Società Chimica Italiana
Sezione Liguria e
Sezione Piemonte e Valle d'Aosta

Société Chimique de France
Section regional
Provence-Alpes-Côte d'Azur

GIORNATE ITALO-FRANCESI DI CHIMICA

GIFC 2010

ATTI DEL CONVEGNO

Genova, 26-27 aprile 2010

Sala del Minor Consiglio - Palazzo Ducale

Presentazione

La Sezione Liguria della Società Chimica Italiana, in collaborazione con la Sezione Piemonte-Valle d'Aosta e la Sezione PACA della Société Chimique de France, organizza a Genova nei giorni 26 e 27 aprile 2010 nella Sala del Minor Consiglio del Palazzo Ducale, la quinta edizione delle ***Giornate Italo-Francesi di Chimica***.

Questa manifestazione, che si svolge con cadenza biennale e viene organizzata alternativamente dai due Paesi, si è precedentemente svolta a Juan-les-Pins (2002), Genova (2004), Torino (2006) e Nice (2008).

Le Giornate hanno un carattere interdisciplinare ed hanno stabilito un duraturo contatto tra ricercatori delle regioni francesi Provenza, Alpi e Costa Azzurra e quelli delle regioni italiane Liguria e Piemonte-Valle d'Aosta in vista di una sempre più stretta integrazione, non solo scientifica e culturale, a livello europeo.

Nell'ambito di queste Giornate saranno illustrati, sotto forma di relazioni orali e posters, i più recenti risultati delle ricerche attualmente in corso presso Università, Enti di Ricerca, Aziende ed Industrie di questa macroarea transfrontaliera anche allo scopo di individuare temi di interesse comune da sviluppare congiuntamente. Sono inoltre previste conferenze plenarie che illustreranno lo stato dell'arte e le prospettive future di alcuni importanti settori della Chimica.

I temi trattati nel corso del Congresso rivestono un particolare interesse non solo per gli addetti ai lavori ma anche per l'opinione pubblica in quanto riguardano, tra le altre cose, la tutela della salute umana, il controllo degli alimenti, la protezione dell'ambiente e dei beni culturali, lo sviluppo sostenibile, nuovi materiali e nuove fonti di energia.

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Ringraziamenti

Le ***Giornate Italo-Francesi di Chimica 2010*** si sono svolte sotto il patrocinio e con il contributo di:

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PROGRAMMA

Lunedì 26 aprile

8.30 - 9.30 Registrazione
9.30 Apertura dei lavori e saluti ai partecipanti

9.50 **Uwe MEIERHENRICH**
Amino acids from ultraviolet irradiation of interstellar ice analogs (**PL-1**)
10.30 **Marco MINELLA**
Photocatalytic transformation of melamine: a useful tool to test the direct hole transfer ability of photocatalysts (**CO-1**)
10.50 **Bahcine BAKIZ**
Catalytic reactivity of LaOHCO3, La2O2CO3 and La2O3 phases interacting with CH4-air or CO-air gas flows (**CO-2**)

11.10 Coffee break - Sessione Poster

11.40 **Cristina ARTINI**
Structural and phase stability study of rare earth mixed oxycarbonates and oxides (**CO-3**)
12.00 **Huma ZILL-E**
A step forward in Green Chemistry: Clean recovery of onion flavonoids with novel technologies (**CO-4**)
12.20 **Chiara ROTOLO**
Parallel sequential four-component one-pot regioselective synthesis of diversely and densely substituted pyrazoles (**CO-5**)
12.40 **Jamal AL ABDULLAH**
Natural radioactivity in sediments of the Var river, SE France (**CO-6**)

13.00 Pausa pranzo - Sessione Poster

14.30 **Michele FORINA**
Non-specific physical information in analytical chemistry (**PL-2**)
15.10 **Ilaria MONFARDINI**
A mass spectrometry study (ESI-MS and CID) of metal triflate and metal triflimide catalysts (**CO-7**)
15.30 **Antonello BIGNASCA**
Evaluation of a biomimetic approach to study metals bioavailability in marine sediments (**CO-8**)

15.50 **Muhammad Kamran KHAN**

Chemical synthesis of flavanone glucuronides and chalcones and investigation of their affinity for human serum albumin (**CO-9**)

16.10 **Marina DI CARRO**

Fast liquid chromatography-tandem mass spectrometry for the determination of endocrine disrupting compounds in waters (**CO-10**)

16.30 **Nicolas GALY**

Diallylation of Ketones via the 2,2-Dialkylbenzodioxoles (**CO-11**)

16.50 Coffee break - Sessione Poster

17.20 **Anna PIATEK**

Fluorescent Benzofurazanic Chiral Reagents for Analysis of Biologically Important Chiral Carboxylic Acids by HPLC (**CO-12**)

17.40 **Bertrand SANCEY**

Industrial wastewater treatment by biosorption on starch-based material: chemical abatement and environmental impact (**CO-13**)

18.00 **Nadia BARBERO**

A sensitive and practical fluorimetric test for CNTs acidic sites determination (**CO-14**)

18.20 **Vincent MALNUIT**

Synthesis of Modified Nucleosides Using a Novel One Pot-Three component Reaction (**CO-15**)

18.40 **Carlo SCAPOLLA**

Thioisomunchnones derivatives of mandelic acid and vanilmandelic acid : a serendipitous discovery with interesting applications (**CO-16**)

Martedì 27 aprile

9.00 **Marcello BARICCO**

Materials for hydrogen storage (**PL-3**)

9.40 **Ilie HANZU**

Electrochemical properties of self-organized titania nanotubes: applications to energy storage (**CO-17**)

10.00 **Tania MONTANARI**

Hydrogen from renewables: Ethanol steam reforming over Co-Ni-Zn-Al catalysts (**CO-18**)

10.20 **Antonio CRAVINO**

Small and Soluble Molecules as Donor Materials in Bulk Heterojunction Organic Solar Cells (**CO-19**)

10.40 **Gianmarco IELUZZI**

Transfer and Transformation of Chemical and Physical Knowledge. A Crucial Case in the History of Superconductivity (**CO-20**)

11.00 Coffee break - Sessione Poster

11.30 **Elena CELIA**
Grafting of silica nanoparticles on polyethylene (**CO-21**)

11.50 **Luca BORAGNO**
Blocky ethylene/4-methyl-1-pentene copolymers from single center catalysts: microstructure and crystallization behaviour (**CO-22**)

12.10 **Damien MAILHOL**
Chiral sulfoximines in Multiple Bond-Forming Transformations (**CO-23**)

12.30 **Dario CAVALLO**
Polymer Crystallization under Processing Conditions (**CO-24**)

12.50 **Vito VECE**
In(III)-Catalyzed Tandem C-C and C-O Bond Formation between Phenols and Allylic Acetates (**CO-25**)

13.10 **Elisa ROBOTTI**
Identification of a multivariate target function representing S/N from complex mass spectra – Optimisation by regular simplex (**CO-26**)

13.30 Pausa pranzo - Sessione Poster

15.00 **Jean-Luc PARRAIN**
Metal complexes catalyzed preparation of heterocycles: application to the synthesis of spirolactones (**PL-4**)

15.40 **Alberto MINASSI**
Multicomponent reactions beyond the iminium ion trail: total synthesis of arzanol, the anti-inflammatory principle of eternelle (Helicrysum italicum L.) (**CO-27**)

16.00 **Maria del Mar SANCHEZ DUQUE**
Highly Enantioselective Organocatalyzed Michael Addition of ß-Ketoamides onto Enones (**CO-28**)

16.20 **Andrea BASSO**
E PLURIBUS UNUM: A pluripotent multicomponent approach to DOS libraries (**CO-29**)

16.40 **Julien GODEAU**
Synthesis of polycyclic compounds by cycloisomerization of polyenes catalyzed by Lewis superacids (**CO-30**)

17.00 Chiusura dei lavori

Conferenze Plenarie

Amino Acids from Ultraviolet Irradiation of Interstellar Ice Analogs

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Amino acids, the molecular building blocks of proteins, certainly played a key role in both the emergence of cellular life on Earth and the development of biomolecular asymmetry. We experimentally simulated the abiotic formation of amino acids and diamino acids in interstellar ices by the effect of UV irradiation on CO, CO_2, CH_3OH, NH_3, as well as H_2O and identified 16 amino acids among the remaining products (Muñoz Caro et al. 2002; Meierhenrich, 2008). The presence of diamino acids in the Murchison meteorite verified the above simulation experiment (Meierhenrich et al. 2004). The identified amino acids were racemic, since the experiment was performed under symmetric conditions. However, interstellar electromagnetic radiation is asymmetric, namely circularly polarized. Here we report on enantioselective photolysis of chiral amino acids under interstellar conditions. Circular dichroism CD spectra of amino acids were recorded in the amorphous solid state. In order to achieve vacuum UV asymmetric photodecomposition of racemic mixtures of solid state amino acids, circularly polarized synchrotron radiation was used to irradiate the samples. After photodecomposition, the enantiomeric excess was found to be + 2.6 % in the case of leucine (Meierhenrich et al. 2005). The results will be verified by the 'chirality-experiment' onboard the Rosetta Lander, which will allow the quantification of chiral organic molecules on a cometary surface (Thiemann and Meierhenrich, 2001).

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Thiemann, W. H.-P., Meierhenrich, U. J. (2001) ESA mission ROSETTA will probe for chirality of cometary amino acids. *Orig. Life Evol. Biosphere* 31:199–210.

Non-specific physical information in analytical chemistry

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The procedures generally used to measure the relative or absolute quantity of an analyte are based on a more or less complex set of chemical and physical treatments with the elimination of interferents. A final state is obtained where a suitable physical quantity is specific, i.e. an univocal, possibly linear, function of the quantity of the analyte. The parameters of the function are obtained by means of calibration, using samples with known concentration of the analyte.

These “classic” procedures requires generally a long time, sometimes days, and the use of pure chemicals, so that their cost is large.

Presently, especially in the control of rough materials, quality control, process control, environmental and clinical analysis, analytical techniques able to give the desired result in a very short time (sometimes seconds) at a very low cost (sometimes fraction of €) are required.

For this reason, in the recent years analytical chemistry developed method based on the determination of non-specific physical quantities, frequently spectra (visible, near infrared) obtained in a very short time on the original sample, without or with a minimum rapid pretreatment.

The physical information is constituted by many predictor variables, e.g. one thousand absorbances from a spectrum. A chemometrical tool, an hidden system of equations, is used to obtain the response, i.e. the chemical quantity. The system of equations takes into account all the possible interferences. The result is a function that computes the response from the value of the predictors. As in the classical procedure, the parameter of this function are obtained by means of calibration, where the secondary standards are samples where the chemical quantity has been measured by means of a reference technique.

Today these techniques, especially near-infrared spectroscopy (NIR) are used for billions of determinations, generally executed with the blind use of the chemometrical tool, a black box in the software associated to the instrument.

Here we present some examples of the application of analytical procedures based non-specific physical information (NIR, visible spectra, artificial nose, electronic tongue), with special attention to the risks associated to the use of complex methods of Chemometrics without sufficient knowledge of their characteristics and limits.

Materials for Hydrogen Storage

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Hydrogen is conventionally stored in high pressure gas cylinders and, as a liquid phase, in opened tanks. These methods present several economic and security problems. So, hydrogen storage in solid state materials is a suitable method for future clean mobile applications.

Hydrogen may be inserted as a solid solution in Laves phases (AB_2 type: ZrV_2), which have a “sponge-like” behaviour. In this case, H_2 is up-taken and released without changing the crystal structure of the compound, but only increasing the lattice parameters. Some pure elements (Mg) and intermetallic compounds (AB_5 type: $LaNi_5$) form an hydride phase upon hydrogen absorption. For these systems, the thermodynamic aspects of hydride formation from gaseous hydrogen may be described by pressure-composition isotherms (P-C-T). In fact, when solid solution and hydride phases coexist, there is a plateau in the isotherms, the length of which determines the amounts of hydrogen stored. Recent research work is addressed to the selection of suitable catalysts in order to increase the desorption rate.

Recently, attention has been focused on complex hydrides, which are interesting because of their light weight and their high number of hydrogen atoms per metal atom. In this case, chemical reactions are involved in the up-take and release of H_2 gas. These compounds are based on complex anions, containing hydrogen bonded to a base element, which are balanced by metal cations. Examples are given by alanates, $M(AlH_4)_n$, and boron tetrahydrides, $M(BH_4)_n$. These compounds, by decomposition reactions or by reaction with H_2O, release H_2 from their structure. Usually, fast desorption and reverse reactions need suitable catalysts.

In order to be used for applications, the thermodynamic stability of a candidate hydrogen storage material should be suitable for hydrogen sorption at room conditions. By mixing different hydrides, it is possible to promote the hydrogenation/dehydrogenation processes. On the other hand, small changes in composition allow a tailoring of thermodynamic parameters. So, knowledge of thermodynamic stability of hydrides is fundamental to study the hydrogenation/dehydrogenation processes. Moreover, thermodynamics and phase diagrams are useful to rationalize synthesis reactions of these compounds and to suggest possible alternative reaction routes.

In this presentation, the fundamental aspects of hydrogen storage will be presented. Examples of experiments and thermodynamic calculations on different hydrogen storage materials will be presented.

Metal complexes catalyzed preparation of heterocycles: application to the synthesis of spirolactones

J.-L. Parrain

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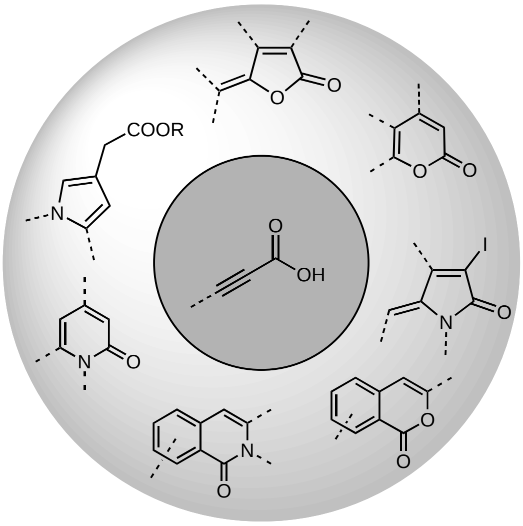
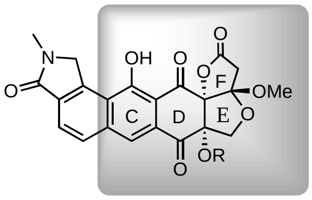
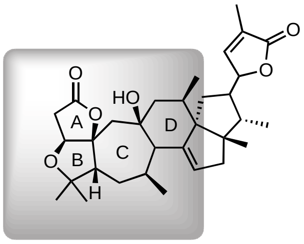
The present talk deals with some metal catalyzed organic transformations from simple α,β-alkynoic building blocks which might be of interest in selective synthetic chemistry. In this context, the palladium catalyzed tandem cross-coupling /annulation tandem reaction of β-haloalkenoic acids or amides with organostannanes provides a convenient route to alkylidenebutenolides, pyrrolones, pyranones, pyrroles, coumarins, isocoumarins and isoquinolones with a good control of regio- and dia-stereoselectivity. Changing the palladium complex to copper salt has also revealed particular reactivity for the preparation of γ-alkylidenebutenolides from terminal alkynes.



Application toward the core of complex natural spirolactones (lactonamycine and lancifodilactone) will also be detailed.



Lactonamycine



Lancifodilactone A

Comunicazioni Orali

Photocatalytic transformation of melamine: a useful tool to test the direct hole transfer ability of photocatalysts

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The transformation of 2,4,6-triamino-1,3,5-triazine (melamine) was studied by using different advanced oxidation technologies (AOTs).[1] Particular attention was devoted to photocatalytic transformation of melamine under UV-irradiated TiO_2. The systems involving homogeneous hydroxyl radicals, as generated by H_2O_2/hν, Fenton reagent, sonocatalysis, are ineffective. However, melamine is degraded by TiO_2 photocatalysis or by $SO_4^{\bullet -}$ ($S_2O_8^{2-}$/hν or $S_2O_8^{2-}$/heat). The time evolution of long-living intermediates, such as 2,4-diamino-6-hydroxy-1,3,5-triazine (ammeline) and 2-amino-4,6-dihydroxy-1,3,5-triazine (ammelide), have been followed, being 2,4,6-trihydroxy-1,3,5-triazine (cyanuric acid) the final stable product.[2] During both photocatalytic and $S_2O_8^{2-}$/hν experiments, in the early steps a fairly stable intermediate evolving to ammelide is observed in a large extent. This intermediate was identified as 2,4-diamino-6-nitro-1,3,5-triazine. This indicates that the amino- is oxidized to nitro-group through several consecutive fast oxidation steps, and that a hydrolytic step leads to the release of nitrite in solution.

In the presence of irradiated TiO_2, hole scavengers, such as methanol and bromide ions, completely stop the degradation, whereas chloride and fluoride[3] ions decrease the degradation rate. A drastic abatement of the melamine transformation rate was observed in conditions of instability (coagulation) of the TiO_2 colloid: the contact points between the particles behave as recombination centers reducing the quantum yield of the process.

The melamine transformation is initiated by an electron abstraction, whose formal potential lies in the range 1.9-2.6 V vs NHE. The experimental data imply that the photocatalytic transformation starts with a direct hole transfer (DHT) to the melamine, suggesting that both direct electron transfer and $^{\bullet}OH$ mediated mechanism can operate depending on the nature of the organic substrate. Melamine cannot absorb at the TiO_2 surface and so an outer sphere DHT mechanism is suggested.

The study of the photocatalytic degradation of melamine using two different commercial titanium dioxides, such as P25 by Degussa (the standard in the field of photocatalysis) and TiO_2 by Merck, showed a marked different in the melamine degradation rate. In the presence of TiO_2 by Merck the initial rate decreases drastically showing the inability of this photocatalyst to oxidize efficiently the substrate by a direct hole injection mechanism. These data suggest that the peculiar properties of the P25 TiO_2 derive from its ability to photooxidize efficiently the substrates not only by $^{\bullet}OH$ mediated mechanism, but also by a direct hole injection pathway. Then, the photodegradation of melamine is an efficient tool to evaluate the direct hole transfer ability of a photocatalyst.

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Catalytic reactivity of LaOHCO3, La2O2CO3 and La2O3 phases interacting with CH4-air or CO-air gas flows

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The general aim of this study was to investigate the potential application of solid phases belonging to the La_2O_3-H_2O-CO_2 system in gas sensors or CO_2 absorbing devices for CO_2 capture. This lanthanum-based system could be sensitive to three types of gases, including H_2O and CO_2, by using a specific temperature range in which the hydroxycarbonates $LaOHCO_3$ or dioxycarbonates $La_2O_2CO_3$, or oxide La_2O_3 are stable.

Catalytic interactions between flowing gas mixtures of air and CH_4 or CO and three catalytic powders – lanthanum oxide, lanthanum hydroxycarbonate, and lanthanum dioxycarbonate – were studied as a function of time and temperature using Fourier Transform infrared (FTIR) spectroscopic analyses of emitted CO_2 gases. The three powdered materials were synthesized following a specific coprecipitation route[1],[2] and then characterized by X-ray diffraction as well as scanning and transmission electron microscopy. The thermal decomposition of the hydroxycarbonate, $LaOHCO_3$, was studied using thermal differential analysis coupled with thermogravimetry. The catalytic efficiencies were determined from the intensity variations of a vibrational CO_2 FTIR band.

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Structural and phase stability study of rare earth mixed oxycarbonates and oxides

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Rare earth (RE)-based oxides are widely studied materials because of their luminescence properties and their use as HTSC precursors. Many oxides, such as $Y_3Al_5O_{12}$ (YAG) and the Lu_2O_3, Gd_2O_3 and Y_2O_3 sesquioxides[1], can in fact become luminescent if properly doped by optically active ions; besides, as many HTSC contain RE ions (YBCO, Ru-based superconductors[2]), RE oxides are extensively used in the HTSC synthesis. Moreover, due to their thermodynamic stability and chemical durability against H_2O and CO_2, oxycarbonates in the hexagonal form can act as hosts of optically active ions, and their structural similarity with the hexagonal rare earths sesquioxides, that are good hosts of luminescent ions, make them possible candidates in the search for new phosphors[3].

In the search for new possible luminescent and superconducting materials, a thorough study of the structural and stability properties of several rare earth mixed oxycarbonates and oxides has been performed. In particular the Gd/Nd, the Gd/Ce and the La/RE (RE=Dy Ho, Er, Tm, Yb, Lu) systems have been analyzed; all the samples have been obtained by thermal decomposition of the coprecipitated mixed oxalates. The phase stability of the system Gd_2O_3-Nd_2O_3 up to 1350°C has been studied[4], as well as the $Gd_2O_2CO_3/Nd_2O_2CO_3$ pseudobinary phase diagram up to 660°C[5]. A stability study of perovskitic $LaREO_3$ oxides (RE=Dy, Ho, Er, Tm, Yb, Lu) as a function of temperature has been undertaken[6]: a correlation between the Goldschmidt t value and the perovskitic stability field amplitude was found. Magnetic measurements, performed on all the perovskitic samples, showed that t is also related to the exchange interactions. In all the aforementioned cases a correlation between the crystal form and the average cationic radius has been established.

Gd/Ce mixed oxides, on the contrary, show a much more complicated structural behaviour because of the closeness of Ce^{4+} and Gd^{3+} radii and the resemblance of CeO_2 and Gd_2O_3 structures[7]. This system has been studied collecting diffractograms at the Elettra synchrotron facility: the results have revealed that Vegard's law is not followed and that a continuous transition between the two structural forms takes place via the growth of small microdomains of one structure in a matrix of the other structure.

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[5] Artini C., *J. Alloys Compd*. **2009**, *477*, 532-536

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A step forward in Green Chemistry: Clean recovery of onion flavonoids with novel technologies

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Solvent free extraction of onion (*Allium cepa L.)* flavonol content, whose antioxidant activity relates to human health promoting effects, has been done first time with a novel technology microwave hydrodiffusion and gravity extraction (MHG)[1]. Effectiveness of this innovative method in extraction of onion total phenolic content and major and minor flavonoids content have been evaluated and compared with conventional solvent extraction. Microwave extraction offers important advantages like shorter extraction time (23 mins), cleaner feature (no solvent or water used) and extraction of valuable onion crude juice retaining fresh organoleptic properties with higher phenolic content at optimized power (500W). Along with this, efficiency of this novel method have also been checked by analysing the antioxidant capacities of extracts of different colored onion varieties by using different assays like DPPH, ORAC and inhibition of linoleic acid peroxidation tests.

MHG is an attractive novel technology that clearly offers opportunities for food processing industries to meet the growing demand of consumers for healthier food products as it works in absence of any solvent[2]. Along with microwave we have also performed the extraction of onion antioxidants with ultrasound, another novel technology. A response surface methodology was launched to investigate the influence of process variables on ultrasound assisted extraction followed by a central composite design approach. Furthermore, the extracts was also analysed by above stated tests for their antioxidant activities.

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Parallel sequential four-component one-pot regioselective synthesis of diversely and densely substituted pyrazoles

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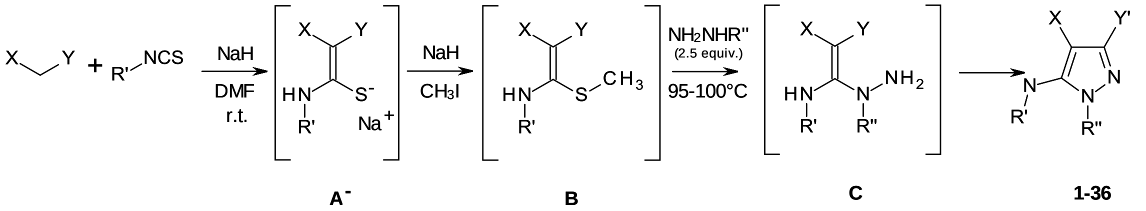
Functionalized pyrazoles and their fused analogues constitute the core structures of blockbuster drugs such as Acomplia, Celebrex and Viagra, as well as promising compounds endowed with different activities such as anti-inflammatory, analgesic, antibacterial and anti-cancer[1]. Although the usual synthetic methods for the preparation of pyrazoles (condensation between an hydrazine derivative and a 1,3-dicarbonyl compound or by 1,3-dipolar cycloaddition of diazoalkanes or nitrile imines to olefins or acetylenes) are simple and efficient, the use of unsymmetrically substituted precursors often leads to a mixture of regioisomers[1]. As a part of an extension of our studies on synthetic applications of polarized ketene *N,S*-acetals[2], a parallel one-pot regioselective protocol has been developed (Scheme 1) to prepare a small pyrazole library by using a Carousel synthesizer.

Scheme 1.



X: COOMe, COOEt, SO_2Ph, SO_2(4-Me-)Ph, SO_2Me, $CONH_2$, CN, COPh; **Y'**: Me, t-Bu, Ph, (4-Cl-)Ph, (3-Br-)Ph, (4-Br-)Ph, (4-F-)Ph, (4-NO_2-)Ph, NH_2, 2-Thiophen-; **R'**: C_6H_{11}, $PhCH_2$, Ph, (4-NO_2-)Ph, (4-OMe-)Ph, (3-NO_2-)Ph, (3-OMe-)Ph, (2-NO_2-)Ph, (2-OMe-)Ph; **R''**: H, Me

The condensation of active methylene building blocks X-CH_2-Y with cycloesil-/benzyl-/aryl-isothiocyanates in the presence of sodium hydride gave the corresponding ketene aminothioacetal sodium salts **A**$^-$. The subsequent alkylation of **A**$^-$, as enethiolate anions, with methyl iodide produced (isolable) *push-pull* ketene alkyl/aryl-amino methylthio acetals **B**. Displacement of the methylsulfanyl group by either the nitrogen of hydrazine or the more nucleophilic nitrogen of methyl-/benzyl-hydrazine led to the enehydrazine intermediates **C** (some of which could be isolated). In the final step, **C** underwent intramolecular regioselective cyclization to afford highly or fully substituted pyrazoles **1-36**, as a result of chemoselective addition of the amino group to Y (assuming that its unsaturated carbon is more electrophilic than that of X). The observed reactivity trend: Y = R-/Ar-CO > X = CN; Y = CN >> X = COOR, is in accordance with electrophilicity of the sp^2 and *sp* carbons of these functionalities. On the whole, the nature of X, Y, R' and R'' can influence the overall yield or the formation of the final products (e.g., the reaction does not work with X, Y = COOR; or R'= Me; or R''= aryl). This new procedure is scalable and could be routinely carried out without chromatographic purifications.

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Natural radioactivity in sediments of the Var river, SE France

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Human beings have always been exposed to natural radiation, which is mainly due to the activity of primordial radionuclides ^{238}U, ^{232}Th and ^{40}K, and of natural decay series, present in the earth's crust, in building materials, air, water, food and in the human body itself[1]. Natural radionuclides are wide spread in the earth's environment and exist in various chemical forms in soil, sediments, rocks, plants, water and air[2] [3], Most of the sediments that settle in river beds originate from weathering and erosion of rocks and soils. The natural radionuclide concentration in sediments should be representative of the mean distribution of radionuclides in the river catchment. The study of the activity distribution of primordial radionuclides ^{238}U, ^{232}Th and ^{40}K allows the understanding of the radiological implication of these elements due to-the γ-ray exposure.

A core of about 9.5 m depth, collected in sediments of the lowest dam of the Var river (SE France), was the subject of detailed geochemical studies. The activity concentrations of natural radionuclides in sediment of the Var river were measured using γ-ray spectrometry with the aim of estimating the radiation hazard and establishing a database for radioactivity levels of river sediment. The activity concentrations of ^{238}U, ^{232}Th and ^{40}K in sediment samples ranged from 14.5 to 28.0 Bq kg^{-1}, 14.5 to 31.7 Bq kg^{-1} and 485.9 to 833.0 Bq kg^{-1}, respectively. Concentration of uranium measured by inductively coupled plasma mass spectrometry (ICP-MS) was compared with concentrations of uranium calculated from activity concentrations measured by gamma spectrometry and a good correlation was found. Concentrations of uranium were 1.16-2.24 mg kg^{-1} and 1.2-1.5 mg kg^{-1} by spectrometry gamma and ICP-MS respectively.

