 3.42 (ddd, J=2.5, 4.5 and 9.0 Hz, H-5GlcI), 3.69 (dd, J=4.5 and 11.5 Hz, H-6aGlcI), 3.82 (dd, J=2.5 and 11.5 Hz, H-6bGlcI). For ^{13}C NMR see Table 1.

Acknowledgments

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