Granite exists in the Var river catchment that may sensibly increase the U concentration in sediments. The activity concentrations of these radionuclides obtained in the present study were compared with those determined in other areas of the world (Albania, Spain, Algeria and Italy) [4]. The ^{238}U and ^{232}Th concentrations are similar to Albania and Algeria and lower than others. The ^{40}K concentration is higher than others.The overall mean outdoor terrestrial gamma dose rate is 40.8 nGy h^{-1} and the corresponding outdoor annual effective dose is 0.05 mSv. These data can be used to detect end measure accidental radionuclide contaminations in the Var catchment in the future.

Keywords: Radionuclides - River sediment – gamma Spectrometry-Annual effective dose.

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A mass spectrometry study (ESI-MS and CID) of metal triflate and metal triflimide catalysts

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Metal triflates and triflimides behave as "Lewis superacids" and are currently employed as catalysts in the domain of organic synthesis.[1,2] Their superacidic character is often correlated to the efficiency of their catalytic activity. Several hypotheses about the nature of the reaction intermediates involved have been made, but in most of the cases the reaction mechanism remains unclear.

Electrospray Ionization Mass Spectrometry (ESI-MS) is one of the most performing tools for the study of chemical reactions.[3] The ESI soft ionization conditions are suitable to detect all the species present in reaction medium directly from solution to the gas phase. It can afford therefore reaction mechanism investigation through reaction intermediates identification and characterization.

At first, we focused on the study of the interactions of metal triflates and triflimides with neutral ligands (e.g. ketones, aldehydes, amides, phosphates). It was observed that an equimolar mixture of a triflate (or a triflimide) metal salt and a neutral ligand gives a mass spectrum corresponding to a complex of the general formula: $[M^{n+}(OTf^{-})_{n-1}(L)_{m}]^{+}$ (or $[M^{n+}(NTf_2^{-})_{n-1}(L)_{m}]^{+}$).

A further characterization of metal complexes was possible using collision induced dissociation (CID) that provided the complete fragmentation pattern of the complex precursor peak. The relative intensity of the product peak corresponding to the loss of the neutral ligand compared to the intensity of the product peak, corresponding to the counterion triflate or triflimide loss shows the gas phase affinity of the metal ion for the neutral ligand versus the counterion.

The ESI-MS behavior of the formed complexes suggests a criterion to set up a relative affinity scale of a series of neutral ligands for a specific metal, assuming that the formation and fragmentation of the complexes $[M^{n+}(OTf^{-})_{n-1}(L)_{m}]^{+}$ or $[M^{n+}(NTf_2^{-})_{n-1}(L)_{m}]^{+}$ correspond to the Lewis acidity of the selected metal.[4] The adopted ESI-MS approach for the study of triflate and triflimide catalysts leads therefore to many interesting perspectives, giving rise to a better understanding of the mechanism still unknown of some reactions currently in use.

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Evaluation of a biomimetic approach to study metals bioavailability in marine sediments

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Most researches concerning the availability of trace metals in sediments employ single reagents or selective extractions methods, using chemical reagents such as unbuffered electrolytes, dilute organic acids, acidified reducing or oxidizing agents. These approaches certainly give more detailed information on metals mobility in respect to total determination. However, although the geochemical selectivity of chemical reagents has been shown, their biological significance has not been rigorously demonstrated [1]. Indeed, such reagents are not able to mimic the conditions encountered in the digestive environment of benthic deposit-feeding animals (organisms that obtain food particles by sifting through sediments) where hydrolytic enzymes, surfactants and chemicals derived from pre-digested food abound [2]. In these conditions, not only food particles are solubilised, but also other components, as metals and other contaminants, can be released from the sediments. Therefore, it seems that a more appropriate means of studying bioavailability is the use of enzymes representative of those encountered in the gut of marine organisms [1]. This biomimetic approach can lead to more realistic information about the bioavailability of pollutants (in particular trace metals) in sediments.

With these premises, a comparison study was undertaken in order to evaluate metal bioavailable fractions in marine sediments, operationally measured both by a sequential selective extractions scheme and a biomimetic approach. Different experimental conditions were investigated and the enzyme was employed both untreated and thermally denatured, in order to study release mechanisms of metals. As expected, the bioavailable fraction evaluated with the biomimetic approach was often significantly lower than the one relating to the first step of sequential selective extractions. Moreover, a good correlation was found between the fraction of metal available to the enzyme and the enrichment factors in the gut fluids of deposit-feeding organisms, suggesting that an enzymatic approach is qualitatively more reliable than a chemical extraction in replicating the mechanisms of metal mobilization that occur in deposit-feeders guts.

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Chemical synthesis of flavanone glucuronides and chalcones and investigation of their affinity for human serum albumin

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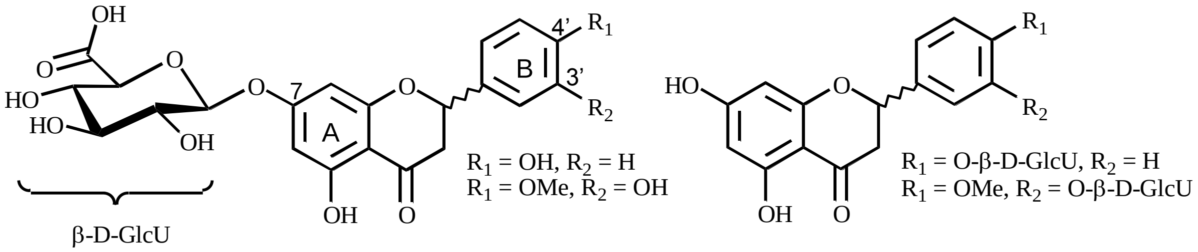
Polyphenols could help prevent the development of cardiovascular diseases and cancers by reducing reactive oxygen species (antioxidant activity) and interacting with specific cell proteins. However, a critical point in understanding their potential health effects is the knowledge of their bioavailability, i.e. their intestinal absorption, metabolism, tissue distribution and excretion[1]. The interaction of polyphenol metabolites with human serum albumin (HSA) is an important factor in their transport to biological sites[2].

Despite the high consumption of citrus fruits and juices worldwide, the bioavailability of flavanones, the major class of citrus polyphenols, is still incompletely known. Currently, there is a great need of polyphenol conjugates for bioavailability studies and investigations of specific cell effects. In the present study, glucuronides of hesperetin and naringenin (Scheme), the major flavanone aglycones in orange and grapefruit respectively, were chemically synthesized and investigated for their affinity for HSA.



Scheme: structure of the flavanone glucuronides synthesized in this work

Synthesis: First, the OH group at C-7, which is the most acidic, was protected by regioselective benzoylation to allow subsequent glucuronidation of the OH group at C-3' or C-4' (B-ring). On the other hand, the regioselective debenzoylation at C-7 of the perbenzoylated flavanone aglycones allowed glucuronidation at the same position (A-ring). After careful deprotection in mildly alkaline conditions, the target compounds were purified and characterized by NMR and MS.

Binding to HSA: The affinity of the four glucuronides for HSA was tested via their ability to quench the intrinsic fluorescence of HSA (single Trp residue in sub-domain IIA). The binding constants were estimated and compared with those of the aglycones. Investigations of competitive or noncompetitive binding of the glucuronides in the presence of fluorescent HSA ligands used as probes allowed us to get some insight in the binding sites. The study was also extended to the hesperetin and naringenin chalcones (synthesised using optimized alkaline conditions), which are the biosynthetic precursors of flavanones.

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Fast liquid chromatography-tandem mass spectrometry for the determination of endocrine disrupting compounds in waters

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The determination of five endocrine disrupting compounds (nonylphenol, bisphenol A, estrone, 17β-estradiol and 17α-ethinylestradiol) in water was performed by means of fast liquid chromatography-electrospray ionization-tandem mass spectrometry (LC-ESI-MS-MS).

The method was developed testing different columns; the chromatographic separation of the analytes was optimized using a water–acetonitrile gradient elution on a Pinnacle DB Biphenylic column, which allowed the separation of the analytes in less than six minutes.

Quantitative analysis was performed in Multiple Reaction Monitoring (MRM) mode; two transitions for each compound were monitored.

Calibration curves using bisphenol A-d_{16} as internal standard showed good correlation coefficients (0.9993-0.9998). All figures of merit of the method were satisfactory; limits of detection were in the low pg range for all analytes.

The method was applied to the determination of the analytes in a drinking water treatment plant in Liguria (Italy) using a passive sampling approach. POCIS (Polar Organic Chemical Integrative Samplers) were deployed both in the influent and in the effluent; results showed low concentration of the analytes in the influent and negligible in the outlet, reflecting the expected function of the treatment plant.

Diallylation of Ketones via the 2,2-Dialkylbenzodioxoles

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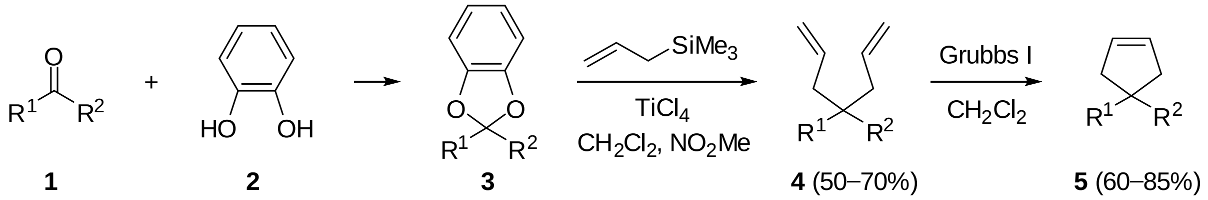
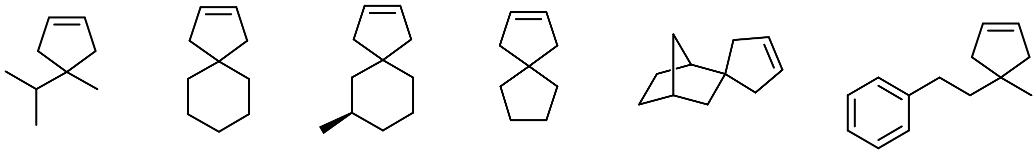
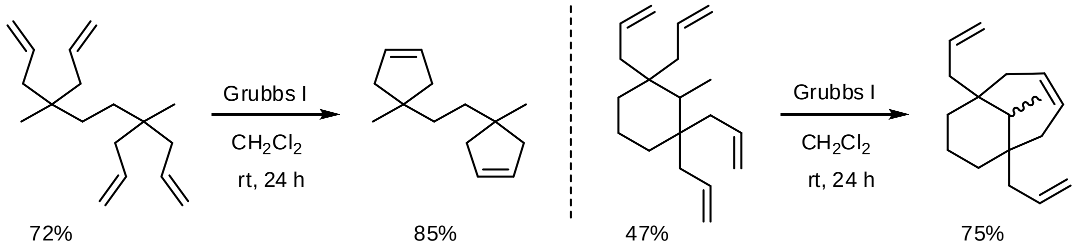
Reaction of aliphatic ketones **1** with catechol **2** afforded 2,2-dialkylbenzodioxoles **3**. Treatment of these benzodioxoles wirh allyltrimethylsilane in the presence of $TiCl_4$ led to 4,4-dialkylhepta-1,6-dienes **4** resulting from a diallylation process. Ring-closing metathesis gave rise to 4,4-dialkylcyclopentenes **5**.[1]



By this process we obtained, from simple dialkylketones, many original products in 3 steps. To our knowledge, it is the first general procedure which afforded this kind of product from ketones.





In conclusion, we found that, while ketals are mainly known as a protective group, in the specific case of the $TiCl_4$-mediated allylsilane reaction, they could be a useful tool to control the selectivity of this reaction and to allow the formation of various 4,4-dialkyl-1,6-dienes. Now, we focus our efforts on the cycloisomerisation of such 1,6-dienes.

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Fluorescent Benzofurazanic Chiral Reagents for Analysis of Biologically Important Chiral Carboxylic Acids by HPLC

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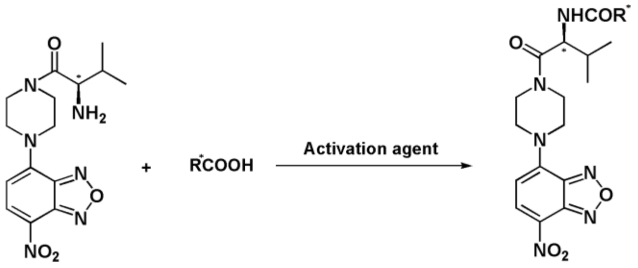
The sensitive and selective determination of biologically active compounds carboxylic acids such as fatty acids, bile acids, prostaglandins, and drugs is very important in biological and biomedical sciences. High-performance liquid chromatography (HPLC) has been most widely used for the analysis of chiral molecules. Enantiomeric resolutions and quantitations of enantiomeric drugs and biologically active compounds have been achieved with the direct HPLC technique, using chiral stationary phase (CSP) columns. However, the direct resolution of racemates is usually not adequate for trace analysis in biological specimens, in terms of sensitivity and selectivity and resolution by means of direct methods of some enantiomeric compounds such as amines and carboxylic acids is often difficult.[1] Higher cost, shorter lifetime and intrinsic difficulty in selecting the most adequate column are also disadvantages of CSP columns.[2] In this context, and on the basis of our previous experience in this field,[3,4] we have synthesized some new chiral labeling reagents having benzofurazane structure and investigated their reactivities towards both endogenous compounds such as lactic acid and nonsteroidal anti-inflammatory drugs (NSAIDs) such as ibuprofen. We found that our derivatization reagents reacted with carboxylic acids in the presence of activation agent under mild conditions at room temperature to form the corresponding fluorescent diastereomeric amides. These products can be easily separated by RP-HPLC, thus allowing accurate quantification of the corresponding acids.



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Industrial wastewater treatment by biosorption on starch-based material: chemical abatement and environmental impact

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Among the industrial activities, the surface treatment enterprises are today considered to be one of the largest water consumers and polluters. In fact, their process waters contain both organic and metallic pollutants, coming from rinsing and washing baths, which are quite difficult to remove. In practice, many industrial wastewater treatments involve three main successive stages: *i)* a pre-treatment or specific treatment using chemical methods (dechromatation, decyanidation); *ii)* a decontamination step using conventional chemical methods (neutralisation, precipitation, extraction, evaporation, oxidation, flocculation); *iii)* and the treatment of the obtained sludge (i.e., supervised tipping). Generally, the second stage is achieved by increasing the pH to convert soluble metals into an insoluble form (i.e., hydroxides). In certain cases, an additional treatment of the treated water can be required to remove the remaining metal ions, mainly by means of adsorption onto commercial activated carbons. Because of active carbons high costs, in recent years a big interest on the development of alternative sorbents has intensified. Attention was focused on various natural solid supports, such as polysaccharides, able to remove pollutants from contaminated water at low cost.

In our group, we have studied the use of starch-based materials as new sorbents for pollutant removal such as dye molecules, metal ions and aromatic compounds[1,2]. These low-cost polymers possess interesting high sorption properties and rapid kinetics. Moreover, the material can be easily regenerated after use.

In this communication, we propose the use of this starch-based material for the sorption of fluoride metal ions and organic compounds, responsible of the chemical oxygen demand (COD), present in industrial water discharges coming from surface treatment industries. Carrying out our experiments using the batch method, the sorption of pollutants on starch-based materials was studied as function of mass of sorbent, contact time and pollutant load. Results of sorption experiments showed that the polymer exhibited high sorption capacities and interesting environmental effects, which were proved by toxicity tests. Indeed, germination rate of a specific lettuce (*Lactuca sativa*) was used as laboratory indicator of phytotoxicity. All these chemical and biological results confirmed the ability of starch-based materials to abate water pollutants, both of organic and inorganic nature.

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A sensitive and practical fluorimetric test for CNTs acidic sites determination

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Since their discovery in 1991[1], carbon nanotubes (CNTs) have attracted considerable attention because of their unique structural, mechanical and electronic properties exploited in many applications, especially in the field of nanotechnology, nanoelectronics, composite materials and medicinal chemistry[2].

However, to expand and optimize the use of CNTs in many fields, it is necessary to chemically modify and functionalize their graphitic outer walls. Due to the great chemical inertness of CNTs, caused by the graphitic walls consisting of thousands of carbon atoms in an aromatic delocalized (π-conjugative) system, a harsh environment is required to effectively functionalize their surface. Since the abundance of carboxylic groups, increased with treatment time, temperature and the degree of lattice defectiveness, is critical for the final application, it is important to determine the amount of surface acidic groups.

Recently, we developed a very sensitive, practical, fast and accurate method for quantitative determination of acidic sites on CNTs using thionin acetate (THA), a positively charged redox dye[3]. When THA solution is put in contact with functionalized CNTs, either well dispersed or not, the positive charge of the molecule allows its adsorption on the negative charged surface of the CNTs[4]. Since the adsorption on CNTs can occur by both a specific electrostatic interaction with carboxylic groups and an unspecific hydrophobic interaction with the graphitic structure of the nanotubes, we applied this method to different oxidized and non oxidized carbon nanotubes. The method has revealed particularly useful as a fluorescence routine test to monitor oxidation processes of both single and multiwalled CNTs. The specificity of the interaction is also analyzed and supported by Raman Spectroscopy and mapping[5] and Thermogravimetric analysis (TGA).

Furthermore, we propose the use of other two commercial fluorophores, such as Rhodamine 6 and a Cyanine dye, for the titration of carboxylic groups on carbon nanotube samples. Since their structure is different from THA, we propose this method as a comparison with our previous results.

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Synthesis of Modified Nucleosides Using a Novel One Pot-Three component Reaction[1]

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Nucleoside analogues are an important class of bioactive compounds. They are widely used as antiviral, anticancer and antibiotic drugs. For example, ribosides, such as ribavirin, thiazofurin and pyrazomycin[2] (Figure 1), proved to be potent bioactive compounds with a broad spectrum of activity. Nevertheless, there are still persistent limitations (toxicity, resistance, emergence of new viral strains…) to their therapeutic application, requiring the synthesis of new molecules that could overcome these problems.

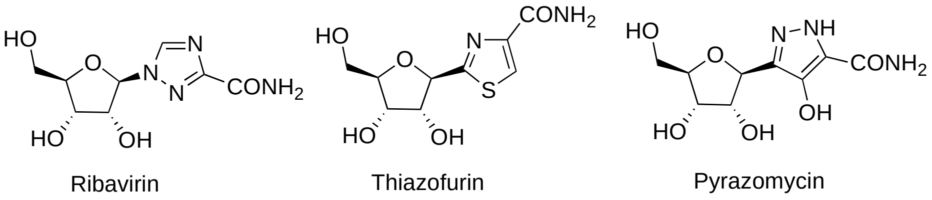

Figure 1. *Structure of bioactive five-membered-ring nucleosides*

Azide-alkyne 1,3-dipolar cycloaddition catalyzed by Cu(I) is a rapid and effective method for the synthesis of triazole heterocycles. Sharpless and co-workers[3] suggested the formation of a cuprous intermediate during the catalytic cycle. Based on these results, we developped an azide-alkyne 1,3-dipolar cycloaddition-electrophilic addition tandem reaction by quenching the cuprous intermediate with an electrophile to get highly functionalized triazole derivatives (Figure 2).

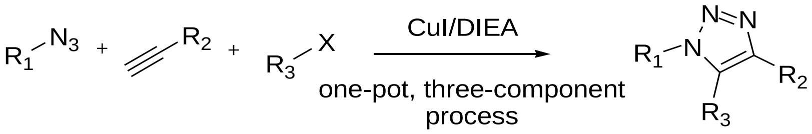

Figure 2. *Synthesis of functionalized triazolyl-nucleosides*

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Thioisomunchnones derivatives of mandelic acid and vanilmandelic acid : a serendipitous discovery with interesting applications

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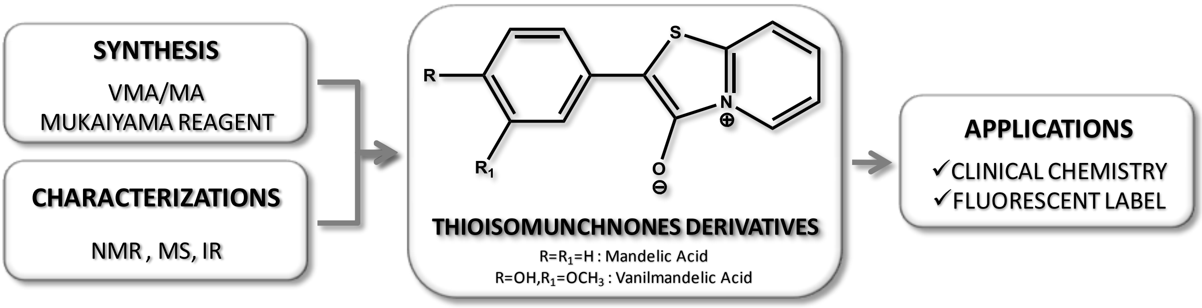
Up today many coupling reagents are used for the formation of amide bond including the mixture between triphenylphosphine and 2,2'-dipyridyl disulfide (Mukaiyama reagent)[1], an oxidation-reduction condensation reagents. In the reaction of the DL-Vanilmandelic (VMA) and DL-Mandelic Acid (MA) with (S)-α-Methylbenzylamine in presence of the Mukaiyama reagent over the expected diastereomeric amides some fluorescents by-products are formed. The latter have been isolated and characterized with Nuclear Magnetic Resonance (^{1}H-NMR, ^{13}C-NMR, COSY, HSQC, HMBC), Mass Spectrometry (High Resolution MS e Tandem MS/MS) and Infrared Spectroscopy for structure identification. The obtained spectroscopic data sustained by some literature references allow to assign the structure to mesoionic like compounds as "thioisomunchnones" (1,3-thiazolium-4-olates)[2,3]. Whereas DL-Vanilmandelic Acid is important clinical biomarker (for neuroendocrine tumor screening test)[4] we thought to derivatize it as thioisomunchnone for its quantification in liquid chromatography coupled with a fluorescence detector. Moreover the mesoionic derivative of vanilmandelic acid has been used as fluorescence labeling reagent for derivatize carboxylic acids as ibuprofen, an important anti-inflammatory drug.



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Electrochemical properties of self-organized titania nanotubes: applications to energy storage

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Titanium oxide nanotubes were manufactured by anodization of Ti thin films DC sputtered on a Si substrate and by anodization of Ti foil. The anodization bath consisted of a solution of H_3PO_4 1M + NaOH 1M which contained 0.3%w HF. The anodic oxidation was carried out by applying a voltage of 20V across the electrochemical cell.

Regular arrays of self-organized titania nanotubes ~80nm in diameter and having a wall thickness of ~20nm were obtained on the surface of the titanium. The nanotubes obtained are amorphous although they can be converted partially to anatase by heating at 450°C for 3 hours.

Sn electrodeposition was carried out upon the as-prepared titania nanotube array as well as on compact titania layers obtained by performing the anodization in an HF-free electrolyte. The baths used for Sn electrodeposition were highly diluted (from 36mM to 9mM Sn^{2+}) and contained $SnCl_2$. The Sn^{2+} was complexed with sodium citrate that was added to the electrodeposition bath. The electrodeposition of Sn was carried out galvanostaticaly using current densities close to the limiting current.

It was found that it is possible to obtain wire-like high aspect ratio crystallites having widths as narrow as 100nm and lengths of several micrometers. This behaviour is not observed when compact titania layers are used as substrates.

Nucleation and growth was further investigated using the electrochemical method developed by Scharifker and Hills which is based on potentiostatic current transient analysis. The determined instantaneous nucleation process corroborated with the crystallite count vs. electrodeposition time indicates that the nucleation locus is at the bottom of the nanotubes.

The use of self-organized TiO_2 nanotube arrays is investigated for the fabrication of an alternative Li-ion negative electrode. Discharge/charge curves and cycling performance are studied in lithium-anode electrochemical test cells for both amorphous and crystalline titania nanotubes as well as for titania-tin composites in both pristine and oxidized form.

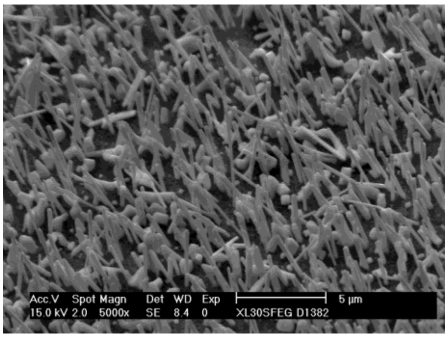

Figure 1: SEM tilted view of Sn nanowires electrodeposited on TiO_2 nanotubes substrate.

Hydrogen from renewables: Ethanol steam reforming over Co-Ni-Zn-Al catalysts

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Hydrogen is industrially produced through steam reforming of hydrocarbons catalyzed by alumina supported Ni based catalysts. Such systems were found active in ethanol steam reforming (ESR) reaction, as well. Large scale hydrogen production from renewables, such as bioethanol, is highly desirable to decrease general dependence on fossil fuels and greenhouse gases emissions. According to our previous studies[1,2,3], over Ni catalysts, at enough high temperature (770 K and above) and in excess of water, ethanol undergoes decomposition (directly or in steps) to CH_4, CO_x and H_2 followed by the water gas shift and the methane steam reforming reactions which approach equilibrium. The formation of CH_4 is a critical aspect, because it limits H_2 formation at low and intermediate temperature: CH_4 steam reforming is completed only at higher temperature. Under this respect Co based catalysts seem to give better performances. Nanostructured and well crystallized Co-Ni-Zn-Al hydrotalcite-like compounds, with different Co/Ni atomic ratio (a.r.), were prepared through the urea method[4]. The calcination in air at 973 K of the layered precursors gives rise to high surface area mixed oxides, active in ESR. All the catalysts were characterized and their catalytic activity was studied in flow reactor experiments. At 873 K the selectivity to H_2 increases with Co loading. The most selective catalyst is the Ni-free Co-Zn-Al mixed oxide. The most active catalyst has a Co/Ni a.r. of 2.6. Yield to H_2 exceeding 90% is obtained with this catalyst at 823 K with a water to ethanol feed ratio of 6. To gain some deeper insight in the reaction mechanism, the interaction between the catalyst surface and water/ethanol and water/acetic acid vapour mixtures were studied through FTIR experiments. It was found that the most relevant selectivity determining step is the evolution of surface acetate species assumed to be the key intermediate. Two different routes are possible leading to the formation of CH_4 and CO_x or, alterantively, CO_2 and H_2, depending on the oxidation state of the surface active phase. Under this respect the feed composition plays a role, being ethanol a reducing agent and water a potential oxidant. The high selectivity to H_2 and CO_2 obtained in the 770-870 K range, is attrubuted to the high oxidation state of Co under reaction conditions, allowing the evolution of acetate species to CO_2 and H_2. Water is supposed to have the main role of allowing surface sites to stay in an unreduced state. On more reduced surface (with Ni and/or less water in the feed) acetates decompose producing CH_4 and CO_x.

The catalytic systems here described are showing activity also in glycerol steam reforming reaction.

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Small and Soluble Molecules as Donor Materials in Bulk Heterojunction Organic Solar Cells

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Conjugated polymers are of high interest as donor materials in state-of-the-art organic bulk-heterojuncton solar cells and their optimization should be still pursued. However, low molecular weight materials offer several advantages: their are well defined and inherently monodisperse, their purification is generally achieved by standard techniques such as recrystallization or column chromatograph. In addition, their dimensionality can be varied from 1- to 3-D, in the latter case attaining easy processable and isotropic semiconductors.[11] In particular, using 3-D cores such as tetrapods quaterthiophene or propeller-shaped triphenylamines with attached linear conjugated branches we have demonstrated the feasibility of field-effect transistors, electroluminescent diodes, and both bilayer and bulk-heterojunction solar cells.[2] As follows-up, bulk-heterojunction solar cells based on small soluble conjugated molecules as donor materials are currently investigated worldwide and indeed competing with polymer based devices.

Recently, we have for the first time implemented fluorescent BODIPY dyes as donors in bulk-heterojunction solar cells. Blending them with fullerene derivatives as electron acceptors, we have obtained power conversion efficiency values up to 1.34%. Using an original approach - *multidonors* with complementary absorption spectra - these values have been raised to 1.70%.[3]

The above research will be reviewed, and emphasis will be given to the most recent results. Moreover, issues such as the "importance of devices size and layout" as well the "origin of the open circuit voltage in D-A solar cells" will be briefly addressed.

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Transfer and Transformation of Chemical and Physical Knowledge. A Crucial Case in the History of Superconductivity

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The recent history of superconductivity is an interesting case of movement of scientific knowledge and technological innovation. In a landscape dominated by scientific experimental activism and theoretical curiosity of Bernd Matthias[1], who brought to the attention of the scientific community type A_3B intermetallic compounds (with A = B = Nb and Sn, Si, Al), superconducting materials with critical temperature of 23 K, stands the important discovery of the Swiss A. Müller and G. Bednorz. Indeed in 1986 at the IBM in Rüschlikon they found that mixed oxides perovskitic were superconductors at 35 K.[2] Their inspired idea came from reading an article written by the French C. Michel, B. Raveau and L-Er-Rakho[3] on the resistivity presented by the oxide of metallic BaLaCu perovskitic structure at high temperatures. In about a year the discovery of the phenomenon of superconductivity in compounds Y1Ba2Cu3O7 at 98 K by Americans C.W. Chu[4] and M.-K. Wu[5] was also extraordinary because it made sufficient cooling with cheaper liquid nitrogen.The outlined cognitive situation, for our retrospective view, has several points of interest: first, Bednorz and Müller were not well know specialists in the field of superconductivity, secondly, the phenomena present in the mixed oxide was not provided by the BCS (Bardeen, Cooper e Schrieffer) theory, thirdly in small workshops like Rüschlikon, laboratories that were not created as centers of excellence, became instead places to discover. Another remarkable feature is the progressive increase in the importance of chemical sciences and materials acquired in the field of superconductivity, at the expense of the centrality of physics. Additionally, it came to creating research teams composed of scientists from various disciplinary training, united by the same research purposes and witnesses of the cognitive complexity of work in progress and needs of science and technology working together. In this light it is understandable that the reality of extended labs has been cut and has taken more and more space. This network (extended labs) connected in fact the research laboratories, as research groups consisting of scientists from different disciplinary fields, with the economy, politics in the service of scientific development and economic development. The working group of the Department of Chemistry of the University of Turin is situated in this research plane, and disciplinary proficiencies at stake are chemistry, physics and materials science. The general framework in which this work was presented was well defined by the work of H. Nowotny and U. Felt (*After the Breakthrough*,Cambridge: Cambridge University Press, 1997) and J. Matricon and G. Waysand (*The Cold Wars. A history of superconductivity*, New Brunswick: Rutgers University Press, 2003).

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Grafting of silica nanoparticles on polyethylene

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Modification of surface properties of some polymeric materials is an important issue. Modified polymer surfaces may show new properties as adhesion improvement, wettability and functionalisation. Surface modification can be realized by surface grafting of suitable monomers containing functional groups that can be used for other reactions. A further grafting of nanoparticles can enhance specific surface of the material and leads to a hierarchical integration of nanoscale textures functionalized silica nanoparticles, resulting in stable high surface area materials that can be easily functionalised by a large number of other active molecules.

In this work, the modification of surface properties of polyethylene by grafting of functionalized silica nanoparticles (figure 1) is reported and further the wettability of film was switched from hydrophilic to hydrophobic by grafting of a semi-fluorinated compound.
Therefore it is believed that this work offers new short term prospects for the fabrication of highly active materials in technologies such as catalysis, sensing or antibacterial surfaces.

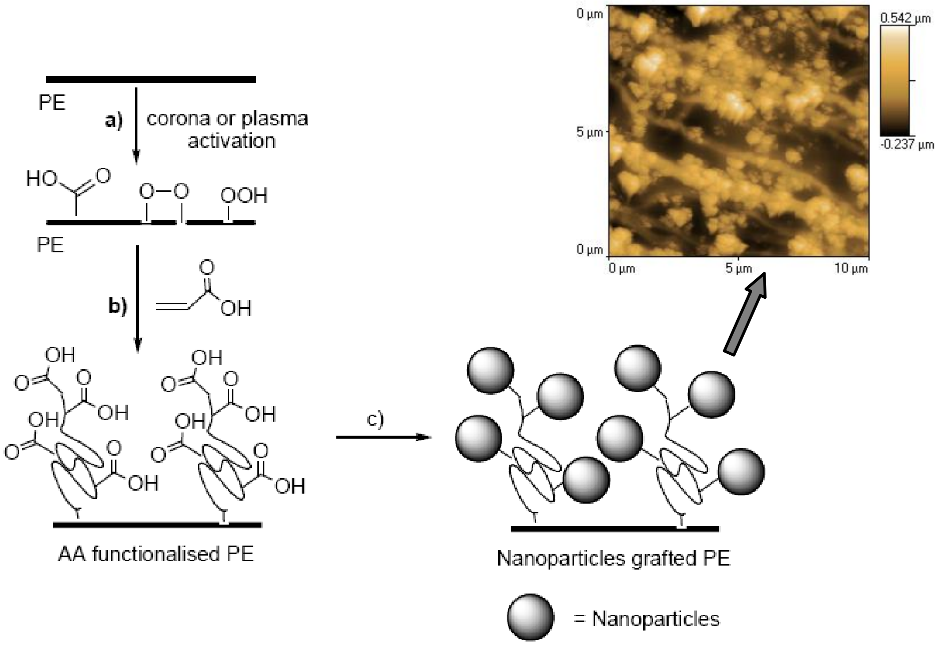

Figure 1*: Grafting of silica nanoparticles on polyethylene (synthetic pathway and AFM image)*

Blocky ethylene/4-methyl-1-pentene copolymers from single center catalysts: microstructure and crystallization behaviour

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The peculiar microstructural features of a series of novel copolymers from ethylene (E) and 4-methyl-1-pentene (4M1P), prepared by means of isospecific metallocene catalytic systems, were correlated with their melt crystallization behaviour. The isospecificity of the employed catalysts favours the formation of homosequences of both E and 4M1P, because of the easy isospecific propagation of the 1-olefin. Statistical elaboration of the copolymerization according to a 2*nd* order Markov model demonstrates that in the presence of a sterically hindered 1-olefin, a penultimate unit effect is responsible of the copolymer's blocky microstructure, even with moderately isospecific metallocenes.[1,2,3]

In this contribution, standard DSC analyses conducted on a series of copolymers prepared with the *rac*-ethylenebis(tetrahydroindenyl)zirconium dichloride [*rac*-(EBTHI)$ZrCl_2$] isospecific catalyst, revealed the presence of crystalline structures up to uncommonly high comonomer contents. Moreover, the heating traces obtained on the *as-polymerized* samples exhibited endothermic signals even in the equimolar composition range. In samples with high 4M1P contents, wide angle X-ray diffraction patterns acquired at room temperature evidence, the presence of reflections due to Form I and Form IV of poly(4-methyl-1-pentene).[4] In E-rich copolymers, the orthorhombic structure of PE was found. These data are consistent with the abovementioned blocky microstructure of the copolymers, that make them able to crystallize up to high comonomer concentrations owing to the presence of homosequences long enough to arrange in a crystalline lattice.

A DSC-based technique, namely *Successive Self-Nucleation and Annealing* (SSA)[5] procedure, was adopted to thermally fractionate the copolymer specimens on the basis of the length of the crystallizable sequences and to enhance the overall crystallinity in samples in which low or no crystallinity develops upon standard DSC cooling. In the copolymers within the range of equimolar composition, the SSA procedure revealed the presence of two distinct series of endothermic signals, one in a temperature range below room temperature and the other between 50 and 100 °C, which were ascribed to the contemporary presence of E and 4M1P crystallites.

The overall results demonstrate that a new family of multiphase semicrystalline polyolefins can be synthesized by a single center nonliving catalytic system.

This study was supported by Regione Lombardia (Project 4161-MOD-IM-PACK, 2008 - 2009).

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Chiral sulfoximines in Multiple Bond-Forming Transformations

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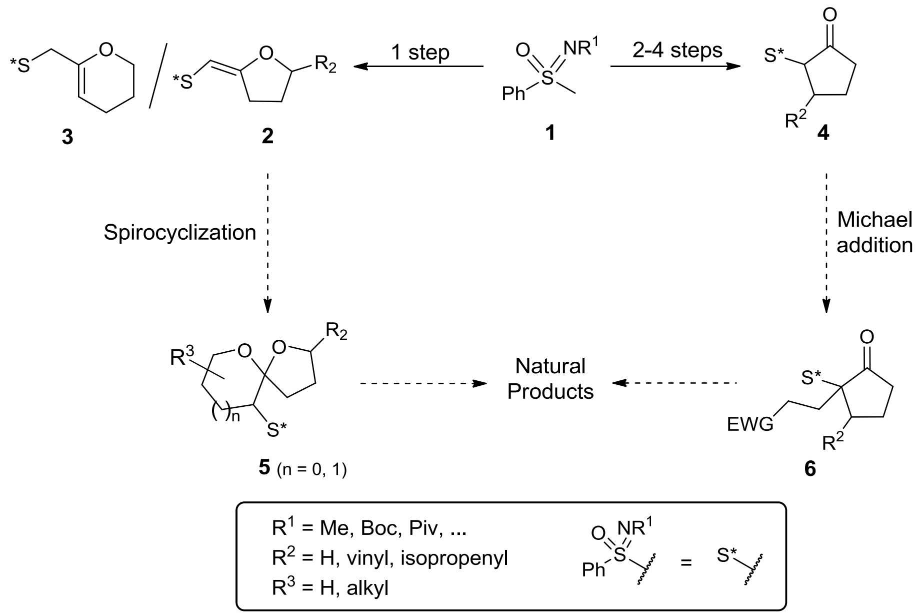
Sulfoximine chemistry has been developed since the 1950's. These molecules are chiral analogs of sulfones. They attracted our attention due to the presence of an electronically and sterically modulable stereogenic sulfur atom which makes them useful in asymmetric synthesis,[1] and more specifically in multiple bond-forming asymmetric transformations.[2]

In this work the reactivity of α,α-dilithiocarbanion of sulfoximines **1** with *bis*-electrophiles has been studied. A series of 2-sulfonimidoylylidene tetrahydrofurans (**2**) and 6-sulfonimidoylmethyl-3,4-dihydro-*2H*-pyrans (**3**) has been obtained from sulfoximines **1** following a consecutive reaction with α,ω-haloesters.[3] Two distinct approaches to 2-sulfonimidoyl cyclopentanones (**4**) were also developed. The synthetic exploitation of compounds **2-4** in subsequent stereoselective transformations has led to a variety of spiroethers of type **5** and polysubstituted cyclopentanones **6** that may prove useful in natural products total synthesis. The syntheses of compounds **2-4** and their applications will be presented.



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Polymer Crystallization under Processing Conditions

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The properties of semi-crystalline materials depend on the extent, type and morphology of the crystalline phase. In turn, the formation of crystals is largely affected by the molecular structure, with its different types of defects; however, the strict control of chain microstructure alone does not allow tailoring product's properties because a processing step, in which the polymer melt is subjected to high stresses and rapid cooling, is always involved. The imposed extreme external conditions are often decisive for the structuring of the material since they dictate orientation, size and structure of the crystals.

In this work, the interplay between chain constitution and processing conditions which dictates polymer crystallization behavior is investigated. Near-processing conditions have been reproduced by means of in-house designed laboratory equipments probing the structuring of the material with suitable tecniques. The experimental work was mainly focused on two aspects. The first one concerned the structuring of i-PP based materials, containing various type of microstructural defects, under conditions of very fast cooling. The collection of Continuous Cooling Curves (CCC diagrams) with on-line thermal analysis and in-situ/ex-situ structural characterization has enabled us to infer the role of co-units and stereo defects on the polymorphism of quenched samples.[1] The second aspect dealt with the effect of flow on polymer crystallization. Mild shear pulses applied to a polymer in the molten state largely affect crystallization kinetics and morphology. These evidences suggest the formation of metastable bundles of aligned chain segments which are able to act as nucleation sites in subsequent cooling.[2] Formation and stability of these shear induced precursors has been investigated in-situ by coupling rotational or pressure driven shearing devices with optical microscopy and X-ray diffraction.

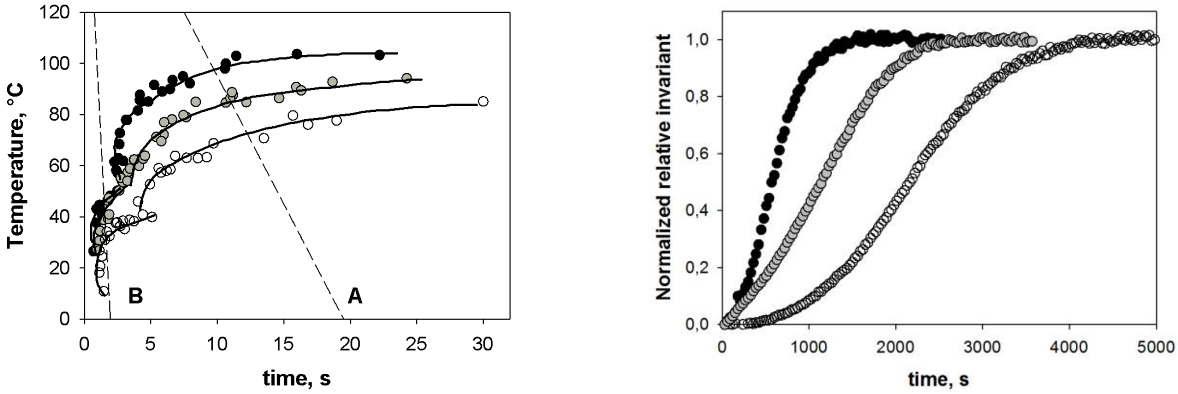

Figure: (Left) CCC diagrams of propene/ethylene random copolymers; (Right) Crystallization kinetics of sheared and partially relaxed isotactic polypropylene

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In(III)-Catalyzed Tandem C-C and C-O Bond Formation between Phenols and Allylic Acetates

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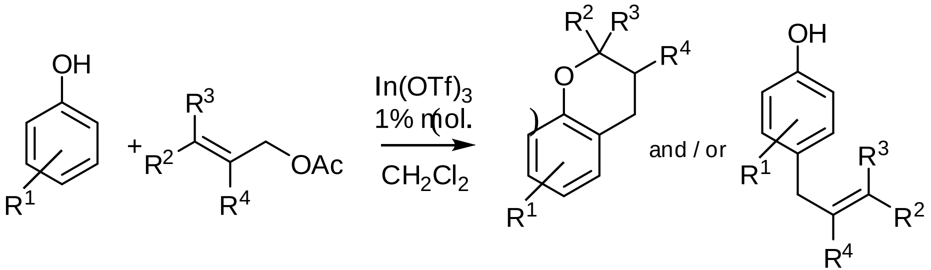
The laboratory reported the synthesis of various metallic triflates and triflimidates, using electrochemical[1] or chemical procedures.[2]

We recently developed a catalytic methodology for the Friedel-Crafts allylation of aromatic compounds with allyl acetate derivatives, using metal triflates and triflimidates.[3] In the case of phenol derivatives, we directly obtained chromane-type products, resulting from a tandem reaction, starting with a classical Friedel-Crafts allylation followed by an intramolecular cyclisation.



R^1 = H, CH_3, OCH_3, COOEt, Cl
R^2, R^3, R^4 = H, alkyl, Ph

A few catalytic methods are described in the literature to access chromane structures from phenol derivatives in one step. Thus Ag(OTf)[4] was reported to promote hydroarylation-hydroalkoxylation, starting from linear and cyclic dienes. $Sc(OTf)_3$ was found to be an efficient catalyst for the [3+3] cyclocoupling of trimethylhydroquinone with isophytol to afford vitamin E.[5] We developed a mild and simple method for a selective synthesis of chromane-type derivatives. Some of these structures, such as vitamin E, present interesting bioactivity, whereas other chromane-derived molecules have some anticancer properties.

Mechanistic, kinetic and theoretical calculations were also carried out with a model reaction, between phenol and prenyl acetate, in order to get more insight on the proposed mechanism.

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Identification of a multivariate target function representing S/N from complex mass spectra – Optimisation by regular simplex

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When mass spectrometry is not combined to separation techniques, the evaluation of signal and noise in a complex mass spectrum is not trivial. The tuning procedure usually adopted for automatic tuning makes use of a standard mixture covering the overall range of m/z values provided by the analyzer. The automatic tuning which is usually based only on the increase of the signal of a selected number of m/z values does not ensure the achievement of the best experimental conditions: signal could improve and noise could increase as well.

The scope of this work is the development of a function separating signal and noise (for evaluating the S/N) in complex mass spectra, for potential use as target function for the automatic tuning of the instrument.

The procedure exploited here makes use of Principal Component Analysis (PCA) to separate the signal (present in the significant components) from the noise (present in the residuals). The spectra provided by the instrument when a set of scans of the same standard mixture are carried out, are separated into two contributions: one due to signal and one due to noise. A S/N ratio can therefore be computed and exploited as target function for the automatic instrumental tuning.

The target function thus obtained is then tested to evaluate its applicability and identify the best experimental procedure to carry out a subsequent tuning: in particular, the presence of memory effects and the best concentration of the standard adopted during tuning are evaluated.

Once the target function is obtained, a multivariate tuning is applied. The work was carried out by a mass spectrometer Finnigan LCQDuo equipped with an ESI Ion Trap mass analyzer. The tuning of the instrument involved 10 parameters and was carried out by a regular simplex optimization procedure. The optimization carried out allowed a relevant increase (about 70%) of the S/N ratio recorded.[1]

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Multicomponent reactions beyond the iminium ion trail: total synthesis of arzanol, the anti-inflammatory principle of eternelle (*Helicrysum italicum* L.)

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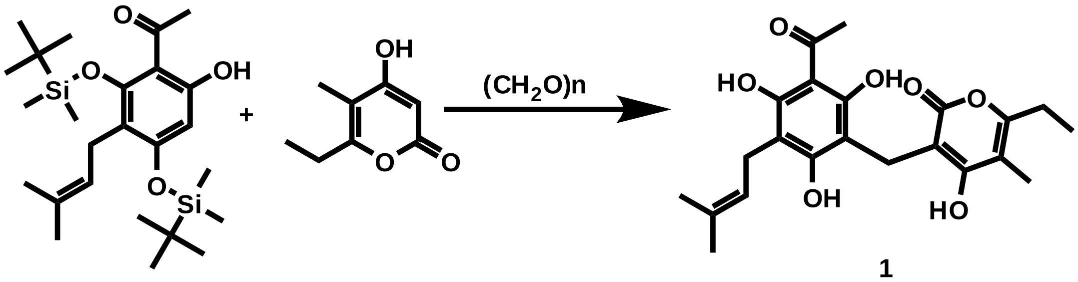
Multicomponent reactions (MCR) are based on the combination of more than two starting materials, and are characterized by high atom economy. Therefore, they represent a premium strategy compared to one-pot reactions. Most MCR are based on the formation of amide and ester bonds, do not generally involve the generation of more than two carbon-carbon bonds, and are triggered by nucleophilic attack to an iminium ion. Non-iminium ion based MCR have not yet received systematic attention, despite their relevance in polyphenolic chemistry. To fill this gap, we have started a methodology study aimed at the generation, in a MCR-fashion, of aryl-heteroarylmethanes, an important class of natural products.

Our interest for this class of compounds was fostered by the remarkable bioactivity of the prenylated phloroglucinyl(pyronyl)methane arzanol (**1**) the major anti-inflammatory, antibiotic, and anti-oxidant principle of everlasting (*Helichrysum italicum*).[1] With the ultimate aim of developing a total synthesis of **1** and related heterodimeric pyrones, we have embarked in a systematic study on the synthesis of *gem*-(β-dicarbonyl)arylmethanes, evaluating the possibility of obtaining this type of compound in a multicomponent fashion by combination of a carbonyl derivative with equimolar amounts of a β-dicarbonyl and an electron-rich aromatic derivative.[2] We will present our methodological studies in the area and their application to the total synthesis of arzanol and to the generation of analogues suitable to clarify the structure-activity relationship of the natural product, a potent mPGE2 syntase inhibitor.



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Highly Enantioselective Organocatalyzed Michael Addition of β-Ketoamides onto Enones

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Over the years, the Michael addition[1a,b] has attracted a high interest, especially its enantioselective process. The first enantiomeric excess in this field have been induced with organometallic species back in 1975 by Wynberg.[1c] Over the last decade, asymmetric organocatalysis[2] has found an increasing interest in the enantioselective Michael addition, mainly in the field of addition of malonate derivatives and □-ketoester onto Michael acceptors.[3]

In the context of ongoing projects,[4] we are interested in Michael addition of □-ketoamides onto □,□-insaturated carbonyls in such a way that the newly created chiral center would be controlled stereoselectively. In this study, different types of organocatalysts have been tested, such as proline, cinchona alkaloids and thiourea derivatives. Out of the different catalysts studied, we found that thioureas give the best results with excellent enantiomeric excess.

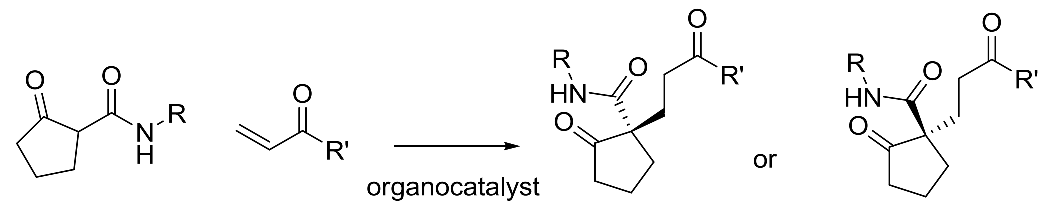

Figure 1 : Control of the newly created chiral center - Organocatalyzed addition of β-ketoamides onto α,β-insaturated carbonyls.

Financé par ANR

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E PLURIBUS UNUM: A pluripotent multicomponent approach to DOS libraries

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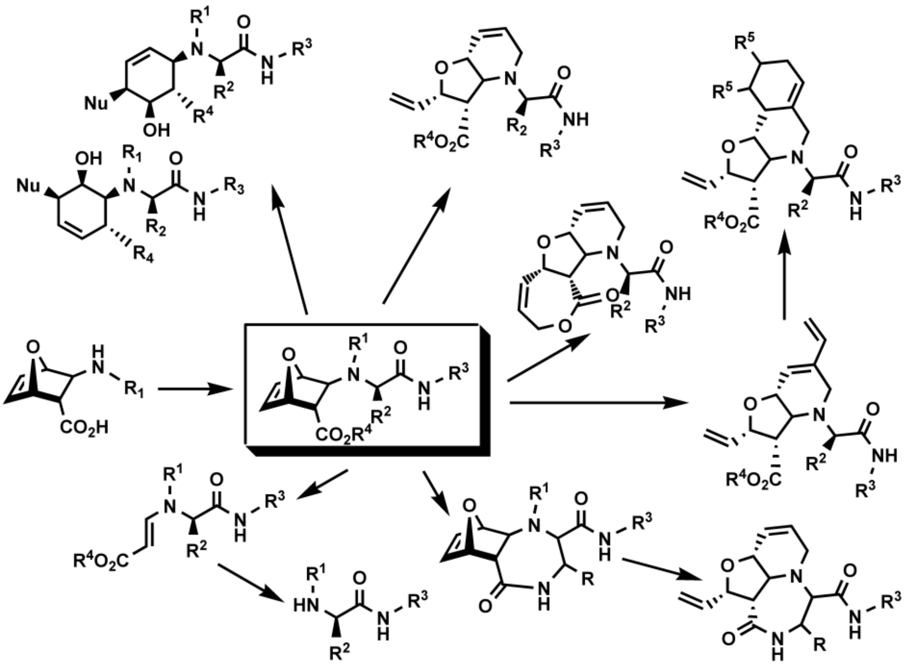
Diversity Oriented Synthesis (DOS) represents a new methodological approach that in recent years is gaining more and more importance in the field of organic synthesis. Its goal is the efficient and automatizable preparation of collection of substances characterized by high diversity content, in terms of skeletons, appendages and stereochemistries. One way to achieve this is to employ *pluripotent substrates*, which are molecules that can be synthetically elaborated in many different and indipendent ways, each one leading to a distinct molecular skeleton. In our approach the pluripotent substrate is not a single entity but a collection of molecules with a common core, generated in a combinatorial fashion with the aid of multicomponent reactions: this library of compounds is then further elaborated to generate 'n' different combinatorial libraries, each with a different skeleton. The final compounds, although deriving from a common substrate, are structurally different and therefore can cover a higher portion of the chemical space, compared to classic combinatorial libraries where all the members of one library are characterised by the same core. The use of this approach to the design, synthesis, elaboration and biological applications of a diverse library of pluripotent oxanorbornene derivatives will be discussed in details.[1]



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Synthesis of polycyclic compounds by cycloisomerization of polyenes catalyzed by Lewis superacids

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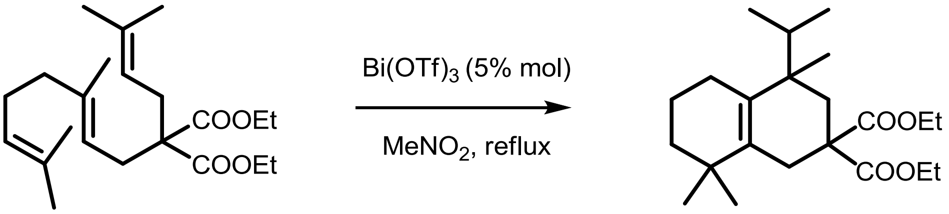
Based on recent work in the laboratory for the cyclization of dienes,[1] a cycloisomerization reaction has been developed on polyunsaturated systems such as 2-geranyl-2-prenyldiethylmalonate (*E*)-**1a** (Equation 1) or 2-cinammyl-2-geranyldiethylmalonate using different metallic triflates and triflimidates as the catalysts. The reactions are carried out with 5 mol% $M(OTf)_n$ and $M(NTF_2)_n$ (M = Sn, Al, Bi, Yb, La, Cu, Fe ...). The results show the formation of polycyclic compounds such as **1b** in a original catalytic cyclization process of biomimetic type.[2,3]



(*E*)-**1a** **1b,** 72%

Equation 1 *: 2-Geranyl-2-prenyldiethylmalonate cycloisomerization.*

Tandem cyclization reactions including catalytic Friedel-Crafts arylation processes were also performed for substrats bearing aromatic substituents. Depending on the nature of the catalyst used (metal center M, counter-ions and solvatation),[4] significant variations in yields and selectivities were observed. Mechanistic and kinetic studies wiil be presented on the influence of these parameters on the different cyclizations.

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Comunicazioni Poster

Comparative Study on the Volatile Constituents of Marine Sponges of The IRCINIIDAE Family Collected From Gibraltar

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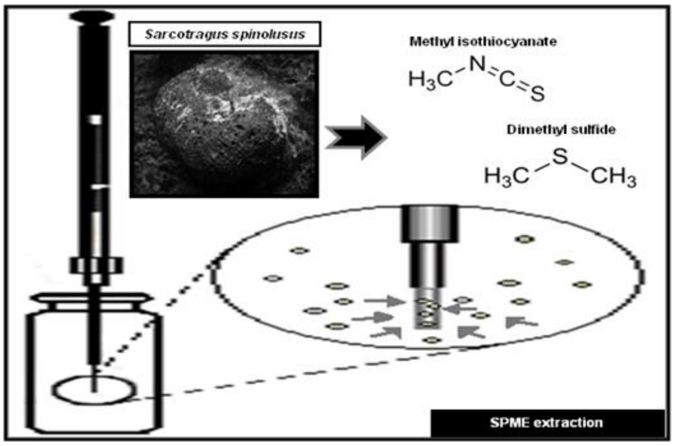
Marine sponges of the Irciniidae family (Porifera, Dictyoceratida) represent a rich source of unusual bioactive terpenes exhibiting antibacterial, antiviral, cytotoxic and anti-inflammatory activities. For several species among this family, the knowledge on their volatile constituents and their potential ecological role remains very scarce. Sponges of the genus Ircinia were described to exude low-molecular-weight volatile compounds (e.g., dimethyl sulfide, methyl isocyanide, methyl isothiocyanate) that give these sponges a characteristic strong and unpleasant odor.[1] Their ecological role as potential defenses against predatory fish has been evaluated.[2] To date, the volatile constituents of sponges of the genus Sarcotragus have not been studied, though their odor is no lighter than the associated genus Ircinia from the same family.

We report a comparative GC-MS analysis of the volatile components of S. spinolusus, I. oros, I. variabilis and I. dendroides, collected from Ceuta and Casablanca (Gibraltar, Mediterranean Sea), using static headspace solid phase microextraction (HS-SPME). The impact of different parameters (e.g., sample weight, fiber coating , extraction time and temperature) were evaluated to determine the best conditions of analysis.

Comparison of the volatile chemical fingerprint of the studied species showed some significant differences that can represent a valuable complementary identification tool when combined with the associated non volatile secondary metabolites composition and the morphological characters of the sponges.



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Alumina doping effects on the growth of superconducting YbCO whiskers

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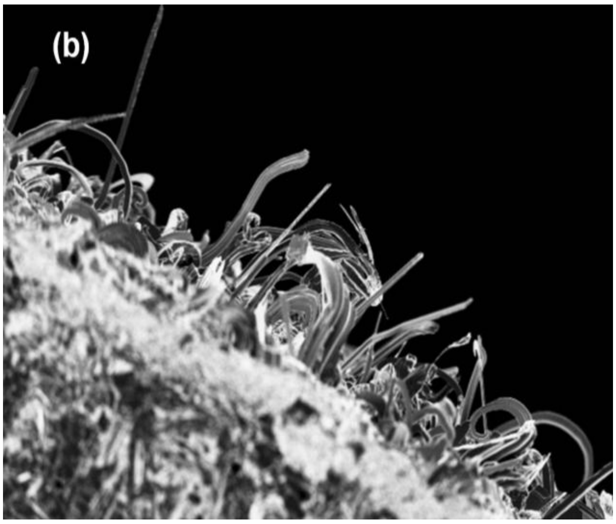
Terahertz sensing, imaging and spectroscopy devices represent a top priority nowadays and layered HTSC perovskites offer a good alternative for these kinds of applications[1,2,3]. Moreover, chemical doping represents an efficient way of improving the properties of HTSC compounds. In the present work, Al_2O_3 doped Y_{1-y} (Ca_y) $Ba_2Cu_3O_x$ (YBCO) whiskers were synthesized using a solid state reaction technique. Al_2O_3 addition was systematically varied in the nominal cationic stoichiometry of $Y_1Ba_2Cu_3Ca_1Te_{0.5}Al_x$, with $0 \leq x \leq 0.5$. It was observed that moderate amounts of alumina increase the number density of the grown whiskers. The X-ray diffraction measurements revealed a minimum in the c-axis lattice parameter value for alumina contents around $x = 0.1$. These results point out a possible incorporation in the crystal structure of Al ions, which may occupy Cu (I) sites and sustain a different oxygen stoichiometry. This is also confirmed by the electrical transport measurements, which show a decrease in the critical temperature with increasing the alumina amount. Any superconducting feature disappears in the whiskers for alumina content above about x=0.05. Two different main results can be summarized. The first concerns the increase in the amount of produced whiskers, which is attributable to the role played by alumina in the creation of nucleation centers for the whisker growth. The second is related to the cell parameter modifications, which show that some changes are possible in the system while preserving its superconductivity.



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Functionalization of sol gel bioactive glasses carrying Au nanoparticles: an unusual Au affinity for amino-groups

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Herewith we report on the functionalization with 2-mercaptoethanol, 2-ethanolamine, cysteine and cystine of a novel type of potentially bioactive glass containing gold nanoparticles (hereafter referred to as AuNPs).

The glass has been designed to carry on a double function: to favour the repair of bone tissues, and specifically release functionalized AuNPs in the human body. Indeed, the successful functionalization of gold surface is expected to allow *(i)* the design of controlled drug-releasing systems, and *(ii)* the development of protein-functionalized materials to be used as bio-mimetic materials with bio-ligands that can favour cell adhesion and proliferation at the biomaterial surface[1,2].

The functionalization of gold surfaces with thiol (-SH) groups has been widely investigated, and a large variety of thiolate molecules have been claimed, and often demonstrated, to be preferentially adsorbed at the gold surface through thiol linkage[3-5]. In opposition to a fair number of works present in the literature[4-8], we will report spectroscopic evidence that, in our glass systems, AuNPs form a linkage with the amino-group of small organic bio-molecules rather than with thiol functionalities.

The present results open the door to the creation of a new class of composites that, for their realization, do not require the presence of the thiol functionality, but can be produced (at least in theory) starting from any primary amine.

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New organo-modified silicas for the reinforcement of SBR compounds

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Since the 90's silica has constantly gained importance as reinforcing filler for rubber compounds in tyre applications.[1,2] Compared to carbon black (CB), the use of silica results in lower hysteresis losses, leading to lower rolling resistance and consequent fuel saving. Since CB and silica possess their own advantages, the use of blends of silica and CB in rubber compounds can assure benefits from each filler. However, the compatibility of hydrophilic silica with the hydrophobic rubber matrix is generally poor. The addition of multifunctional coupling agents, typically bis(triethoxysilylpropyl)tetrasulphide (TESPT),[3] enhances silica-matrix compatibility and consequently the reinforcing effect of the filler. During compounding, the coupling agent links onto the silica surface, rich in silanol groups, and, in the subsequent step, the organosilane contributes to the vulcanization process by sulphur donation and by reaction of the sulphide groups with the rubber matrix.

In this framework our research activity has been focused from several years on understanding the role of the filler-matrix interactions on morphology and ultimate properties of rubber compounds.[4]

In the present work new organosilanes chemically bonded to different liquid polybutadienes are tested in order to replace TESPT and obtain modified silicas with a reduced hydrophilic character, which can, at least in principle, improve filler-matrix interactions and, consequently, tyre performances. Moreover, these new organosilanes could be usefully employed in compounds obtained by vulcanization processes which exploit peroxides or radiations instead of sulphur.

SBR-based compounds containing these new organo -modified silicas were prepared through a three steps mixing method by using an internal batch mixer and then press cured into flat sheets. For reference purpose samples filled with unmodified or TESPT-modified silica were also prepared. The morphology of the samples was investigated by TEM and mechanical properties as well as cure characteristics were determined.

This work was supported by the Italian National Program MIUR-ELASTORAD FIRB and Pirelli Tyre S.p.A.

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Development of new analytical methods based on ICP-MS for the determination of rare earth elements in geological samples

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Rare earth elements (REE) are a group of elements which includes the lanthanides and yttrium. They exhibit similar physical and chemical properties, including low solubility and immobility in the terrestrial crust; hence, their pattern of abundance provide a great deal of information about the source and evolutionary processes of sedimentary rocks and consequently about the geochemical and geological history of the Earth[1]. REEs are also used in a number of industrial and technological applications, so they are released into the environment and can be accumulated in soil, sediments and, possibly, biota[2]. Furthermore, the REE signature has been suggested as suitable marker of anthropogenic inputs from oil refineries[3]. Therefore the accurate quantification of REEs in sediment samples is of great interest both from a geological and environmental point of view.

Inductively coupled plasma mass spectrometry (ICP-MS) is an analytical technique which has been widely used to determine REEs in geological and environmental samples[4] because of its high sensitivity, multi-element determination capability and wide linear dynamic range. However, the accuracy of the analysis can be affected by the occurring of spectral interferences, due to the formation in the ionization source of various polyatomic species having the same m/z value as the analytes.

In the present study direct determination of REEs in geological samples by ICP-MS after microwave-assisted acid digestion was investigated. For the removal of spectral interferences two new approaches were explored. In the first one, a cooled spray chamber set at a temperature of 0 °C was utilized in order to reduce the interfering oxide species. This system led to a halving of the percentage oxide formation for almost all the interfering species, thereby allowing the analysis of all the REEs without significant interferences. The second approach was the application of the dynamic reaction cell technique[5]. Oxygen was used as the reaction gas to convert REEs into their oxides and to detect the REE pattern at m/z +16. Reactions of REE ions with oxygen inside the quadrupole cell were investigated and the interferences due to the dioxides and un-reacted ions were carefully evaluated by taking into account the actual concentration of REEs in sediment samples. This approach led to the interference-free determination of Y, La, Ce, Pr, Nd, Sm, Tb, Dy, Ho, Er and Tm.

The developed methods were validate by the analyses of both certified reference materials and Antarctic marine sediment samples, using ICP atomic emission spectrometry (ICP-AES) and ICP sector field mass spectrometry (ICP-SFMS) for comparison. Good accuracy, low limits of detection and high precision make the proposed procedures suitable for the analytical task, providing interesting alternatives to methods which require prolonged matrix-separation procedures or high-priced instrumentation.

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Synthesis of new antioxidant flavonols with cardioprotective and antioxidant activity: in vitro and in vivo studies

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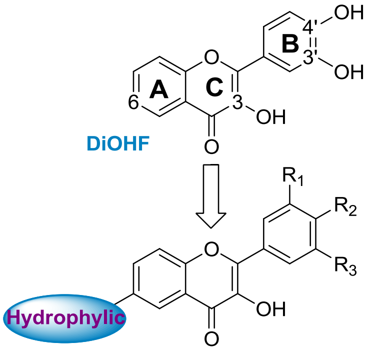
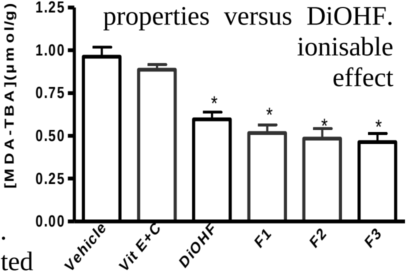
Flavonoids are polyphenolic compounds, derivatives of benzo-γ-pyrone that occur ubiquitously in food from plants. Epidemiological and pharmacological studies have shown that flavonoids intake is associated with many beneficial effects, such as antiviral, antitumor, anti-inflammatory, hepatoprotective activities, and the prevention of cardiovascular diseases. Flavonoids have several properties including autoxidation reactions inhibition and scavenging free radicals (FR). Several studies[1, 2] have reported that scavenging FR requires the 3-OH group adjacent to the 4-carbonyl on the C ring which allows electron delocalization across the molecule and stabilization of the aryloxyl radical. Qin *et al*[3] and Wang *et al*[4] have studied the possible mechanisms involved in the cardioprotective effect obtained when 3',4'-Dihydroxyflavonol (DiOHF) is infused during the experimentally-induced in vivo coronary artery occlusion in sheep. The reduction of infarct size was attributed to its concurrent vasorelaxant, antioxidant and anti-inflammatory actions. Taken together the results suggest that DiOHF could be considered as an important lead compound for the treatment of cardiovascular diseases, despite its poor water solubility that could prevents its use as a drug in many situations. Therefore, the aim of this project was (i) to design a series of novel flavonols by introducing different ionisable substituents into the DiOHF structure according to a modification of a described procedure[5] aimed to increase water solubility; (ii) to investigate the antioxidant activity of the compounds by undergoing DPPH and ORAC test-tube assays; spin-trapping/ESR determination of superoxide scavenging using the phosphorylated nitrone DEPMPO, and testing the inhibitory effect of flavonols on superoxide generating xanthine and NADPH oxidases (iii) to assess the biological activities in vitro and in vivo, i.e. vasorelaxant and antioxidant effects on excised aortic rings and cardioprotection, lipid peroxidation and antioxidant status in ischemic-reperfused hearts obtained from orally-treated rats or in vitro-perfused with the selected flavonols. We obtained several flavonols bearing various electron releasing or withdrawing substituents on A and B rings. The antioxidant activity of the new flavonols was first tested using the DPPH and ORAC assays as a preliminar screening step showing that three of the new compounds (named F1, F2 and F3) exhibit improved (+20%, p<0.05) properties versus DiOHF. In a second step, in vitro ESR studies revealed that the insertion of ionisable substituent at the 6-position increases the solubility and the antioxidant effect (DEPMPO-adduct inhibition) compared to DiOHF in a model of endothelin (ET)-mediated superoxide production in the rat aorta. The data support the hypothesis that since ET-dependent FR production enhances vasoconstriction through NADPH oxidase activation, flavonols could display a strong protective effect on the vascular tone and function. In a third step, we showed that the addition of physiological doses of selected flavonols in the perfusate of ischemic hearts exhibits cardioprotective and antilipoperoxidant effects (MDA-TBA test). In vivo studies are now in progress to check if the cardioprotective effect observed consecutive to oral administration is mediated by gene expression.





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A NMR method to identify and classify Michael acceptor sites in multifunctional compounds. Identification of the obnoxious terpenoid umbellulone as a reversible Michael acceptor

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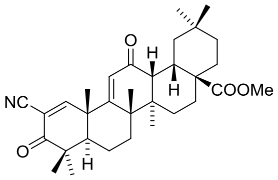
Michael acceptors are traditionally shunned in modern drug discovery. Yet, covalent thiol trapping represents an important mechanism of bioactivity, and many biologically relevant and druggable pathways, are targeted by thiol-reactive compounds (MAPK phosphatase, PTP-1B, NF-κB, Akt).[1] Research on Michael acceptors, long confined to the realm of toxicology, was rekindled by the development of the antioxidant inflammation modulator (AIM) triterpenoid bardoxolone methyl (RTA402, **1**). [2] This very reactive homo-oleanane Michael acceptor was awarded orphan drug status by FDA for the treatment of pancreatic cancer, and is also in late clinical development for the treatment of diabetes-associated chronic kidney disease. The hallmark of the biological profile of **1** and related homo-triterpenoid nitriles is a puzzling reversible reaction with thiol groups, a mechanistically unexplained feature. [3]

Spurred by these observations, we have developed and validated biologically an expeditious NMR method to identify Michael acceptors and sort them out in reversible and irreversible thiol sinks. The results of the assay were validated biologically in a thiol sensitive biological assay (TRPA1 activation), and the potential of the method is exemplified by the unexpected identification of the monoterpene umbellulone (**2**) as a reversible Michael acceptor. Based on these findings, a molecular explanation for the offensive properties of umbellulone is proposed.



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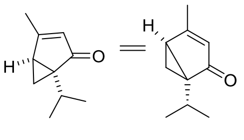

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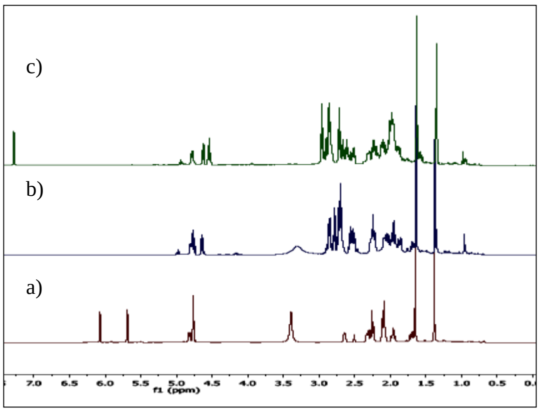

Irreversible reaction of costunolide with cysteamine in DMSO. a) ^{1}H NMR spectrum of costunolide b) ^{1}H NMR spectrum of a 1:2 mixture of costunolide and cysteamine in DMSO c) the same mixture after dilution 1:25 with $CDCl_3$.

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Multidisciplinary techniques to certify Taggiasca olives.

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Chemical and genetic approaches were applied to find the best technique for a molecular authentication of Taggiasca olives. A set of 46 samples of Taggiasca and 43 samples of table olives of different cultivars was used to perform a study on fatty acids composition and NIR analysis, while a genetic assay involved a reduced set of samples. The first technique was carried out by gas chromatography, following the Commission Regulation (EC) No 1989/2003, while the second technique, already applied for the geographical authetication of Ligurian extra virgin oil[1], is used here for the first time to characterize table olives. The fatty acids profile is too similar among the different cultivars, so this analysis is not a selective marker to cultivar discrimination. Instead, excellent results were obtained applying to the NIR data, after feature selection and data pretreatment, LDA and SIMCA as classification and class-modelling techniques, respectively. In the genetic study, the best results were obtained with microsatellite analysis, short tandemly repeat DNA motifs, spread in the whole eukaryotes genome. Variations in the length of microsatellite was identified by PCR with different primers. We found that DCA09 primer has the best discrimination power, in agreement with an other study[2], and it discriminates Taggiasca from all other cultivars. This technique is, however, very time consuming, expensive and not reliable for routine testing. Summarizing, the NIR and chemometrics seem to be a rapid and effective tools in the identification of Taggiasca cultivar and they are a very innovative techniques for molecular authentication of table olives.

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Studies directed towards the synthesis of the polycyclic core of the molecules isolated from Schisandra Lancifolia

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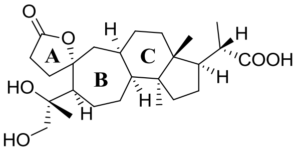
The **spiro [6.4.0] ring system** is a recurring structural motif in numerous natural products such as Lancifodilactones, Micrandilactones. Despite their interesting biological activities (anti-HIV for instance), the reason why we decided to focus on developing an approach toward the synthesis of the **ABCD** core of compounds **2** and **3** and the **ABC** core of target **1** comes from the fact that such compounds represent a synthetic challenge for organic chemists. Indeed, these polycyclic structures present at least nine stereogenic centers including several quaternary one. Several groups are working on their approach,[1-2] and to date, no total synthesis has ever been reported in the literature.



Lancifodilactone F

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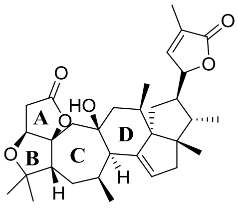
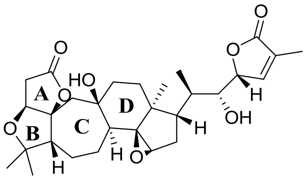


Lancifodilactone A

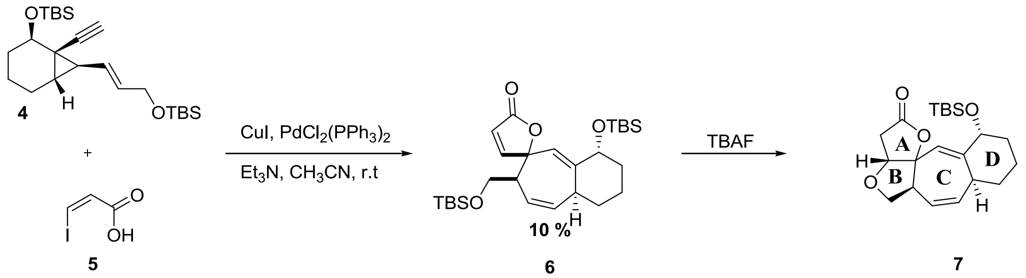
2



Micrandilactone B

3

We developed a new palladium-catalyzed domino reaction as a key step to obtain quickly and efficiently the [6.4] spiro moiety. This one pot three steps sequence afforded the desired tricyclic (6,7,5) structure **6** with a total diastereoselectivity although in only 10 % yield. The latter, in presence of TBAF evolves, by an oxo-Michael addition, into the lactone **7** affording the **ABCD** skeleton of Lancifodilactone A and Micrandilactone B in quantitative yield. Of course the yield of the domino reaction has to be improved but such a result validates the sequence during which the one-carbon ring expansion is accompanied by the creation of three carbon – carbon bonds and two stereogenic centers.



The synthesis and the cyclisations of these polycyclic compounds will be described and discussed.

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Semiclassical WUG corrections to the interaction energy of two coupled dipoles at low temperatures

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Well before the classical paper by London[1] on the dispersion attraction of two ground state hydrogen atoms, Keesom[2] showed that if two dipolar molecules a distance R apart undergo thermal motions they attract themselves with a law going as R^{-6} according to:

$$<V\exp(-V/kt)>\approx -\frac{2}{3kT}\frac{\mu_A{}^2\mu_B{}^2}{R^6}=\frac{\mu_A\mu_B}{R^3}\frac{2}{3}a.$$

The Keesom formula is easily derived by taking the first two non-vanishing terms in the Boltzmann average of the classical potential of interaction of the two molecules[3] for *small* values of the dimensionless parameter *a* (high temperatures and small values of the dipole strengths) and was recently extended to the higher multipole interactions[4]. Battezzati and Magnasco[5] modified the classical Keesom result for *large* values of the parameter *a* (low temperatures and large values of the dipoles) giving the three-term formula:

$$<V\exp(-V/kt)>\approx -2\frac{\mu_A\mu_B}{R^3}+2kT+\frac{2}{3}\frac{R^3}{\mu_A\mu_B}(kT)^2=2a\,kT+2kT-\frac{2kT}{3a}=<V>_{\rm cl}\,.$$

In the limit of small oscillations, the leading terms of this result can also be obtained by using the quantum Bloch density matrix expanded in the limit of small $\hbar$ [6,7].

In this paper, quantum corrections to the interaction potential energy of two permanent dipoles in the moderately low temperature régime are obtained through the Wigner-Uhlenbeck-Gropper (WUG) semiclassical expansion of the density matrix [6] up to $O(\hbar^2)$, an asymptotic expansion in the limit of $|a|\to\infty$ whose leading term is proportional to $\hbar^2$, the dipoles being assumed in oscillatory motion around their position of minimum energy, giving:

$$<V>=<V>_{\rm cl}-\frac{\hbar^2}{I}\left(\frac{a}{3}+\frac{1}{9a}\right)+\text{h.o.t.}$$

The quantum effects need to be considered in proximity of the turnover temperature T^* to the purely quantum régime and are always repulsive. Numerical applications to a series of heterepolar diatomic molecules of the first row (LiH, BH, CH, NH, OH, FH) show that the quantum corrections at $R=8a_0$ are not negligible, being particularly relevant for BH and OH (9.2% and 8.6%, respectively).

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Synthesis of 3- and 3,4-disubstituted chiral 1,2-benzenedisulfonimides

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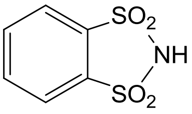
The catalysis with small organic molecules, named organocatalysis, has become a highly dynamic area in chemical research.[1] In the light of these, we have recently reported the use of *o*-benzenedisulfonimide (**1**) in catalytic amounts as a safe, non volatile and non corrosive Brønsted acid in some acid-catalyzed organic reactions under very mild and selective conditions.[2] This organocatalyst, highly soluble in both organic solvents and water, is easily recovered and purified from the reaction mixture and, owing to its complete solubility in water, it is ready to be used in further reactions, with economic and ecological advantages.[2]



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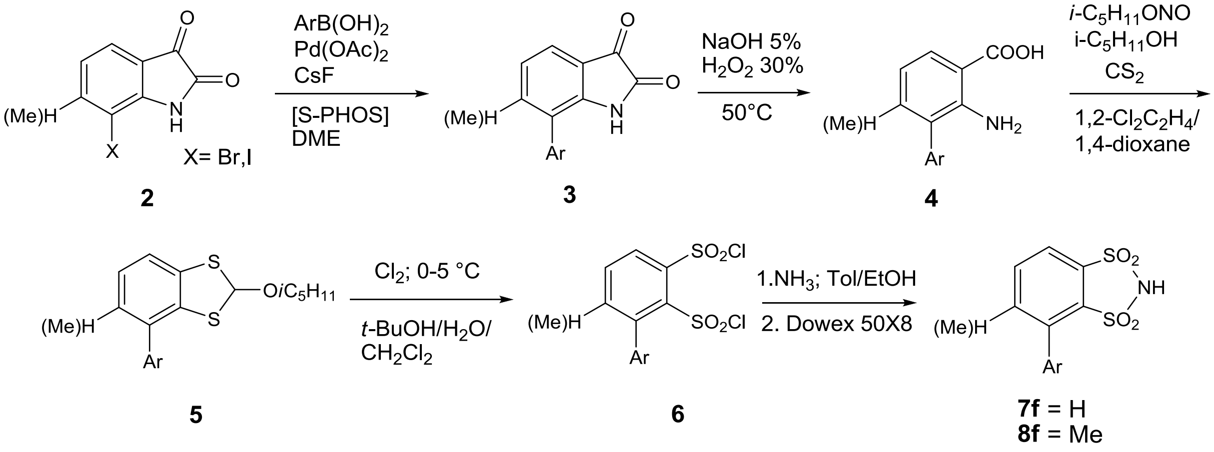
During the last years, some chiral Brønsted acid catalysts have emerged as a new class of organocatalysts for a number of enantioselective carbon-carbon bond forming reactions.[1] In the perspective of design of new and chiral acid organocatalysts with the structure of 1,2-benzenedsulfonimide, we propose a synthesis of hindered 1,2-benzenedisulfonimides bearing an aryl group in 3td position with fairly good overall yield.

The general scheme of the reaction is described below:



Ar= a C_6H_5; b 4-MeOC_6H_4; c 4-ClC_6H_4; d 2-*i*PrOC_6H_4; e 2-MeC_6H_4; f 1-naphthyl

The chirality of this acid is due to the hindered rotation of the aryl group placed in 3- position (atropisomery). Especially in the compound **8f**, theoretical studies demonstrate that the rotational barrier responsible of this property should be high enough to lead to stable enantiomers.

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Iron oxides: new perspectives as heterogeneous photocatalysts

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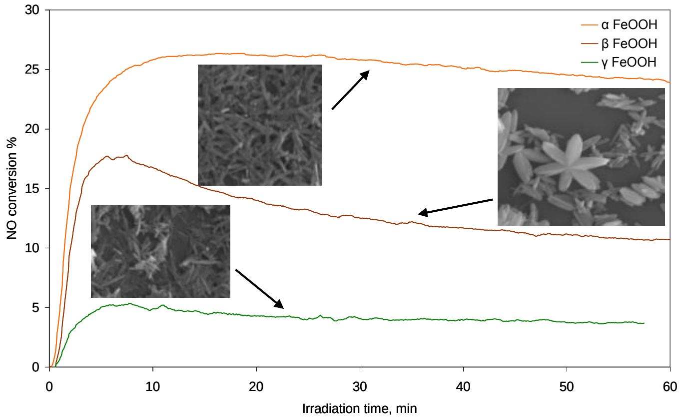
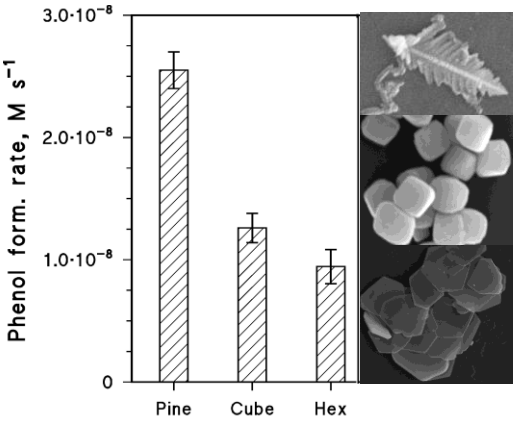
Iron oxides and hydroxides are widespread in nature and play an important role in a variety of disciplines, including environmental and industrial chemistry, corrosion science, soil science, biology and medicine.[1] Iron oxides have been widely studied in metallurgy and soil chemistry for their importance as colloids to adsorb a broad variety of chemical species. Non-systematic or incomplete studies are present in the literature regarding their photocatalytic activity.[2 3] In particular, the correlation between different shapes of iron oxides colloids and their catalytic activity has not yet been explored.[4] The present study demonstrates that two photocatalytic reactions carried out in the presence of iron oxides, namely solid-gas phase decomposition of NO and benzene hydroxylation in aqueous media, can be considered as valid methods to assess the photoreactivity of novel iron-based materials and as possible solutions to the problem of pollution in urban areas.





The growth of well-defined iron polymorph nanostructures can be obtained through simple hydrothermal processes, using an aqueous medium and anions or organic compounds as shape controllers. The synthesized materials shows very different shapes and expose different planes. Although it is still difficult to establish a correlation between the shape of the nanoparticles and their photocatalytic properties, species with a high concentration of surface hydroxyl groups such as α-FeOOH and β-FeOOH show the highest photoactivity. In contrast, α-Fe_2O_3 specimens show generally minor or poor photoreactivity. It has also been observed that iron oxides undergo photodissolution processes. In particular, the higher the photoactivity, the higher is the catalyst photodissolution or photoreductive dissolution in the presence of organic ligands and reductive agents. Future studies will be devoted to the understanding of the role of the exposed planes at the semiconductor-reaction medium interface and of how they affect both the efficiency of the photooxidation reactions and the rate of photodissolution through the presence of singly, doubly or triply coordinated surface hydroxyl groups.

The author is thankful to Rockwood Italia, Divisione SILO for the financial support of his Ph.D. thesis.

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HPLC-DAD-MS^n to investigate the photodegradation pathway of Nicosulfuron aqueous solution

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Sulfonylurea herbicides are used to control a variety of broad-leafed weeds and grasses in cereals and other row crops and for industrial weed control. They can be considered such "as new formulation pesticides" because of their high selectivity and low persistence in the environment.

The environmental interest derives not only from the possibility of diffusion and penetration of these herbicides in the deepest layers of ground, in particular in sandy or clay-poor soils, up to reach ground waters (their sorption depends on different factors, among which soil pH, soil texture, temperature etc.) but it is also very important to study the natural degradation that can form new species potentially more toxic and stable than the precursor herbicides; in this case a lower persistence in the environment unfortunately does not correspond to a lower toxicity[1]-[2]: from hence the importance of the identification of the species that can potentially form.

In this study the nicosulfuron, a typical sulfonylurea herbicide, is considered in order to follow the fate of the molecules in the environment simulating one of the natural process that can occur, the photoinduced degradation. Aqueous solutions of the herbicide in study underwent a simulated sun irradiation, the new species formed during the degradation process were identified by HPLC-DAD-MS/MS technique and a degradation pathway was proposed. Moreover the effect of temperature and the contribution of the hydrolysis were evaluated.

The use of ESI and APCI in both PI and NI mode permits to obtain integrated information about the metabolites that can be formed; moreover, a study of the total ion chromatogram followed by the extraction of the SIM chromatograms of the most intense m/z signals have made possible the identification of five possible photodegradation metabolites.

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Evaluation of surface carboxylic groups for oxidized Single Walled Carbon Nanotubes using Raman Spectroscopy

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The ability of Single Walled Carbon Nanotubes (SWCNTs) to permeate cell membranes without damage i.e. by passive diffusion[1,2], as a nanosyringe, with an energy and receptor indipendent mechanism, together with their proved biocompatibility, strongly suggests their utilization as carriers for cellular internalization of drugs, nucleic acids, proteins, etc.

But, to be used, pristine SWCNTs have to be oxidized, in order to eliminate toxic metal residues and to increase the number of carboxylic groups present on their graphitic walls that can be utilized for further covalent functionalization[3]. Oxidized SWCNTs can be then functionalized with several moieties, depending on the specific application. SWCNTs linked to drugs can be used for therapeutic purposes in several pathologies (including tumor treatments) [4,5]. In particular, SWCNTs functionalized with nucleic acids, such as DNA or small interfering RNA (siRNA), can be used for applications in gene therapy and interference[6], while SWCNTs functionalized with several labels (i.e. fluorescent tags) can be used for diagnostic purposes[7].

The abundance of available surface carboxylic groups is a critical point which depends on several factors, such as time, temperature and the type of the oxidative treatment used.

Here we use Raman Spectroscopy, coupled to a correct labelling[8], to develop a reliable method to evaluate the oxidation degree of chemically oxidized Single Walled Carbon Nanotubes.

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New supported recyclable material for reduction of disulfide derivatives

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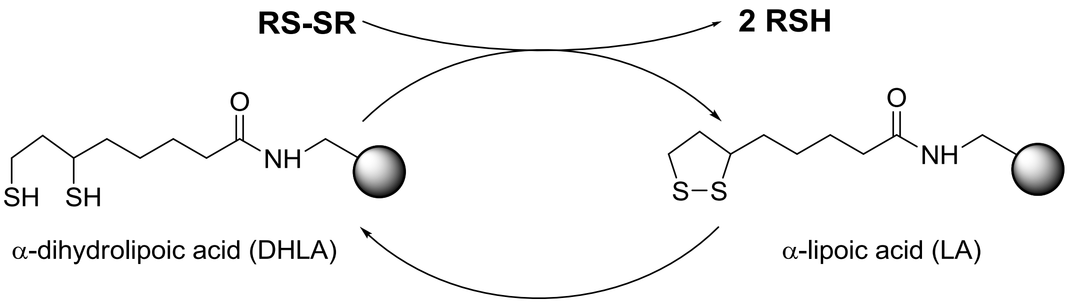
Delivery of genetic materials into a target cell is a major challenge for gene therapy that may be done with non viral systems or synthetic/artificial viruses.[1] For this aim, we are highly interested in the reduction of disulfide. Actually, (perfluoroalkylated) thiols or conjugates deriving from cysteine were used for the formulation of nanometric monomolecular DNA complexes obtained via detergent dimerization through thiol-disulfide process.[2].Often, these later are obtained in the disulfide form and have to be transformed into thiols before uses. Through the numerous method able to transform the disulfide into thiol, the more attractive one involves thiols themselves[3], this latter being used in a thiol-disulfide exchange reaction, that may be considered formally as an oxidation-reduction process. Moreover, to obtain a very easy work up, this thiol/disulfide function [□-dihydrolipoic acid (DHLA)/□□-lipoic acid (LA) redox couple] was attached on a resin so that the reduced prepared compound (disulfide → thiol) can be easily removed and the oxidized resin reutilized after reduction (Cf Scheme).



The resin we chose, the PEG Aminomethyl-ChemMatrix® one useful in aqueous media as well as in organic solvents, was grafted with the lipoyl residue on the remaining amino function. Various disulfides were reduced with this modified resin and we will present the first results obtained.

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Gas-phase reactions of GeF_3^+ with H_2O and NH_3: an experimental and theoretical study

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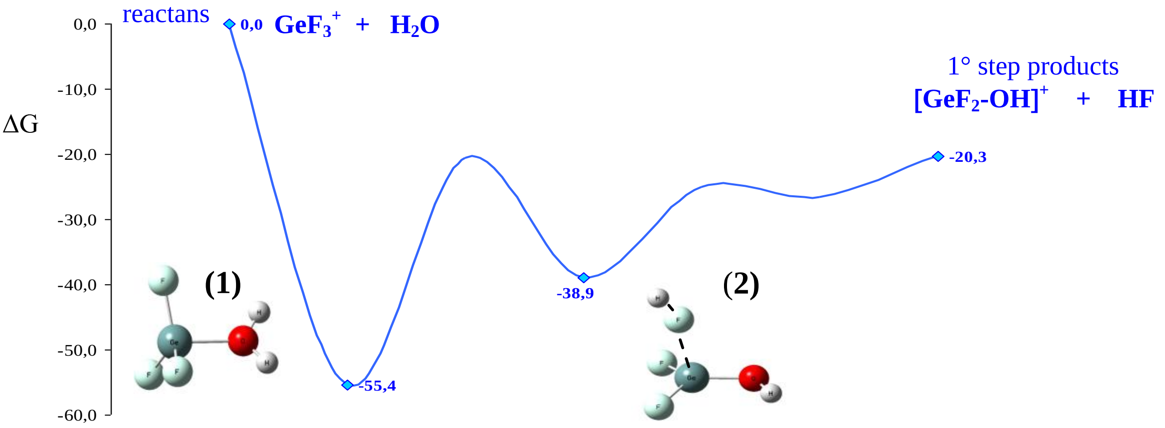
Neutral and ionic germanium fluorides $GeF_n^{+/0/-}$ (n=1-5) are of considerable interest not only for fundamental reasons but also for their role in the fine processing of semiconductors[1,2]. We discuss here the reactions between GeF_3^+ and the exemplary oxygen and nitrogen bases H_2O and NH_3. These processes were experimentally ascertained by ion trap mass spectrometry, and their mechanisms were elucidated by ab initio calculations. We optimized in particular the geometries of the involved intermediates and transition structures at the MP2(full)/6-311G(d,p) level of theory, and refined their total energies by CCSD(T) single-point calculations. The Figure shows the exemplary profile of the first step of the reaction between GeF_3^+ and H_2O. The process commences by formation of the F_3Ge^+-OH_2 complex (1), which interconverts into $F_2Ge(OH)^+$-FH (2), and eventually dissociates into F_2GeOH^+ and HF:



The F_2GeOH^+ cation further reacts with H_2O, and yields $FGe(OH)_2^+$ and $Ge(OH)_3^+$ by the following sequence of efficient reactions:

$$F_2GeOH^+ + H_2O \rightarrow FGe(OH)_2^+ + HF$$

$$FGe(OH)_2^+ + H_2O \rightarrow Ge(OH)_3^+ + HF$$

The reactions between GeF_3^+ and NH_3 are strictly analogue and consists of three subsequent and efficient addition-eliminations, with formation of $F_2Ge(NH_2)^+$, $FGe(NH_2)_2^+$, and $Ge(NH_2)_3^+$, respectively. The reactions between GeF_3^+ and H_2O and NH_3 closely resemble the corresponding processes involving SiF_3^+, investigated so far by SIFT mass spectrometry and ab initio calculations. This suggests further conceivable similarities between the still essentially unexplored reactivity of GeF_n^+ and the rich and variegated chemistry of SiF_n^+ (n=1-3).

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Synthesis of original amidoximes as antileishmanial agents

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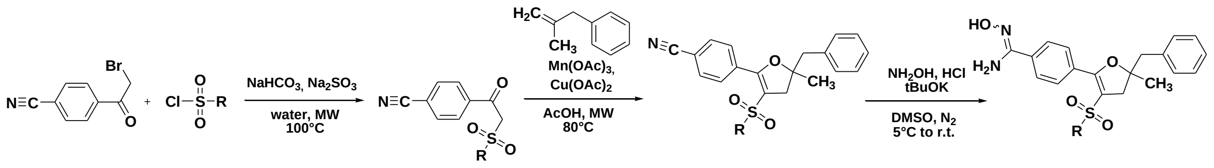
Leishmaniasis is one of the most important parasitic diseases worldwide. Research for molecules that act on new target remains thus necessary.[1] Recently, furamidine and its prodrug pafuramidine have shown interesting therapeutic activities in several parasitic infections including leishmaniasis.[2]

Previously, we explored the antileishmanial potential of several amidoximes derivated from pafuramidine, bearing a sulfone moiety and a 2,3-dihydrofuran scaffold. It appeared that some of these amidoximes revealed good properties against *Leishmania donovani* promastigote. Taking into account these studies, we present herein the synthesis of new amidoximes substituted by different sulfonyl groups, in order to explore the influence of sulfone on the antiparasitic activity.

The synthesis is carried out in three steps. First of all, eight β-ketosulfones were synthesized in water under microwave irradiation. Then, thanks to manganese(III) acetate based oxidative cyclisation, the eight dihydrofurans derivatives, substituted in position 4 by different sulfonyl groups, were obtained in moderate to good yields.[3] The last step consisted in converting these nitriles into amidoximes. The antileishmanial activity of these compounds is under active investigations.



R = p-CF_3-C_6H_4-, p-F-C_6H_4-, p-Cl-C_6H_4-, p-Br-C_6H_4-, p-I-C_6H_4-, p-CH_3O-C_6H_4-, p-NO_2-C_6H_4-, n-C_4H_9-

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Microwave Hydrodiffusion and Gravity (MHG): A Solvent free extraction of essential oils

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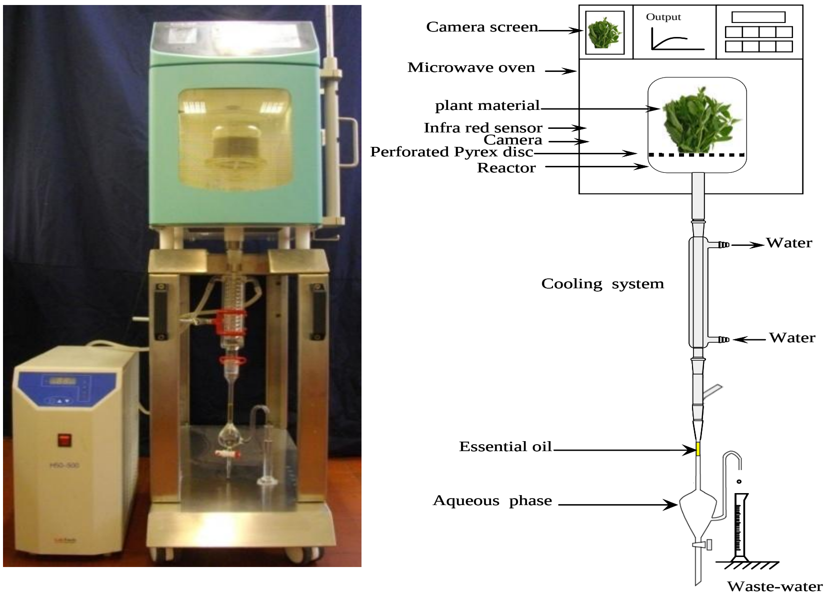
A recent patent describes a new and green technique for the extraction of essential oils from different kinds of aromatic plants. The microwave hydrodiffusion and gravity (MHG) system is an original combination of microwave heating and earth gravity at atmospheric pressure. Based on a relatively simple principle, this method involved placing plant material in a microwave reactor, without adding any solvent or water.

The internal heating of the *in-situ* water within the plant material distends the plant cells and leads to the rupture of glands and oleiferous receptacles.

The physical phenomenon, known as hydrodiffusion, allows the extract (water and essential oil) diffused outside the plant material, to drop by earth gravity out of microwave reactor and fall through a perforated Pyrex disc.

A cooling system outside the microwave oven cools the extract continuously. Water and essential oil are collected and separated in a vessel traditionally called the "Florentine flask".

This green method allows the extract essential oils without distillation and evaporation which are the most energy consuming between the unit operations.



Microwave Hydrodiffusion and Gravity (MHG)

Farid CHEMAT**,** Maryline ABERT VIAN, Francesco VISINONI, **European Patent, EP** 1 955 749 A1

2-Phenyl-1-Arylcarbamoyl-2,3-dihydro-1*H*-imidazo[1,2-*b*] pyrazoles 7-substituted as potential neutrophil chemotaxis inhibitors

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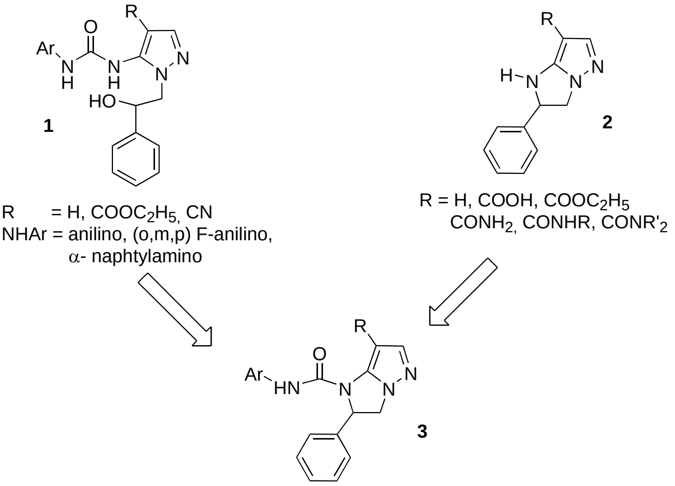
Neutrophils chemotaxis is a multi-step process induced by chemokines as interleukine 8 (CXCL8) and non-chemokine agents as N-formyl-methionyl-leucyl-phenylalanine (fMLP). Since the over-regulation of neutrophil chemotaxis is responsible for a series of inflammatory diseases, including many autoimmune pathologies, many researchers are involved in the search for new potential anti-inflammatory drugs interfering in neutrophil migration. In this context, we recently reported many pyrazolyl-urea derivatives (compounds **1**) active *in vitro* as IL8-induced chemotaxis inhibitors at nM concentration.[1] The chain modification on the N1 position of the pyrazole scaffold, gave us new very potent inhbitors (at nM-pM concentrations) both in the IL8- and in fMLP-OMe-induced neutrophil chemotaxis.[2]

At the same time, we reported a preliminary study on new interesting 2-phenyl-2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazoles 7-substituted (compounds **2**) which resulted potent inhibitors of fMLP-OMe chemotaxis.[3]

To increse our knowledges about SAR and mechanism of action of these chemotaxis inhibitors, we designed and synthesized a new series of 2-phenyl-1-arylcarbamoyl-2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazoles 7-substituted (compounds **3**) including in the same structure the rigid scaffold of compounds **2** and the urea moyeties of the most active compounds **1**.



R = H, $COOC_2H_5$, CN
NHAr = anilino, (o,m,p) F-anilino, α- naphtylamino

R = H, COOH, $COOC_2H_5$ $CONH_2$, CONHR, $CONR'_2$

R = H, $COOC_2H_5$, $CONH_2$, CONHR, $CONR'_2$
NHAr = anilino, (o,m,p) F-anilino, α- naphtylamino

All compounds were tested in *in vitro* chemotaxis assays in human neutrophils IL8- and fMLP-OMe-stimulated. Synthesis and preliminary biological studies results will be reported in the poster session.

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Synchrotron μ-beam study of oxygen content modifications in a single Bi-2212 superconducting whisker

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Several studies have been published on possible applications of cuprate high temperature superconductors for THz devices, due to their peculiar crystalline structure consisting of Intrinsic Josephson Junctions (IJJs).[1] In this framework Bi-2212 whiskers have been proposed because of their high crystalline quality and micrometric sizes. We recently reported on structural changes of Bi-2212 whiskers at ambient conditions,[2] and the present work is intended to clarify the correlation between crystalline and electronic effects which could be induced in Bi-2212 whiskers. The experiment was carried out at the ID-22 μ-beam line of the European Synchrotron Radiation Facility: a Bi-2212 whisker has been investigated by μ-XRD, μ-XRF and electrical characterization during a series of in situ thermal processes consisting of three main steps of 0, 6 and 24 hours at 90°C.[3] The electrical characterization data revealed an increase of the sample resistivity and a decrease of its T_c after each ageing step and each exposure to the X-ray μ-beam. The XRD measurements revealed two main crystalline domains (Figure 1) and the data analysis showed an increase of the *c*-axis parameter from 30.59Å to 30.72Å, in agreement with the oxygen depletion mechanism proposed to explain the resistivity increase. The mild temperature annealing of Bi-2212 micro-crystals, proved to be an effective process in modifying the c-axis lattice parameter, envisaging a possible method to modulate the IJJs' properties.

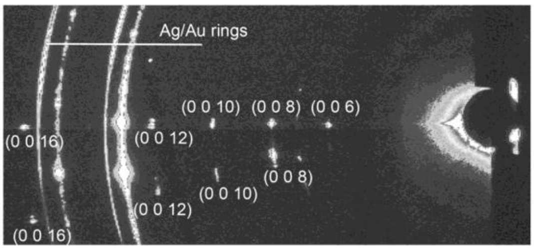

Figure 1: μ-XRD image of the as grown Bi-2212 crystal mounted on the chip.
Two main series of (00l) reflections are visible, corresponding to two domains misaligned by about 14°.

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Synthesis and characterization of Fe-based magnetic nanoparticles

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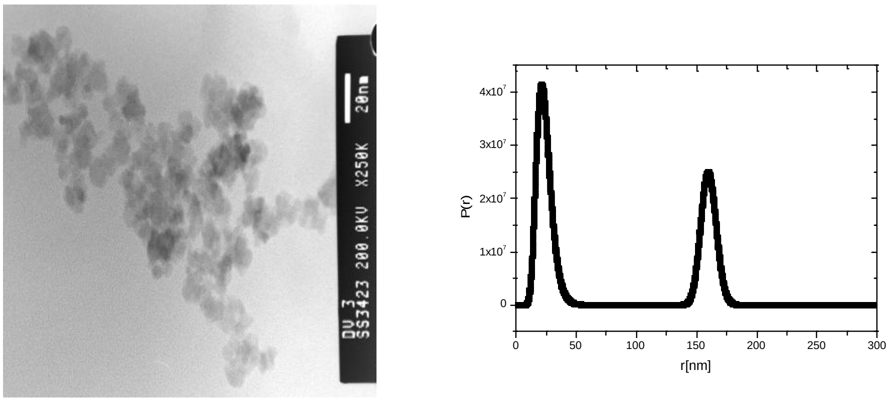
In recent years, the study of Fe-based magnetic nanoparticles has excited the interest of the materials international scientific community either for the peculiar fundamental physical properties shown by these nano-sized materials (electric and magnetic properties strongly affected by dimension and surface effects) and by different technological fields of use of these nanoparticles (high density magnetic storage media, catalysis, medical diagnosis, magnetic drug delivery, magnetic cell separation and so on)[1],[2].

Here, the synthesis and the morphological and physical characterization of magnetite nanoparticles is presented. The nanoparticles were synthesized by a coprecipitation method. The obtained black solution was washed several times with water, at 70°C, to completely eliminate ammonia. Finally, the nanoparticles were again dispersed in water.

Morphological (TEM) analysis was performed to achieve a preliminary information about the size distribution of the nanoparticles. The complete morphological study (size distribution histogram) of the magnetic nanoparticles was obtained by a.c. magnetic susceptibility measurements as a function of the applied frequency of the a.c. field. The particle magnetic dipole may relax with the a.c. field by two different mechanisms: Néel relaxation (rotation of the magnetic moment of the particle without physical rotation of the particle itself) and Brownian relaxation (due to the mechanical rotation of the particle and strongly dependent from radius of the particle and viscosity of the fluid). The mathematical analysis (MathCad 14.0) of the experimental results agree and complete TEM information, showing nanoparticles with a narrow size distribution. Additional magnetic measurements were performed by SQUID magnetometer.

Preliminary results concerning the coating of the magnetic nanoparticles with inorganic materials as gold or silica, in order to decrease the dipole-dipole interactions, are also reported.



TEM image and size distribution (from AC magnetic data) of Fe-based nanoparticles.

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Electrochemical Corrosion Study of Eutectic Sn-Ag-Cu Solder Alloy in NaCl Solution

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Lead-based solders e.g. eutectic or near eutectic Sn-Pb alloys have been used in microelectronics industry for a long time. The global concern on the environmental impact of toxic Pb-based alloys in consumer electronics, however has given an impetus to use Pb-free alternatives[1-4]. With the growing importance of lead-free solder technology, the eutectic alloy of the ternary Sn-Ag-Cu (SAC) system has gained considerable research interest. The eutectic SAC alloy is considered one of the most promising replacement for the Sn-Pb alloy as it offers a number of advantageous properties over other candidate alloys. The key advantages of the SAC eutectic alloy include its relatively low melting temperature (~ 217°C), reasonable wettability and superior mechanical properties compared to Pb-Sn and Ag-Sn binary alloys.

In the literature very little information is available on the corrosion resistance of Sn-Ag-Cu solder alloys[5-7].

The present communication reports a study on the electrochemical corrosion behaviour of the eutectic Sn-Ag-Cu solder alloy in a chloride-containing environment. The electrochemical characterization of the solder alloy was carried out by potentiodynamic polarization and impedance spectroscopy measurements performed in 0,1 M NaCl aqueous solution at room temperature, and a comparative study was made between the Sn-Ag-Cu solder alloy and the intermetallic phases (ε -Ag_3Sn and η- Cu_6Sn_5) formed in the eutectic. Light optical microscopy (LOM), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were used to characterise the microstructure of the samples to determine the coexisting phases and their composition, prior to and after the electrochemical measurements.

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Silylated diarylethenes as building-blocks for the elaboration of advanced optoelectronic structures

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In the last decade, interest toward photochromic diarylethenes, involving a ring closure/opening electrocyclic isomerisation, has been largely developed due to their thermal irreversibility, sensitivity and fatigue resistance. These intrinsic properties make diarylethenes highly promising for various applications. Indeed, besides the reversible change of colour, additional potentialities for technological applications could be offered by this family of compounds such as the preparation of light-triggered switching devices and optical molecular memories. In this regard, a high difference of fluorescence response between the open and closed forms is essential for the design of non-erasable readout systems. Unfortunately this emission difference is generally very weak for the parent compounds and the linkage of a fluorophore unit is often necessary. We assumed that a modification of the structure of the pentatomic cycle could induce this kind of behaviour. Many attempts have been performed to introduce heteroatoms (O, S, N) in the cycle.

The preparation of new photochromic diarylcyclopentenes including silicon atom was investigated. These exhibits appreciably intense fluorescence emission in the visible region, originating from the closed form[1,2]. Based on this work, we described new photochromic building blocks containing silicon atoms. Their photochromic behaviour are in progress.

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Glycosylated bisabolols from a Middle-East *Carthamus*

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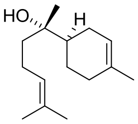
Because of it excellent anti-inflammatory activity, *S,S*-α-bisabolol (**1**), the major ingredient from chamomile oil, is an important cosmetic ingredient, currently obtained synthetically from either farnesol or other terpenoid building blocks to meet its growing demand. Apart from chamomile, several other natural sources of this compound exist, and two of them (*Vanillosmopsis erythropappa* and *Artemisia rutifolia*) are currently exploited industrially to complement the synthetic source.[1] Synthetic α-bisabolol is a mixture of stereoisomers, and concerns exists on the presence of farnesol (**2**), a known skin sensitizer, in the final product. Therefore, the search of new natural sources of this compound is a hot topic, currently pursued worldwide.

We present evidence that the Middle-East weed *Carthamus glaucus* Boiss. is an extraordinarily rich source (*ca* 2% on dry weight basis of the aerial parts) of a fucosidated form of α-bisabolol (**3**)[2] well worth considering as a novel, more water soluble, alternative to the aglucone. Several further acyl decorated analogues were obtained (e.g. **4-7**) , as well as an unusual triglyceride bearing a butenoyl moiety at the central position (**8**) and a B-ring non-oxygenated flavonoid (**9**).



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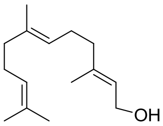

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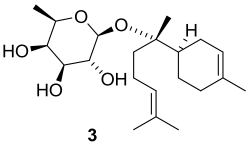

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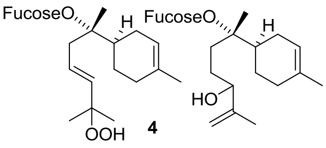

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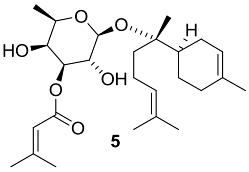

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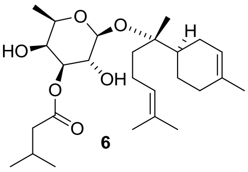

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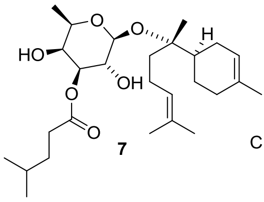

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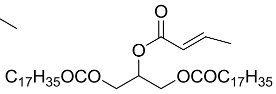

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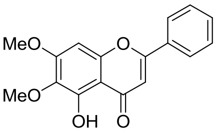

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Multicomponent reaction from 1,3-dicarbonyl for the regiospecific synthesis of highly functionalized pyridines

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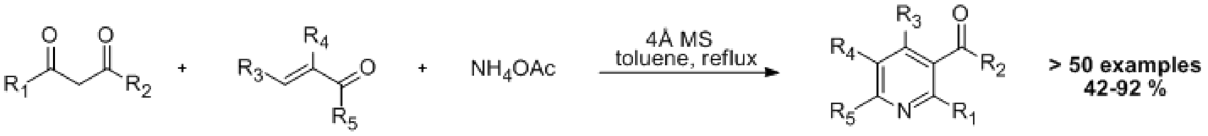
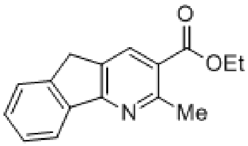
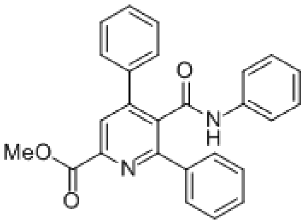
At the moment, the ecological situation of our planet is becoming worrisome and the organic chemists have to go into an "eco-conception" era of molecules, while remaining capable of furnishing products of high molecular complexity. Among the various methods developed for that purpose, multicomponent reactions[1] involving domino processes answer perfectly these constraints. They allow to reach a large number of variously functionalized molecules from at least three substrates reacting simultaneously.

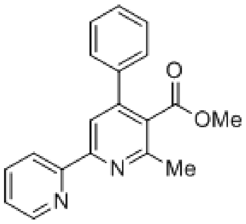
In this context, our Group is interested for several years in the synthesis of new heterocyclic molecules with the aim of using them as building blocks for the development of new leads in the pharmaceutical industry. Thus we developed new Michael addition-initiated domino multicomponent reactions[2] involving a 1,3-dicarbonyl compound,[3] a Michael acceptor and various amines. This sequence allowed the rapid access to highly substituted pyridines when the amine is replaced by an ammonia source : ammonium acetate.[4]

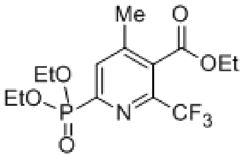


With appropriate starting materials, it is possible to form pyridine derivatives such as azafluorenones, nicotinamides, bis-pyridines or fluorinated pyridines. A wide panel of substituents can be easily introduced on the pyridine moiety in a totally regioselective manner.









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Influence of electrospinning parameters on nanofibrous polymeric membrane formation

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Electrospinning represents a novel technique able to produce single nanofibers and continous filaments with nanometer size diameter (5-500 nm). Indeed, by reducing the fiber diameters from the microscale (10^{-6} m) to the nanoscale (10^{-9} m), peculiar properties are attained, such as high surface area per unit mass, flexibility in surface functionalities and superior mechanical performances.

In the present work, the above technique has been applied to develop electrospun membranes based on poly(vinylidene fluoride) (PVDF). The films were characterized by several experimental techniques including scanning electron microscopy (SEM), wide angle x-ray diffraction (WAXD), infrared (FTIR) and Raman spectroscopy and contact angle measurements. By studying the influence of several electrospinning parameters, such as humidity, air flow rate, type of solvent and voltage tension, on the nanofiber features, the most suitable conditions, which allowed to obtained defect-free and uniform nanofibers, have been assessed (see Figure). In particular, with increasing electrospinning chamber humidity the homogeneity of fiber diameters has turned out to ameliorate together with a reduction of the collector area covered, namely an appropriate control of the above parameter is crucial in the development of electrospun films with suitable characteristics. It is worth underling that the above parameter is generally not taken in proper consideration.

Moreover, the electrospinning process has been found to be capable to promote the formation of β-phase, which is responsible of PVDF piezoelectric and pyroelectric properties.

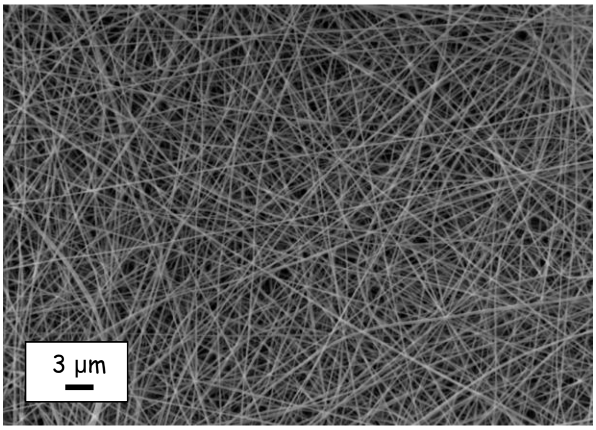

Figure. SEM micrograph by BS of PVDF electrospun nanofibers under optimal working conditions.

Photocatalytic treatment of soil washing wastes containing the herbicide bentazon

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The soil matrix is a constantly evolving environmental compartment deriving from various factors and chemical, physical and biological processes affect more or less profoundly the original nature of the starting material.

The main effect of soil pollution is the extended contamination due to the leaching of toxic and persistent xenobiotic compounds into deeper layers of soil, which may enter the food chain giving rise to bioaccumulation phenomena and moreover, can reach the aquifers, originating obvious risks to human health.

Among all the remediation treatments, soil washing is an ex-situ technology used for the soil decontamination, which employs mechanical processes to separate and wash soil particles. In this context surfactants are often used as solubilising agents in the washing formulations, due to a generally low toxicity which makes them more environmental friendly than washing systems based on organic solvents.

A crucial point is that, after the soil washing, it is often necessary to perform a suitable treatment before discharging the obtained wastewaters. Nowadays increasing attention is devoted to the photocatalytic approach, based on the use of semiconductors under irradiation of light of proper wavelength. Titanium dioxide is extensively applied in heterogeneous photocatalysis since it is a stable, inexpensive, not toxic and highly photoactive material. However, despite of the large number of reported applications of both soil washing and photocatalytic treatments, the possible use of photocatalysis to treat soil washing wastes has not yet been thoroughly studied and no systematic work has been done in this direction.

In this perspective we investigated the removal of bentazon, 3-isopropyl-1H-2,1,3-benzothiadiazin-4-(3H)-one-2,2-dioxide, a post-emergence herbicide used for selective control of broadleaf weeds and seeds especially in rice fields. The application of aqueous solutions containing non ionic surfactants ($C_{12}E_5$, $C_{12}E_8$ and Brij 35: $C_{12}E_{23}$) having the same hydrophobic moiety was initially investigated to remove the pesticide pollutant from contaminated soil samples. The results indicate that all the investigated surfactants, under the examined conditions, can effectively remove the bentazon residues from the soil.

We further considered the possible use of photocatalysis to degrade the pollutant loading present in the washing wastes. A preliminary study of the photodegradation process was performed in aqueous solutions in order to identify the transient intermediates formed and their evolution during the treatment. The formation and evolution of the main end products coming from the mineralization of the pesticide was also monitored.

The effect of surfactants on the kinetics of the photocatalytic treatment was successively investigated. Among the examined surfactants, the more hydrophilic compound Brij 35 showed the lowest inhibition effects, allowing the abatement of bentazon after a reasonable irradiation time and, thus, suggesting the use of this compound as suitable soil-washing candidate in view of the possible photocatalytic treatment of the wastes. Degradation experiments performed on soil washing wastes obtained using Brij 35 confirmed the effectiveness of the coupling between these two examined remediation steps.

Sustainable Preservation of Historical Parchments

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Parchment was used as the common writing support from Ist century BC to XVth century AD. Earliest records of writing on skins date back to the Fourth Egyptian Dynasty (about 2500 BC). With the adoption by Assyrian people (about 800 BC) of Aramaic writing, for which clay tablets were not suitable, the use of parchment spread widely. Ability to write on both sides of parchment and its very lasting structure enabled the replacement of papyrus scrolls. Thus, parchment manuscripts are priceless records of the beliefs and ways of living and governing that form the roots of the European and Mediterranean civilisations. Moreover, as ink and paint had no spill out effect on parchment, illuminated codices have become real works of art.

Nonetheless, parchment documents represent a conservation problem which has not been solved. Recently, characterisation of damage in parchments has been achieved through the examination and comparison of artificially aged and historical parchments in the compass of EU IDAP (Improved Damage Assessment of Parchment) and Italian OPERA (Old Parchment Evaluating: Restoration and Analysis) research projects. Samples (sheets, bookbindings, rolls) were provided by the Archives collaborating in the projects, namely State Archives of Turin, Historical Archives of the City of Turin, State Archives of Genoa, State Archives of Florence, Historical Archives of the University of Turin, for a total of more than 80 subsamples from about 40 historical documents of different origin dating from XIIIth to XVIIIth century AD.

The effects of our accelerated ageing protocols concerned with the action of physical (temperature, humidity, light)[1] and chemical (gaseous pollutants in the atmosphere)[2] factors on the stability of parchment were investigated by advanced physical-chemical techniques: differential scanning calorimetry (DSC), scanning electron microscopy (SEM), infrared spectroscopy (ATRIR, FTIR), unilateral nuclear magnetic resonance (NMR) and thermomicroscopy.[3]

Characterisation of ageing processes has been obtained by non-invasive or micro-invasive, non-destructive or micro-destructive techniques that target molecular, nanoscopic, mesoscopic and microscopic properties of parchment.[4] Such an integrated approach has delivered diagnostic protocols based on the correlation between nano- to microstructural changes and macroscopic damage in parchments.[5] Their proper employment in the assessment and monitoring of historical parchments, restored parchments and those running the risk of irreversible alterations could significantly improve strategies for the sustainable preservation of the parchment funds. For the first time a comprehensive procedure for grading damage in historical parchments has been set up.

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Investigation on annealed amorphous germanium carbide prepared by X-Ray radiolysis of $GeH4/C2H2$ gaseous mixtures

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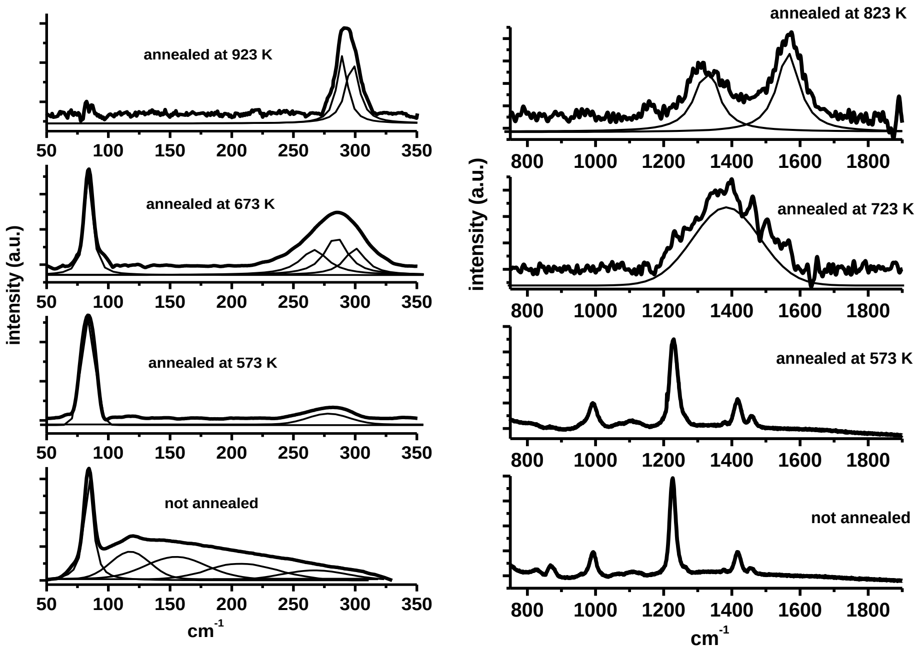
Amorphous germanium carbide films have attracted a great deal of attention because of their interesting physical properties such as electrical and optical semiconducting properties. [1]

In our laboratory, hydrogenated germanium carbides films have been produced by X-Ray activated Chemical Vapor Deposition (CVD) from germane/hydrocarbon gaseous systems.[2] The electronic properties of these films strongly depend on morphological and structural characteristics.[3]

In this work we report the results about the investigations on properties and stability of films obtained by radiolysis-CVD of germane/ethyne mixtures, annealed under inert gas flow at different temperatures. The materials are analyzed with respect to the composition and local bonding configuration and the results are correlated to the optical parameters.



Raman spectra of solid sample obtained from radiolysis of GeH_4/C_2H_2 mixture (50% C_2H_2 percentage) annealed at different increasing temperatures.

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A new entry to polyfunctionalized triazoles.
A Cooperative effect of Iron-Copper co-catalysis and ultrasonic activation

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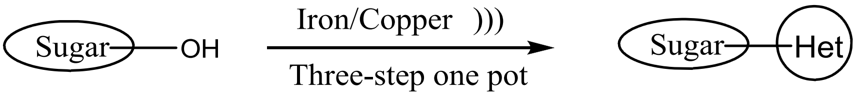
The development of eco-compatible, efficient, and selective catalysis is a fundamental goal in modern organic chemistry. During the last decades, transition metal catalyzed reactions have been reported and have significantly improved numerous chemical transformations. However, most of the reported works are based on precious metals such as palladium, nickel, rhodium, iridium and ruthenium. The limited availability of these metals and their high price makes it highly desirable to search for more economical and environmentally friendly processes. Among the various relevant metals, iron and copper are attractive alternative for the development of sustainable procedures.

The formation of C-N bonds is one of the most important reaction in organic synthesis including natural products, biomolecules and especially in biologically relevant glycosylation reactions. One of the main methods in glyco-chemistry is the Lewis acid-catalyzed N-gycosylation reaction. However, this well-known method suffers from several drawbacks and limitations. Recently, we developed new systems for C- and N-glycosylation reactions able to promote these transformations under mild conditions. As a continuation of our studies directed at the development of straightforward and sustainable methodologies, we presents here a first and original example of cooperative effect of non-conventional activation and Fe/Cu co-catalysis that allows an efficient three-step one pot route to new substituted triazoles (Figure).



Synthesis and spectral properties of fluorescent oligonucleotides, bearing 3-hydroxy-chromones as new modified nucleobases

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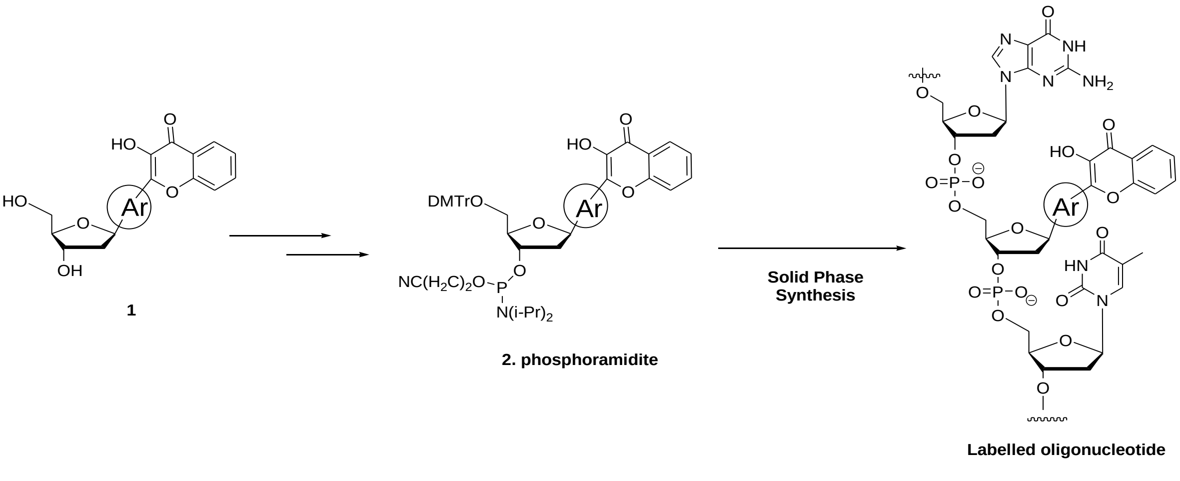
2-Aryl-3-Hydroxychromones (3HC) are oxygen-containing heterocyclic compounds with uncommon fluorescent properties. Due to their functional groups and specific electronic structure, this type of dyes is able to tautomerize after light absorption by an "excited state intramolecular proton transfer", or ESIPT. The two excited tautomers emit photon independently given two well separated bands with difference in wavelength around 100 nm. The equilibrium between the two excited species, therefore the intensity ratio between the two bands, depends on molecular environment properties. This noteworthy property has stimulated usage of 3HC as reporting group in the construction of ratiometrical fluorescent sensors with wide field of applications.[1] 3HC-based ratiometrical fluorescent probes have been used in the studies of solvent and solution polarity, proteins aggregation, lipid membranes properties and others but no studies based on oligonucleotides labelled with 3-HC have never been described. In this research, our goal was to synthesize fluorescent 3HC-containing oligonucleotides and to characterize their photophysical properties. These dyes might find applications for the studies of nucleic acids and their interactions with proteins as well as sensors in diagnostic and screening tests. One way to attain this goal is the covalent replacement of one of the natural bases by a 3-HC derivative.



For this purpose fluorescent nucleoside (**1**) was synthesized in 15 steps from commercially available compounds.[2] It was transformed into phosphoramidite (**2**) and used for solid-phase DNA synthesis. A series of oligonucleotides containing 3HC as modified nucleobase was obtained and the structure and photophysical properties of the labelled oligonucleotides were explored using UV, circular dichroism and fluorescent spectroscopies.

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Microwave Steam Diffusion (MSDf): New and green process for extraction of essential oils

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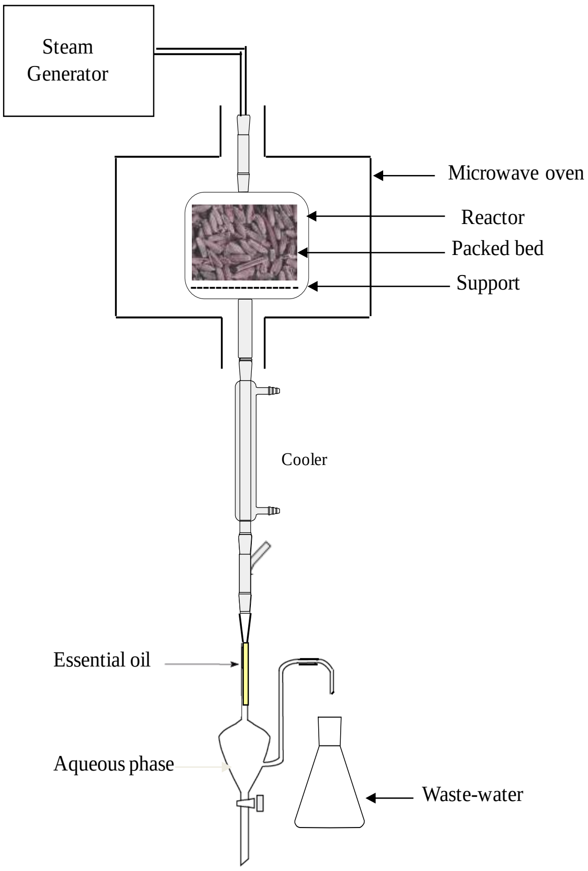
Microwave steam diffusion (MSDf) is proposed as a novel method for green extraction of essential oils from different types of aromatic plants. It is a combination of microwave heating with saturated steam which favours the release of essential oils trapped from the inside to the exterior of the cells of plant tissues and earth gravity to collect and separate. MSDf has been compared with conventional steam diffusion SDf. This green microwave extraction process offers important advantages over traditional steam diffusion, namely; shorter extraction times, lower energy consumption, lower cost and reduced waste water. This study present MSDf as a green, cleaner, environmentally friendly, economic procedure and efficient extraction method of essential oil.



Microwave Steam Diffusion (MSDf)

Phase equilibria in semirigid polymeric systems investigated by applying a revised Flory approach

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Semirigid polymers have focused, during the last decades, an increasing lot of theoretical and experimental scientific work. The main reason is that these polymers display excellent qualities when evaluated as liquid crystals[1,2], owing to the presence, within their macromolecular chains, of rigid and flexible sequences in alternating order, i.e. of intrinsic co-existing anisotropic and isotropic characters.

A very refined approach to the theoretical treatment of phase equilibria in polymeric systems involving semirigid macromolecular chains was developed by Matheson and Flory[3], innovatively using mathematical techniques suitably borrowed from statistical mechanics. Their method is completely general, as it can be applied to deal with any possible semirigid structure and also includes previous results obtained by Flory in treating phase equilibria within systems where the pure flexibility[4,5] or the pure rigidity[6] are specific mutually exclusive features.

The equilibrium equations suggested by Matheson and Flory were found[7], however, to be slightly incomplete, since no enthalpic parameter evaluating possible polymer-polymer interactions was taken into account. Thus their applicability implies a strictly athermal mixing of the involved polymers, endothermic and esothermic processes being not covered.

In order to remove this reduced applicability we have deeply revised the approach proposed by Matheson and Flory, developing an improved version where the thermodynamic contributions coming from polymer-polymer interactions are properly represented.

The reliability of the arising modified equations has been numerically verified by investigating phase equilibria within binary systems involving two interacting polymers.

As it was to be expected, the complete miscibility that the equations proposed by Matheson and Flory would predict cannot survive when the introduced enthalpic parameter accounting for polymer-polymer interactions exceeds a critical threshold. The previously existing single homogeneous phase is consequently replaced by two co-existing phases. Their differentiation, moreover, sensibly increases if the values selected for the enthalpic interactive parameter progressively become larger and larger, the extreme limit being represented by the complete immiscibility of the two polymeric species.

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Siloxane adsorption by solids in biogas purification

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Biogases are methane-rich gases produced by anaerobic digestion of waste materials, such as waste water treatment plants, animal sewage, landfill wastes. These gases can find several energy applications: they can be burnt to produce heat, used as fuels for biogas fuel cell, for spark ignition engines or gas turbine to recover electric power. A possible application to produce hydrogen or syngas by steam reforming of methane can also be envisaged. Whatever the application, the use of biogas is hindered by the presence of a wide amount of impurities, detected in traces or significant amount: amongst them, linear and cyclic low molecular weight siloxanes are commonly found, likely arising from polymethylsiloxanes widely used in the formulation of household, personal care and other industrial products or formed as stable thermal degradation products of polydimethylsiloxane, a member of the silicones family[1]. These compounds are converted upon combustion into quartz and silicate powders, which damage the inner surfaces of the combustion engines and depose at the surface of fuel cell electrodes and combustion or steam reforming catalysts, deactivating them. Their removal can be achieved by condensation, gas liquid extraction or by solid phase adsorption over activated carbons (method of choice), resins, molecular sieves and silica gel.

In the frame of an investigation on the best procedures for biogas purification, we studied the adsorption and thermal decomposition of hexamethylcyclotrisiloxane (HMCTS, one of the most abundant siloxanes in landfill biogases) from wet synthetic biogases (CO_2-CH_4 mixture), at room temperature and in the range 473–673 K over the surface of basic (CaO, MgO) and acidic oxides (zeolites, Al_2O_3, SiO_2), and several commercial active carbons (AC)[2,3]. The adsorption mode of this molecule has been investigated both in a fixed bed continuous adsorber as well as by IR spectroscopy in static conditions. Although at room temperature pure ACs are better siloxane sorbent than inorganic solids such as silica and zeolites, mineralization of silicon atoms occurring at high temperature over inorganic solids can be proposed as an alternative approach to gas purification. In particular, alumina allows the complete removal of HMCTS from synthetic biogases at 673 K. A reactive adsorption occurs with OH groups consumption, surface silication and release of methane until the silication monolayer capacity. On the contrary, silica, which is an excellent adsorbent for siloxanes at room temperature, looses its adsorption ability at high temperature as it is typical of a molecular adsorption behavior. Basic oxides such as MgO and CaO have strong reactivity in decomposing siloxanes in the absence of CO_2, but loose reactivity when in contact with carbon dioxide because of surface carbonation.

Acknowledgements. This work has been supported by MIUR-PNR-FIRB ("Risparmio energetico con valorizzazione dei Bacini Secondari di Energia quale fonte energetica distribuita" - Unità "Natural Energy from Waste (NEW)").

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Chemical modified *Spirulina Platensis* biomass in wastewaters treatment: Chromium (VI) removal.

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The use of biomass to remove toxic metals from industrial wastewaters represent an interesting alternative to the conventional methods, being this technique environmentally friendly, as it offers high selectivity, easiness of operate and effectiveness in the treatment of large volume of wastewaters.

Chromium VI is a common pollutant in wastewaters from textile, leather and metal finishing industries and is mostly found (depending on the pH) as chromate, hydrogen chromate and dichromate species[1]. On the other side, *Spirulina platensis* biomass, an effective biosorbent for cations, cannot be used to adsorb chromate due to its negatively charged surface close to neutral conditions; therefore, a chemical modification reducing the negative surface charge should improve the adsorption capacity towards chromium (VI). Methylation of yeast has been successfully applied by Seki et al.[2] for Chromate and Arsenate adsorption. Following these results we tested methylation process on *S. platensis* biomass and studied the effect of methylation (carried out in methanol/HCl, stirring at room temperature for 24 hours) on the properties of the biomass surface and subsequently its adsorption ability[3] has been investigated in the chromate removal experiments.

In this work we present results from batch tests carried out in the pH range 7–8, in order to focus exclusively on the methylation influence on the biomass adsorption capacity in the absence of any hydrolysis reaction. Results obtained varying both Cr(VI) and methylated biomass concentrations showed that 2–4 g/l of biosorbent were able to remove 8-35 mg/l Cr(VI) with efficiency ≥80%, while higher Cr(VI) levels (43–50mg/l) showed low removal efficiency, in any case yielding substantially better results than the untreated biomass.

The model of Langmuir described the adsorption phenomenon better than the Freundlich one. The values of the overall adsorption capacity of methylated biomass suggested that increased biosorbent availability does not necessarily correspond to larger amount of adsorbed metal.

In order to evaluate how functional groups modifications induced by methylation impact on the biosorption process and to which extent biomass is chemically modified, raw and modified biomasses have been investigated by FT-IR spectroscopy. FT-IR spectra of raw and methylated biomass of *S. platensis* allowed us monitoring the efficiency of the methylation process through the analysis of CH and COO− vibrational stretching modes, taken as diagnostic of this process, thus confirming the decreased number of carboxylate groups at the biomass surface. Moreover, a number of other functional groups, such as "free" carboxy groups (–COOH), amines (–NHR, $-NH_2$) and ether ($-C-OCH_3$), newly formed as consequence of the methylation processes have been detected and could have been involved in the adsorption process, too. Once defined in this study the effect of methylation, further investigation on chromate species adsorption at lower pH values are envisaged.

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A mass spectrometry study of the cationic catalysis of decarboxylation of organic acids in the gas phase

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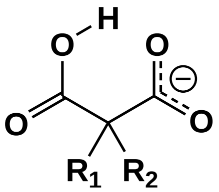
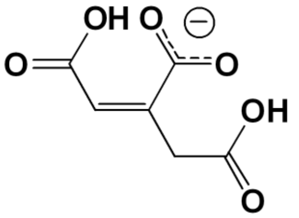
In the context of the transport of ^{137}Cs in the environment, we are currently investigating the interaction between the cesium cation and natural organic matter (humic and fulvic acids). Simple organic acids were utilized as functional models of humic and fulvic acids, and collision induced dissociation (CID) of different adducts of their anions with Cs$^+$, generated by electrospray ionization (ESI), were examined in an ion trap mass spectrometer (Thermo Finnigan LCQ Classic).[1,2]

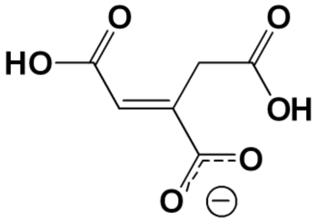
During these studies, we have observed a CO_2 loss in a number of cases, in particular in adducts involving anions of di- and tricarboxylic acids. To check if the coordination of the anions exerts a catalytic effect on the decarboxylation, a comparison between the CID of “naked” anions A$^-$ (negative mode ESI) and of [A$^-$Cs$^+$]Cs$^+$ (positive mode ESI) was carried out. The systems studied included monoanions of malonic acids (substituted or not) and *cis*- and *trans*-aconitic acids, see below.



Malonates (R_1, R_2 = H, alkyl, aryl)



Cis-aconitate



Trans-aconitate

The ion (either A$^-$ or [A$^-$Cs$^+$]Cs$^+$) was selected and subjected to CID, with stepwise increase of the collisional activation (as measured by the relative “normalized collision energy” of the instrument, expressed as NCE%). The catalytic effect is monitored by plotting the amount of dissociation as a function of collisional activation. When a given fragmentation starts at a lower activation, this means that catalysis is operative.

For the malonates, we have observed a significant catalytic effect when the anion is coordinated to two Cs$^+$. The behavior of aconitates is more complex: although the decarboxylation is not significantly catalyzed for the *trans* isomer, another reaction channel concurrent to decarboxylation, loss of H_2O, is catalyzed for the *cis*.

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Organocatalytic synthesis of β-aminovinyl phosphonates

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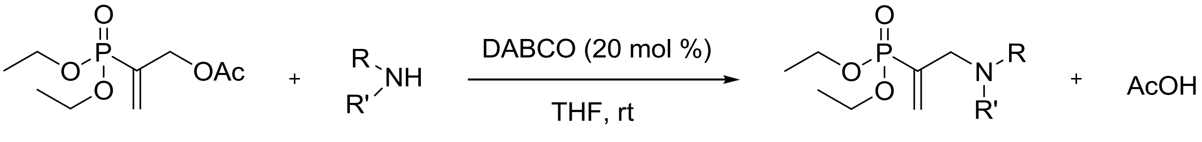
β-aminovinyl phosphonates have received attention due to their use for the preparation of β-aminophosphonic acid derivatives which display diverse biological activities such as antibiotics, enzymes inhibitors, anti-HIV inhibitors,[1] as well as anti inflammatory agents.[2]

Although some β-aminovinyl phosphonates have been obtained by several methods, we present in this study an alternative and general synthesis of diethyl β-aminovinyl phosphonates **2** through an organocatalyzed displacement reaction of acetoxy group from acetoxy phosphonate **1**.



1 **2**

Performed at room temperature, the reaction leads to expected compounds **2** with good to excellent yields in the presence of only a slight excess of nucleophile (1.1 eq). However, we found that the use of DABCO is not essential in several cases.

Under these selected conditions, the scope of this reaction was extended to the synthesis of new highly functionalized β-aminovinyl phosphonates through the use diversely substituted primary an secondary amines.

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Structural characterization of GSK-3β by in silico tools: a crucial step towards the design of selective non-ATP competitive inhibitors

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Alzheimer's disease (AD) is a progressive neurodegenerative disorder and the leading cause of dementia in the elderly. Neurofibrillary intracellular tangles deposition represents one of the main mechanisms responsible for the pathology. This phenomenon is due to the anomalous hyperphosphorilation of τ protein by Glycogen Synthase Kinase-3β (GSK-3β). As a consequence, the design of GSK-3β inhibitors represents a crucial strategy in the treatment of AD. Since kinases are a class of proteins ubiquitously expressed and involved in the regulation of many cell functions, the identification of the structural features defining the active sites of GSK-3β in human brain is mandatory for designing selective inhibitors.

Given this scenario, the aim of our study is the structural characterization of GSK-3β ATP-ase and not ATP-ase binding sites by in silico bioinformatic tools.

Firstly, the 20 crystallographic structures of GSK-3β extracted from PDB were ranked according to their structural quality. For the best of them, the ATP-binding site (Figure 1) was individuated and other potential binding pockets as well.

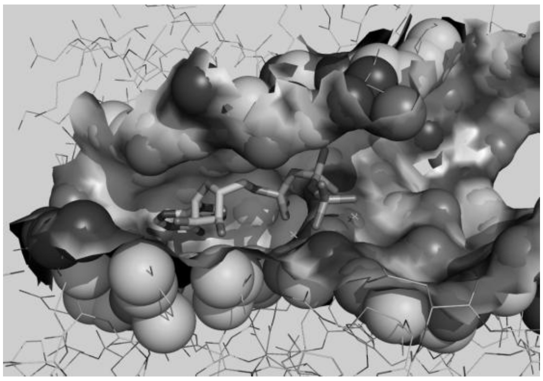

Figure 1. The figure shows the interaction between GSK-3β (ID:1PYX) and the ATP-ase inhibitor phosphoaminophosphoric acid-adenylate ester (ANP).

The nature of the forces involved in the interaction between co-crystallized ligands and the residues of the ATP-binding site was then elucidated. As a further step, the analysis of vibrational motions of GSK-3β was assessed by an anisotropic network model and a particular attention to the active sites residues was paid.

Finally, docking runs were performed to investigate the binding mode of some non-ATP competitive inhibitors reported in the literature.

The study was undertaken with the following bioinformatic tools:

VADAR (http://redpoll.pharmacy.ualberta.ca/vadar/), CAST-p (http://sts.bioengr.uic.edu/castp), Ligand Explorer (http://www.rcsb.org/), ANM (http://ignmtest.ccbb.pitt.edu/cgi-bin/anm/anm1.cgi), DOCK Blaster (http://blaster.docking.org/). MOE 2009.10

Determination of Mercury in Real Samples Using a Gold-modified Glassy Carbon Electrode

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Mercury and its compounds are highly toxic, even at low concentrations, they accumulate in vital organs and tissues and cause kidney injiury, central nervous system disorders, intellectual deterioration and even death. For these reasons, there is an increasing necessity for quantification of mercury in different samples, such as in environmental compartments, food, humans and pharmaceuticals. Therefore it is important to develop sensitive analytical methods for its determination.

The aim of this work is to evaluate the applicability on different real samples of a procedure for the determination of aqueous Hg(II) by anodic stripping voltammetry at a gold -modified glassy carbon electrode. Modification with gold was performed by dipping the electrode into a 50 mg/l $HAuCl_4$ solution and applying a potential of 0.80 V for 6 min. From a previous study[1] optimal values of the square wave parameters for the stripping scan were: step potential 0.004 V, frequency 150 Hz, amplitude 0.003 V. The highest signal with the best baseline shape was obtain with a deposition potential of 0 V. As expected, the height of Hg peak increased with increasing deposition time; a value of 120 s was found to be suitable for concentrations up to 50 µg/l. The renewable gold surface permits to eliminate memory effects, to maintain a stable baseline and response, and to avoid frequent mechanical cleaning steps.

An ocular lubricant gel containing $2\text{x}10^{-3}$% (w/w) of Thimerosal (sodium ethylmercurithiosalicylate, $C_9H_9HgNaO_2S$), equivalent to 0.98 mg of Hg for 100 g of gel, was purchased from a local chemist. The concentration of mercury found (1.00 ±0.06 mg/100 g) was in good agreement with the expected values.

Some certified samples were analysed after dissolution in microwave oven: a) City Waste Incineration Ash (BCR 176, [Hg] = 31.4 mg/kg), b) Tuna Fish (ISPRA T 22, [Hg] = 4.43 mg/kg), c) Sea lattuce (BCR 279, [Hg] = 0.05 mg/kg). Two different solution were tested for the digestion, 6 ml HNO_3/1ml H_2O_2 and 3ml HNO_3/3 ml H_2O_2: the latter permitted to obtain the best results. The concentrations found for Incineration Ash, [Hg] = 31.7±3.4 mg/kg, and for Tuna Fish, [Hg]=4.33±0.38 mg/kg were in good agreement with the certified values. The sample of sea lattuce contains a great amount of I^-, 154 mg/kg, that strongly interfered with voltammetric determination of Hg. The presence of I- caused a decrease of the background current, because of its interaction with the gold surface, a sharp decrease of the mercury signal and a loss of linearity, which hindered the quantification of the analyte, due to the low solubility of Hg_2I_2 ($K_{ps}=1.1\text{x}10^{-28}$)[1].

The determinations were performed also with cold vapor atomic absorption spectrometry and graphite furnace atomic absorption spectrometry to assess advantages and disadvantage of using voltammetry determination in comparison with other techniques.

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Wool fibers as low cost reinforcement in polypropylene matrix

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In the last decade, there has been a growing interest in preparing polymer composites containing natural fibrous reinforcements.[1, 2, 3] Indeed natural fibers have lower density and cost than their inorganic counterparts. Moreover, they make it possible the reuse of waste materials. Among natural fibers, keratin fibers, such as wool, and feathers, are abundantly present in stock-farming and butchery wastes. This biomass, is estimated about 5 million tons per year worldwide.

Good polymer/fibers interaction is required if the filler is expected to either act as a low cost additive or reinforcement of the matrix: in the latter case the tensile modulus of the filler must be higher than that of the polymer matrix.

In the present work polypropylene (PP)-based composites containing wool fibers, grinded, washed and desiccated, were prepared by melt blending in an internal batch mixer. The effect of wool fibers content on the composite mechanical properties was determined. Wool fibers have a hydrophilic character due to the presence of about 70% of hydrophilic amino acids in the amino acidic sequence of keratin.[4] For this reason, in order to increase their compatibility with a hydrophobic matrix, small amounts of PP grafted with maleic anhydride (PP-g-MA) were added to the composites. Adhesion, thermal and mechanical properties of the composites were evaluated as a function of both the grafting degree of the compabilizer and the fiber length.

Research supported by CARIPLO Bank Foundation Project KEBAB 2008.

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Simultaneous determination of twenty amino acids and seven biogenic amines in food by HPLC-MS/MS technique

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In food chemistry, the determination of biogenic amines and amino acids is of relevant interest since their amounts can give useful information about the food aging and storage conditions as well as about potential toxicity of biogenic amines. The study presents a new HPLC-MS/MS method based on a pre-column derivatisation reaction, for the simultaneous determination of the twenty amino acids (namely alanine, arginine, asparagine, aspartic acid, cysteine, glutamic acid, glutamine, glycine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, tryptophan, tyrosine and valine) and seven biogenic amines (namely cadaverine, histamine, putrescine, spermidine, spermine, tryptamine and tyramine) typical of ripened food. During the method validation, limit of detection, limit of quantification, linearity range, repeatability, recovery yield and matrix effect were evaluated for all the analytes: LOD are always lower than 32 µg L^{-1} and LOQ lower than 71 µg L^{-1} (external calibration). In HPLC-MS analysis, the matrix effect is a very important aspect, because it may affect the results of both qualitative and quantitative analyses. The presence of relevant matrix effects can be evaluated using an internal standard: in the present case deuterated tyrosine (d2-tyrosine) was employed.

The method was applied in the analysis of cheese samples. For the determination of biogenic amines and amino acids in cheese, internal calibration plots for each analyte (built adding known amounts of each analyte to an experimentally prepared "blank matrix" of the cheese sample) were used. The internal calibration plot, built on a blank matrix, can be used in routine analyses, especially when both the number of analytes and different types of samples are large and the standard addition method would require too long preparation time.

Isomerization of Epoxides by Titanium Catalysts

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The isomerization of epoxides can lead either to carbonyl[1] derivatives or to allylic alcohols[2] in one step, depending of the reaction conditions.

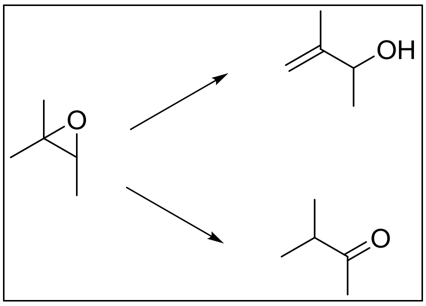

Figure 1 : Isomerization of epoxides

Epoxide derivatives of natural products such as pinene or limonene are of special interest in the fragrance industry as they can give direct access to useful intermediates used in perfumery by further oxirane isomerization.

The aim of this work is the study and the optimization of the catalytic isomerization of terpenoïd epoxides by titanium (IV) derivatives.

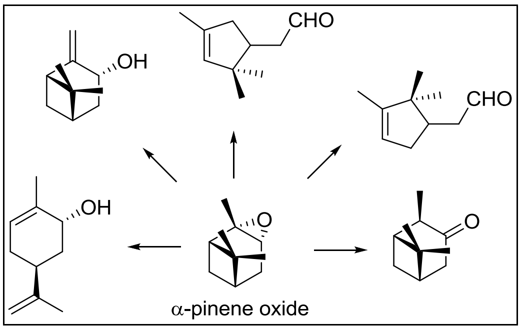

Figure 2 : Isomerization products of the α-pinene oxide

The influence of different parameters on the reaction selectivity of several substrates will be presented.

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Ultrasound assisted extraction of green tea (*Camellia sinensis*)

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Products derived from processed tea leaves (*Camellia sinensis*) have gained a lot of popularity, due to their sensory properties and well documented health promoting and stimulant effects, which stem from the polyphenols present in tea.[1] Catechines are the most important group of tea polyphenols (8-15% of dry leaf weight)[2]. Because of the wide possibility for application of tea catechines in food and cosmetic products, it is very important to devise an efficient extraction technique for these compounds, therefore, different combinations of solvents and high temperature have already been employed. Due to the demand for high throughput, environmentally friendly techniques, other procedures like ultrasonically assisted extraction (UAE), are currently being studied. During extraction, mechanical effect of ultrasound is believed to accelerate the release of organic compounds contained within the plant due to cell wall disruption, mass transfer intensification and easier access of the solvent to the cell content.[3] In tissues where prehydration is necessary to achieve extraction and when desired components are located within cells, like in tea leaves (mesophyll cell vacuoles)[4], ultrasound treatment is critical for achieving rapid and complete extraction[5,6]. Therefore, this study employs different conditions of UAE for water extraction of bioactive compounds from tea. Six different levels of ultrasound power have been applied and compared with control sample, extracted in the same device and under same conditions without application of ultrasound. During each extraction (90 minutes) samples have been taken each 5 minutes and scanned at three different wavelengths (figure 1) to find the optimum extraction time. Extracts obtained at optimum time were also tested for total phenolic content as well as their antioxidant capacity. All samples obtained by UAE showed higher values than control sample in all applied assays.

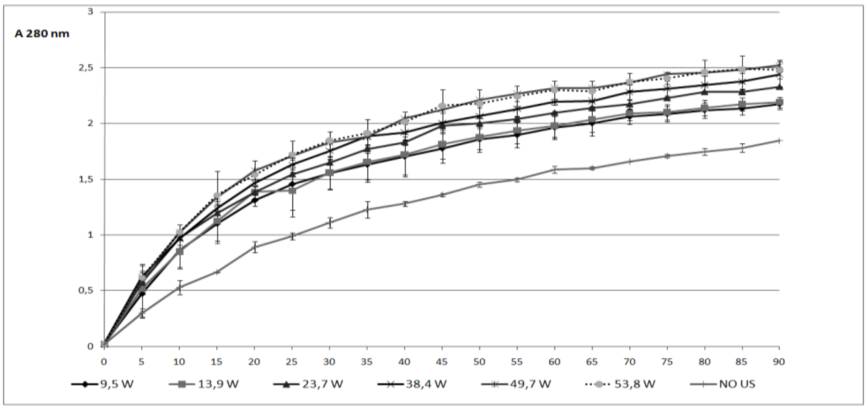

Figure 1. Comparison of absorbance at 280 nm for samples obtained by UAE and control sample

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Long-chain Carboxylic Acids Bearing Fluorescent Groups as Building-Blocks of Self-assembled Monolayers (SAMs)

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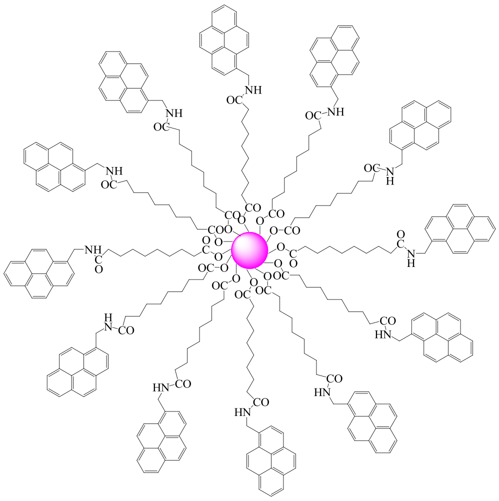
Self-assembled monolayers (SAMs) of organic compounds are 2- (2-D) or 3-dimensional (3-D) organic thin films which are formed by the adsorption of molecular constituents from solution or from the gas phase onto the surface of metals. Organosulfur derivatives such as thiols or disulfides are frequently and especially used for the fabrication of SAMs on gold surfaces.[1] Alternative metals are anyway required as more suitable materials for specific applicative purposes (e.g. for silicon processing in microelectronics). In this case, different anchoring groups might be preferable: as a matter of fact, carboxylic acids seem more useful building blocks for the formation of stable SAMs on surfaces such as silver or, in general, on metals whose oxidation potential is lower than gold.[2-4] Furthermore, the presence of a strongly fluorescent end-group (such as naphthalimid, perylene, or pyrene, as shown in the figure) could hopefully make the resulting SAMs fabricated on nanostructures attractive in the field of sensoring and microelectronic applications.



3-D SAM of a fluorescent long-chain carboxylic acid on a metal nanoparticle.

We will report on our recent results on the preparation and characterization of SAMs on metal nanostructures from long-chain carboxylic acids bearing strong fluorescent end groups.

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TDAE-Initiated reaction of 2-(dibromomethyl)quinoxaline with α-dicarbonyl derivatives

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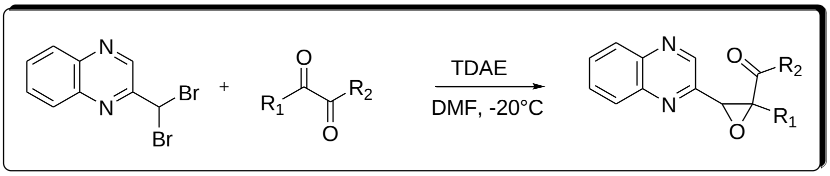
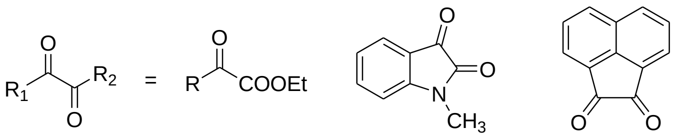
The quinoxaline derivatives show very interesting biological properties (antibacterial, antiviral, anticancer, antifungal, anthelmintic, antileishmanial, anti-HIV, insecticidal) and their usefulness in medicinal chemistry is far from coming to an end. Many drug candidates bearing quinoxaline core structures are in clinical trials in antiviral, anticancer, antibacterial, and CNS (central nervous system) therapeutic areas.

Tetrakis(dimethylamino)ethylene (TDAE) is a reducing agent which reacts with halogenated derivatives to generate under mild conditions an anion *via* two sequential transfers of one electron. We have recently shown that from *o*- or *p*-nitrobenzyl chloride, TDAE could generate a nitrobenzyl carbanion which is able to react with various electrophiles as aromatic aldehydes, ketones, α-keto-esters, α-ketolactams and diethyl ketomalonate.[1] Moreover, we have reported that the reaction of 2-(dibromomethyl)quinoxaline with aromatic aldehydes in the presence of TDAE furnished a mixture of *cis/trans* isomers of oxiranes. In continuation of our program directed toward the study of single electron transfer reactions of bioreductive alkylating agents[1] and the preparation of new potentially bioactive compounds as anti-infectious agents, we applied the TDAE strategy in quinoxaline series with various α-dicarbonyl compounds as electrophiles to form new quinoxalinic oxirane derivatives.





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Photoreactivity of cyanopolyynes study by IR spectroscopy and luminescence: interest for interstellar chemistry

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We are studying the spectroscopy and photochemistry of cyanoacetylenes[1-3] (figure 1) - important astrochemical compounds, present in the interstellar medium and in some Solar System bodies, including comets and the intriguing Saturn's moon, Titan.

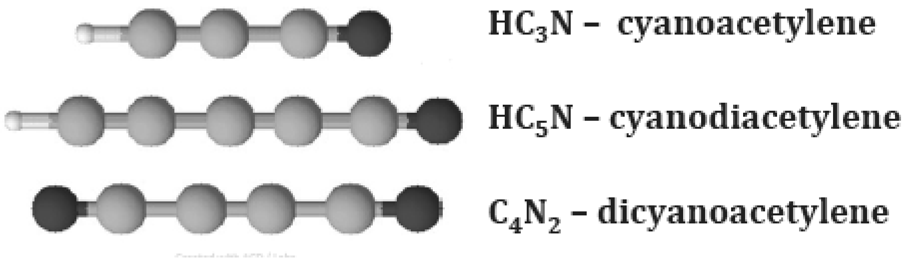

Figure 1

In this contribution we report on the evidence for an in-situ formation of larger unsaturated molecules from HC_3N and C_4N_2 in matrix isolation photolysis experiments.

We report for the first time on the low temperature visible luminescence of matrix-isolated HC_5N which provides a further insight into the electronic spectroscopy of this compound.

Preliminary results regarding the luminescence of C_4N_2 and HC_5N photolysis products are also presented. This topic is currently under study.

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Numerical simulation of the unsteady hydrodynamics of a water droplet in paraffin oil

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The hydrodynamics of a pure water droplet falling in a continuous paraffin oil phase is investigated numerically. The system under focus is two dimensional and consists of a single water droplet, with radius 1 mm, confined in a box with side length 1 cm × 1 cm. Water and paraffin oil are two non-miscible Newtonian and incompressible fluids described by (Eqs. 1 and 2). The complete system is submitted to uniform gravity field and constant temperature conditions.

A falling droplet in a continuous phase is a typical multi-phase unsteady free interface problem. The numerical stability of several finite volume schemes were tested. The most stable is the volume of fluid method. It is based on the use of a color function C that allows the discrimination of the two fluids where C takes value 1 (resp. 0) for the heavy (resp. light) fluid[1,2]. The Navier-Stokes equation is then modified by a coupling term (in bold in (Eq. 2)) that includes the water/oil interface curvature K, the surface tension σ and the color function gradient. The time evolution of the color function is finally determined by an advection equation (Eq. 3) that couples the velocity field inside both phases with the color function. This model gives a stable and good resolution of water/oil interfaces for both rigid and deformable droplets.

$$\nabla V = 0 \qquad (eq.1)$$

$$\rho\frac{\partial V}{\partial t} + \rho\nabla\,(VV) = -\nabla P + \nabla[\mu(\nabla V + {}^{t}\nabla V)] + \rho g + \boldsymbol{2\sigma K n \nabla C} \qquad (eq.2)$$

$$\frac{\partial C}{\partial t} + V\nabla C = 0 \qquad (eq.3)$$

The velocity field in the complete simulation domain is represented in figure 1 at time t = 0.25 s. Figure 2 shows its details inside the droplet. Both figures were obtained with a spatial mesh grid of 200×200 and a time step of $5\ 10^{-4}$ s. The number of convection cells and the structure of the velocity field of Figure 2 are shown to depend of the average velocity of the falling droplet[3]. Besides the description of interfacial phenomena, this work also aims to propose a CFD approach of the mechanisms that enter into play between droplets in flocculation and coalescence phenomena in emulsions. It is conducted within the framework of the ISS/FSL/FASES project and, from this point of view, can be seen as a first step to broader CFD studies aimed to simulate the hydrodynamics and the physicochemical properties of emulsions in microgravity conditions.

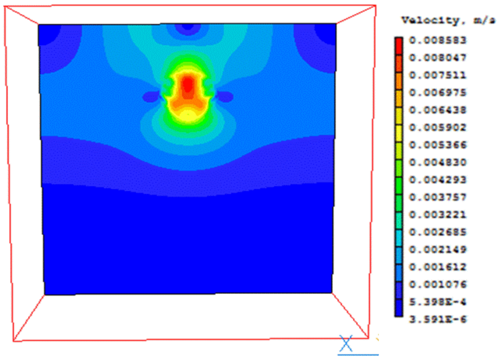

Figure 1: Velocity field inside the complete integration domain at time t=0.25 s. Velocity scale in given in the left column.

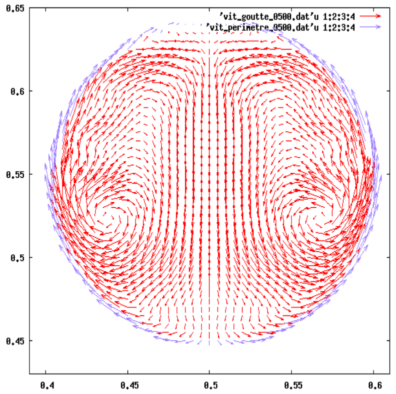

Figure 2: Detail of the velocity field inside and on the interface of the droplet at time t=0.25 s in a reference frame moving at the instantaneous velocity of the droplet.

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Study of Mexican resins "Copals"

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"Copalli" is an Aztec word to indicate any resinous material[1], so the modern "copal" term may refer to any kind of terpenic resins. Most of these substances are produced in Mexico by various botanical genera belonging to the Burseraceae family[2].

In Mesoamerica, the Aztecs considered copal as a spiritual material that was burnt during offerings. The use of copal with reference to rituals can also be observed, in its use as raw material for the manufacture of divine figurines[3]. They also prescribed copal as a medicine to cure different illnesses, and presumably, it was used as an adhesive for different materials, going from dental incrustations to turquoise mosaics.

It is generally difficult to distinguish different resins only by physical criteria and olfactive observations. Moreover, in archaeological materials, the inherent process of deterioration make even harder the interpretation of observations carried out on them. Such samples analysis presents a great interest for the scientist for the knowledge of the techniques employed, in the fabrication of objects, but also for ageing phenomena inherent to these materials.

Next to minor fractions of mono-(C10) and sesquiterpenoids(C15), copal resins are mainly composed triterpenoids with oleanane, ursane et lupane skeletons. Along time an important fraction of the constituent terpens is polymerised, resulting in a hard resin.

A chromatographic method for the chemical analysis of mexican copal was carry out with HPLC and GC/MS. Finally SPE was used as a treatment to copal samples, before HPLC analysis in order to remove non triterpenic compounds.

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Functionalyzed Pyrazoles via Ring-opening / Ring-closing Protocols from Nitrothiophenes

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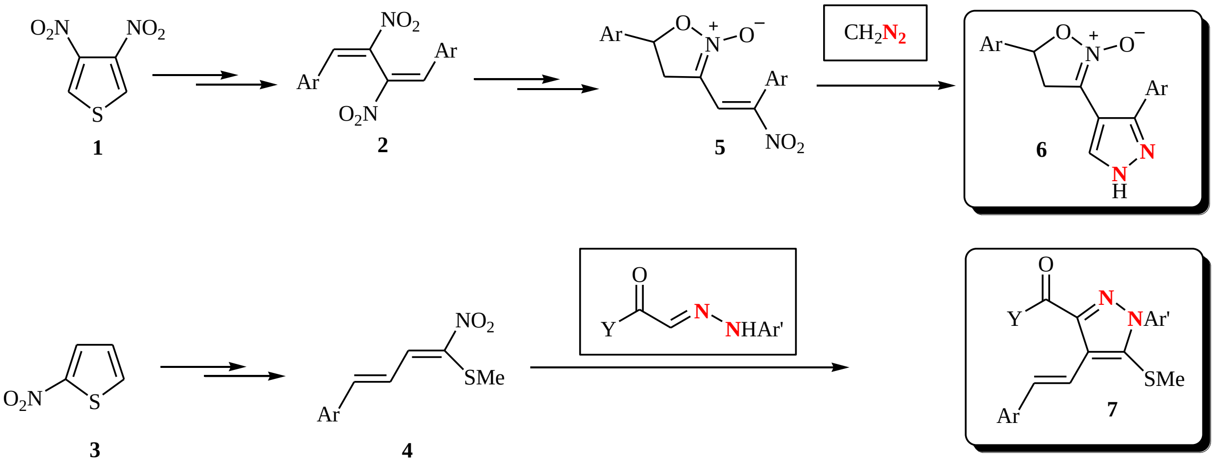
In the past years, nitrothiophenes **1** or **3** have proved to be precursors of very useful linear building blocks such as the nitrodienes **2** and **4**, respectively.[1,2] From these, via suitable functional-group transformations, a number of heterocyclic derivatives have been successfully synthesized, by means of an overall ring-opening / ring-closing protocol.[3] Herein some preliminary, more recent results will be presented, relevant to the approach to interesting pyrazole derivatives (*viz.* **6** or **7**) possibly endowed with biological significance and/or amenable to further modification.



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Hückel transformation theory of sp-hybridization in the ground states of first-row hydrides

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Following early work on CH_4[1], the sp hybridization problem in the ground states of the first-row hydrides (CH_4, NH_3, H_2O, HF) is studied by Hückel transformation theory.[2-5] Optimization of the valence Hückel energy under suitable simplifying assumptions yields simple trigonometric relations between valence angles and hybridization parameters for the first three hydrides and a more complicated trigonometric equation in the hybridization parameter for the last molecule. The optimum sp-content in X–H bond hybrids and $l\sigma$ lone pair hybrids of the different symmetries is established. Examination of the distribution of the electronic charge shows the appearance of Coulson's atomic dipoles[6,7] reducing the importance of the heteropolar component of the electric moment in each molecule.

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CFC determination as an useful tool to study the variability of the water mass ventilation in the Ross Sea (Antarctica)

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Traditionally, water mass characterization and ocean models included temperature and salinity only as physical tracers. More recently, chemical tracers, such as Chlorofluorocarbons (CFCs), have been considered not only into studies on water mass formation and circulation processes, but in ocean models for a variety of applications too.[1] These chemical parameters define the water mass characteristics, the formation region properties and the modifications occurred in the water mass, giving the time scale of the water mass ventilation.

CFCs in seawater samples were determined using a homemade purge and trap-GC-ECD instrument realized in collaboration with Lamont Doherty Earth Observatory (Columbia University, New York) and optimized in our laboratories. The instrumentation is able to determine the analytes in few picomoles concentrations[3]. CFC data collected during three Italian cruises carried out in the Ross Sea (Antarctica) between the austral summer 2001 and 2006 are presented and discussed in the context of water masses distribution and mixing processes.

The distribution of the chemical tracers together with the hydrographic observations showed recently formed Antarctic Bottom Water on the continental slope during all of the cruises. The chemical tracer data allow to calculate the water mass ventilation time and evidenced both a spatial and a temporal variability of the AABW formation processes. The estimated volume of the new Antarctic Bottom Water and the export of gases associated with the overflowing water were different over the examined period, with a higher export observed in 2003.

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The Search of Correctors for Cystic Fibrosis Pharmacotherapy

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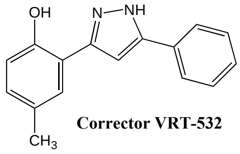
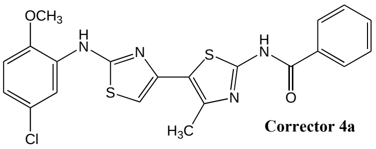
Cystic fibrosis (CF) is an autosomal recessive disorder caused by mutations that impair the function of the CFTR protein (a plasma membrane Cl^- channel). At present, ca. 1500 mutations of CFTR were discovered: in particular, the ΔF508 mutation, observed in over 70% CF patients, leads to a severe and fatal disease. In fact, it causes both a mistrafficking defect (block and demolition of the protein in the endoplasmic reticulum, ER) and a gating defect (decrease of the time spent by the channel in the open state). Some organic molecules with low molecular weight (named "correctors") are able to improve the trafficking of ΔF508-CFTR from ER to plasma membrane. Until now, few correctors have been found, but their use in treating CF is hamperd by toxicity and, moreover, their site of action is unknown.



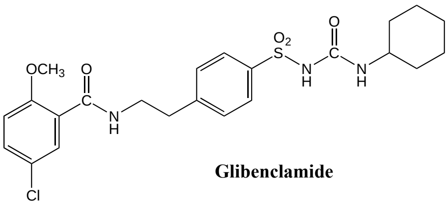
Corrector VRT-532



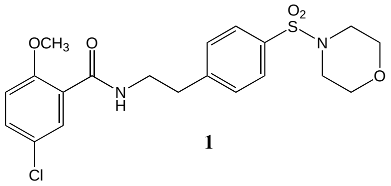
Corrector 4a

Our present study is aimed in finding new correctors by the following strategies:

1) Recognition of pharmacophores present in already known correctors: our attention was pointed at some correctors (in particular, NS004, VRT-532 and 4a) as they have in analogous positions of their structure, some molecular moieties very similar each other (*p*-chlorophenol, *p*-cresol and *p*-chloroanisole). Great attention was paid to *p*-chloroanisole derivatives as such group is present in Glibenclamide, well known hypoglycemic agent and also a CFTR blocker. As Glibenclamide binds CFTR, it is reasonable to think that in CFTR there is, at least, a site in which the *p*-chloroanisole group could adapt itself. Therefore, we synthesized some new Glibenclamide derivatives **1** changing the acidic moiety that, by binding to basic aminoacids of CFTR, leads to the block of the channel. The pharmacological assays done using the synthesized substances do not show a clear sign of correction.

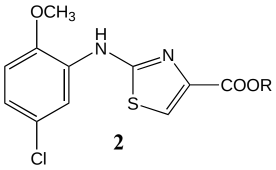


Glibenclamide



1

2) Synthesis of heterocycles structurally related to known correctors: as correctors VRT-532 and 4a hold, respectively, a pyrazole group and two thiazole groups, some new derivatives containing such heterocycles have been prepared. Pyrazole derivatives were found inactive, whereas thiazole derivatives **2** present an interesting potential activity as ΔF508-CFTR correctors.



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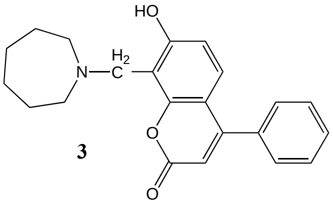

3

3) Computational design: as the HSC70 chaperone is thought to have an important role in addressing misfolded proteins to the degradation pathway, we have initiated a study of inhibitors of the HSC70 starting from a set of substances already synthesized in our laboratory. Therefore, 544 virtual molecules were docked in a hydrophobic binding pocket of HSC70 and a new class of compounds (namely, coumarin derivatives **3**) merged as potential inhibitors of HSC70. On such compounds the research must go on with the chemical synthesis and biological tests. Also other chaperones and co-chaperones (BAG1, BAG3, CHIP) will be the target of our studies on chaperone inhibitors in view to identify the proteins more involved in ΔF508-CFTR degradation.

The Seveso Disaster and the Image of Chemistry in Italy.
An Analysis of the Professional and Daily Press.

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The accident occurred in Seveso on Saturday, July 10th, 1976, at 12:37, at the Icmesa factory, owned by the company Hoffmann La Roche; the factory was located between Meda and Seveso, at about twenty kilometres from Milan. The leakage of the toxic cloud from the reactor which produced trichlorophenol was probably caused by the rising of temperature, which was the result of an exothermic slow reaction, due to the suspended agitation and cooling. Only after a considerable delay, the local authorities realized the seriousness of the accident.

For assessing the impact of the event on the chemical community and on the general public we have analyzed the Italian professional literature and a couple of important newspapers. The first part of the analysis on the professional literature considers the articles published in the official magazine of the SCI *La Chimica e l'Industria*, in the period since August 1976 until December 1982. For a long period of time, the magazine did not provide qualitative and quantitative data on the dynamics of the accident. The first specific article is dated February 1977. Only later articles reported quantitative and analytical methods for thermochemical investigations. In the magazine there are many other contributions, also very important, for correlating the incident with many other aspects: impact on environment, toxicity of chemicals, technological risk, "good practices" for land conservation, etc.

The chosen newspapers are: *Il Corriere della Sera* and *Il Corriere d'Informazione* of the same publishing group. The first one is a morning newspaper, the second is an evening newspaper, more popular. To assess quantitative differences, we use criteria of linguistic analysis and semiotics, which reveal striking differences of style and content between the two newspapers. The analysis covers a sufficiently extended period of time (until the end of 1982) to consider a greater range of issues like the spread of pollution in the area, the measures for land control, the methods of clearance of contaminated sites, the economic aspects, the legal consequences, the human health damage, the death of animals, the new safety and antipollution laws, etc.

In conclusion, it may be noted that the community of chemists was slow to respond and unable to affect the communication process for an event that was a kind of break between the preceding and following periods. It prevailed the public image of chemistry as a producer of toxic substances responsible for the attack to men and environment.

Synthesis of new pyrazolo[3,4-*d*]pyrimidines 6-alkyl substituted Bcr-Abl tyrosine kinase inhibitors

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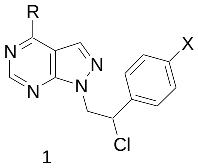
Chronic myelogenous leukemia (CML) is a disease characterized by the presence of the Philadelphia chromosome, which results from a reciprocal translocation between chromosomes 9 and 22. This translocation fuses the breakpoint cluster region (Bcr) and the Abl genes, forming the Bcr-Abl oncogene, that encodes a constitutively active cytoplasmatic tyrosine kinase (TK) Bcr-Abl, present in > 90% of CML. The finding that Bcr-Abl is the cause of the leukemic phenotype and that the tyrosine kinase activity of Abl is fundamental for Bcr-Abl-mediated transformation, made this kinase an important target for the development of specific therapies. Imatinib mesylate, approved by FDA in 2001, became within a few years of its discovery the first line therapy generally well tolerated for the treatment of CML; nevertheless primary refractoriness and acquired resistance to this drug are observed frequently in patients in the accelerated phase or blast crisis. For these reasons overcoming resistance to Imatinib remains a major challenge for successful treatment of CML particularly in the advanced phases.

In this context we previously synthesized a new series of pyrazolo[3,4-*d*]pyrimidines 4-amino-substituted **1** and **2**, derived from our family of dual Src/Abl TK inhibitors[1,2,3]. In derivatives **1** we inserted in the N1 side chain an alogen atom, whereas in compounds **2** we introduced in position 6 of the pyrazolo-pyrimidine nucleus a methyl group. Some of the new molecules showed to be potent Abl inhibitors in enzymatic cell free assays, with IC_{50} values in the low nanomolar range. In order to obtain more potent derivatives and to extend SAR, we synthesized compound **3**, bearing C6 alkyl groups and an alogen atom on the para position of the N1 phenyl ring. In position 4, compound **3** presented the same amino substituents resulted more active in the previous derivatives **1** and **2**.



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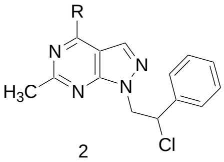

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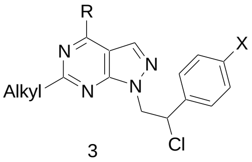

3

R = Amines
X = H, F, Cl

X = F, Cl

Synthesis, some biological results and SAR consideration will be reported in the poster session.

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Memory of chirality in cascade rearrangements of enediynes

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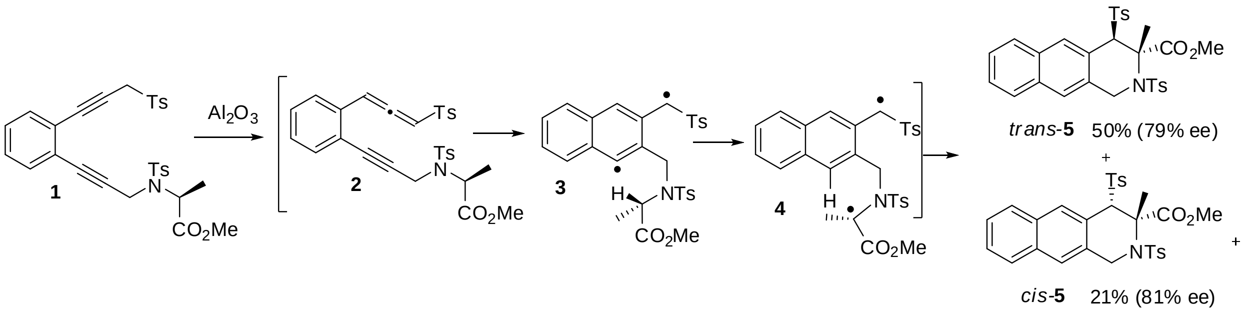
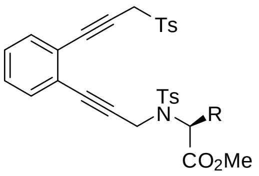
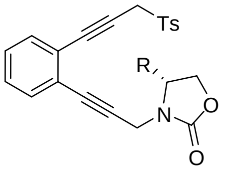
The enantioselective construction of a chiral tetrasubstituted stereocenter is one of the most challenging tasks in current synthetic organic chemistry. This construction *via* enantioselective radical reactions is rapidly advancing with the emergence of strategies making use of either chiral auxiliary or chiral Lewis acids. The third strategy for introducing chirality in radical reactions relies on "Memory of Chirality phenomenon",[1] that is the retention of initial stereochemical information due to slow equilibration of "chiral conformations".[2]

We have devised a new methodology based on a polar-radical crossover rearrangement. In the first step, prototropic enyne-allene **2** formation from enediyne **1** was envisaged. Subsequent, instantaneous Saito-Myers cyclization[3] lead to the (σ,π)-biradical **3** that would give rise after 1,5-hydrogen transfer, to captodative radical **4** ready to couple. Gratifyingly, the later afforded, through intramolecular coupling, the diastereomeric tetrahydrobenzo-isoquinolines *cis*-**5** and *trans*-**5** that were isolated in 71% overall yield with retention of configuration (80% ee).



The use of substrates prepared from chiral amino-acids and other easily available chiral auxiliaries will be discussed.





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Comparison of Four Fingerprinting Techniques for the Characterisation of *Barbera* and *Dolcetto d'Alba* Wines

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Four rapid and low-cost vanguard analytical systems (NIR and UV-visible spectroscopy, a headspace-mass based artificial nose and a voltammetric artificial tongue), coupled with chemometric pattern recognition techniques, have been applied and compared in addressing a food authentication problem: the discrimination between wine samples from the same Italian oenological region, according to the grape variety.

In particular, fifty-nine certified samples, belonging to the two appellations Barbera d'Alba and Dolcetto d'Alba and collected from the same vintage (2007), have been analysed.

The instrumental responses, after a proper data pre-processing, have been employed as fingerprints of the samples for their characterisation: the results from principal component analysis and linear discriminant analysis have been discussed, comparing the capability of the four analytical strategies in addressing the problem studied.

Composition and Antioxidant Properties of the Essential Oil from the Endemic Cape Verdean *Satureja forbesii*

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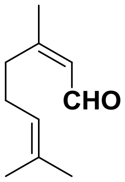
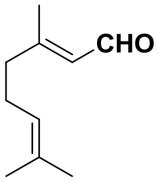
The genus *Satureja* [family Lamiaceae (Labiatae), subfamily Nepetoidae, tribe Mentheae][1] contains more than 200 species of aromatic herbs and shrubs, largely distributed from the Mediterranean region to Europe, West Asia, North Africa, the Canary Islands, and South America, with chemotypes of carvacrol, β-caryophyllene, citral, isomenthone, linalool and pulegone.[2] Eugenol, p-cymene, menthone, γ-terpinene and thymol have also been reported as other major constituents.[3]
During recent years, antioxidant,[2] antibacterial, antifungal, antiviral,[3] Antinociceptive, anti-inflammatory,[4] antispasmodic and antidiarrhea effects have been reported for different species of *Satureja* growing in different parts of the world.[5]

Satureja forbesii (Benth.) Briq., syn. *Micromeria forbesii* (Benth.), is an aromatic and endemic plant known as 'erva-cidreira' and used in folk medicine by Cape Verdeans, mainly as an infusion for the treatment of ailments, such as couth, indigestion and diarrhea.[6]
However, to the best of the author's knowledge, detailed investigation of the volatile compounds of this species has not been undertaken. Therefore, the aim of the present work was to determine the antioxidant properties and chemical profile of the oil obtained from aerial parts of this species from Cape Verde.
Hydrodistillation of air-dried aerial parts of *S.forbesii* (Benth.) Briq. gave an essential oil with a yield of 0.4% (w/w).
The chemical composition of this essential oil was studied by GC and GC/MS. Thirty-nine volatile compounds, representing 90% of the total composition, were identified of which geranial (42.0%) and neral (31.2%) were the major constituents. Using the 2,2-diphenyl-2-picrylhydrazyl free-radical scavenging method and the *in vitro* assay for prevention of lipid peroxidation by thiobarbituric reactive species, significant activities were evidenced.

Satureja forbesii



neral



geranial

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Detection of polycyclic aromatic hydrocarbons (PAHs) in wels catfish (*Silurus glanis*) collected in the Po River Basin, Italy

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Polycyclic aromatic hydrocarbons (PAHs) are of major concern in all environmental compartments, since many of them have been labelled as probable carcinogens by the International Agency for Research on Cancer (IARC)[1]. Their presence in food is quite serious, because food is an important and direct source of human exposure to PAHs[2]. Their occurrence in seawater is limited by their low solubility, but, although their environmental concentrations are low, they tend to bio-accumulate in organic tissues due to their lipophilic character and resistance to degradation[3]: their introduction in seafood chain is well demonstrated since high amounts of these compounds have been found in many aquatic species[4].

This study was conducted on 55 sample of wels catfish (*Silurus glanis*), collected at different sampling stations located in the Po River Basin (northern Italy). The analytical method led to the detection of 9 PAHs (naphthalene, acenaphtene, fluorene, phenanthrene, anthracene, pyrene, benzo[a]anthracene, chrysene, benza[a]pyrene).

According to the Scientific Committee on Food, benzo[a]pyrene can be used as a marker for the occurrence and effect of carcinogenic PAH in food and the Commission Regulation (CE) No. 1881/2006 set a maximum level of it in muscle meat of fish (other than smoked fish) at 2,0 µg/kg on wet weight.

About 5g of freeze dried sample was extracted for about 15 minutes with *n*-hexane/acetone 1:1 (33ml). The extraction procedure was performed using Accelerated Solvent Extraction System (Dionex ASE® 200 Solvent Extractor – Dionex Corporation), which increases the efficiency of the extraction process using conventional liquid solvents at elevated temperatures (100°C) and pressures (102 atm). The solvent was gently removed by evaporation in a rotary evaporator, then the dried residue was added with 50 ml of Ethanol 95% and 6 ml of Potassium Hydroxide 50% and saponification was performed for two hours on a hot plate, connecting the flask with a water-cooled reflux condenser. Once ambient temperature was obtained, a liquid-liquid extraction with *n*-hexane and distilled water was realized in a separatory funnel and PAHs were collected in the non-polar phase. Then the solvent was evaporated to dryness and the residue was loaded on top of a silica cartridge. The elution was carried out with 5 ml of a mixture of *n*-hexane and diethyl ether 9:1 (v/v). Finally, the dried extract was resuspended in isooctane for instrumental analysis, which was performed using an HPLC (1100 series, Agilent Technologies, Santa Clara, CAL, USA) equipped with autosampler, quaternary pump and fluorescence detector . For the separation an Envirosep reversed phase for PAHs column 125 x 4,60 mm, 5 µm (Phenomenex Inc., CA, USA) was used. Acetonitrile and distilled water were used as eluents at a flow rate of 1 ml/min. The gradient elution program was: 50% acetonitrile initially until 5 min, then increasing linearly to 100% acetonitrile in 20 min, holding in 100% for 15 min and finally back to initial conditions in 10 min. Column temperature was maintained at 25 °C. Fluorescence detector was programmed in order to optimize sensitivity for all the peaks while minimizing interferences. The fluorescence intensity was measured at the following excitation/emission wavelengths pairs: 275/325 nm for Na, Ac, F, Phe, 250/375 nm for Ant, Pyr, 285/475 for BaA, Chr and 270/380 for BaP.

The total average concentration of the 9 PAHs was about 25 µg/kg on wet weight, that of BaP 1,0 µg/kg and so well below the fixed maximum level. Chrysene and benzo[a]anthracene, which are classified as probable human carcinogens, were respectively 4,4 µg/kg and under the detection limit of 0,1 µg/kg. The highest concentration was that of Anthracene (14,0 µg/kg), which has been recently included in the Substances of Very High Concern list (SVHC) by European Chemicals Agency because being considered persistent, bioaccumulative and toxic for freshwater and marine ecosystem[6], but is not carcinogenic and so poses a lower threat to human health.

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Highly fluorinated quaternary bisammoniums for biocidal applications

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Highly fluorinated surfactant developments allow to obtain unique properties as compared to their hydrocarbon or silicone counterparts. The research group located in Nice have been interested for several years in unconventional applications[1] of these highly fluorinated surfactants, especially in biocidal domain. Indeed, the introduction of perfluorinated chains in the molecular structure of quaternary ammonium gemini surfactants have led to particularly active antimicrobial agents[2-5]. Through the collaboration between the University of Dakar and the University of Nice-Sophia Antipolis, new highly fluorinated bisammoniums resulting from both expertises were synthesized for a potential biocidal application and characterized.

In this context we will present the results obtained by varying the following molecular parameters: the length of the hydrocarbon connector, the chemical nature of the spacer and the length of the fluorinated chains. Acquired physicochemical properties will be correlated to these structural modifications. Surface and interfacial tensions will be so introduced as the critical micellary concentration (CMC) and will be compared with their counterparts in the literature.

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Synthesis of perfluoroalkyl quaternary ammonium salts

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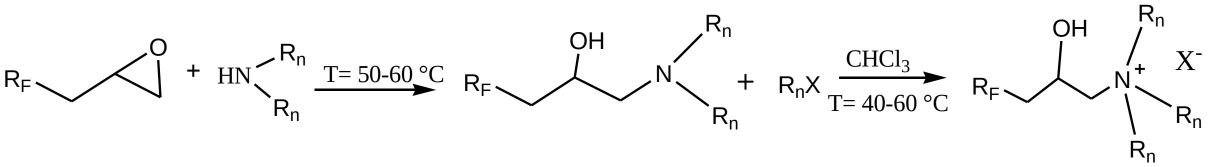
There is an important class of disinfecting surfactants used for antisepsis and active ingredients in formulas claiming to clean and disinfect in human health-related domains and in hospital: they are quaternary ammonium compounds, called Quacs. Their bactericidal activity is related to specific structural characteristics: they have the capability of killing microorganisms by promoting the uptake of these molecules by target organism. These actions involve ionic interactions between positively charged biocides and negatively charged biomolecules. Hydrophobic interactions are also involved in penetration of membrane lipid bilayers and displacement of stabilizing interactions between phospholipids and proteins and so the alkyl chain of quaternary ammonium compounds interactions with the fatty acid chains of membrane lipids. Length of the aliphatic chain, number of carbon atoms in the aliphatic groups, introduction of fluorinated chain are all significant factors.[1] The efficacy of these compounds is conditioned by surfactant properties. There is a well established relationship between cytolitic action and surface tension. The introduction of fluorinated chain in tension-active structure leads to the enhancement of their surfactant properties, for instance lower surface tension and lower critical micelle concentrations[1-3]. The discovery of microbial resistance phenomena against Quacs require the elaboration of new biocide agents with original chemical structures. Fluorinated quaternary ammonium compounds are particularly interesting because they have enhanced surfactants properties such as a high efficiency in reducing the surface tension[4]. Introduction of fluorine and more particularly highly fluorinated part confers to the system intrinsic properties such as chemical inertness, thermal stability, low surface tension which can affect in a favourable manner the biocidal activity[5]. We have synthesized new highly fluorinated Quacs and studied the influence of the semifluorinated and hydrocarbon chain length on the physic-chemical properties.

The structure of the molecule is:



$R_F = C_4F_9, C_6F_{13}, C_8F_{17}$; $R_n = (CH_2)_{1-8}$; X = I, Br

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Intermetallic compounds in the M-Cu-Sn systems (M=Eu,Sr,Ba)

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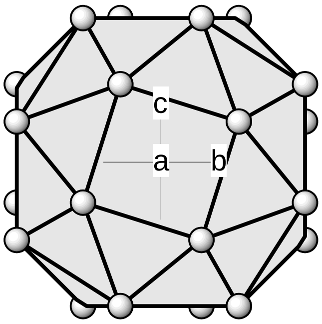
The similar alloying behaviour of the alkaline earths (Ca, Sr, Ba) and divalent rare earths (Eu, Yb) is known since many years (see for example [1]). Following a work on the Ca-Cu-Sn system[2], a preliminary investigation has been carried out on existence and structure of the intermediate phases in the M-Cu-Sn systems with M = Eu, Sr, Ba.

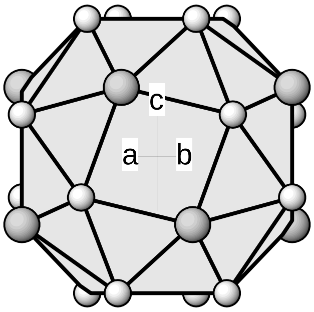
The alloys were prepared from pure elements, handled and weighed in glove box (Ar atmosphere), closed in tantalum containers (arc welded under argon), melted in an induction furnace, annealed at 550°C and checked by standard metallographic techniques. X-Ray analysis was made by means of a powder diffractometer, a Guinier camera and a single crystal diffractometer.

Six new intermetallic compounds have been identified. The crystal structures were solved and refined by single crystal data for **$SrCu_2Sn_2$** ($CaCu_2Sn_2$ type), **$SrCu_4Sn_2$** (KAu_4In_2 type), **$Sr_3Cu_8Sn_4$** ($Nd_3Co_8Sn_4$ type), **$SrCu_9Sn_4$** and **$BaCu_9Sn_4$** ($LaFe_9Si_4$ type). **$EuCu_2Sn_2$** ($CaCu_2Sn_2$ type) was refined by the Rietveld method.

Some crystal chemical remarks are obtained from the comparison of the coordination polyhedra in the different structure types. The analysis of the interatomic distances occurring in series of isotypic compounds show their influence on the phase stability. The figure shows the coordination polyhedron around the barium atom in the cubic $BaCu_{13}$ ($NaZn_{13}$-type) and in the tetragonal $BaCu_9Sn_4$ compound.



Ba in $BaCu_{13}$



Ba in $BaCu_9Sn_4$

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Experimental and Computational Investigation of Symmetrical and Asymmetrical Squaraine Based Sensitizers for Dye Sensitized Solar Cells

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Dye-sensitized solar cells (DSCs) have attracted significant attention as low-cost alternatives to conventional solid-state photovoltaic devices. In these cells, the most successful charge-transfer sensitizers employed are ruthenium polypyridyl complexes, yielding 12% solar-to-electric power conversion efficiencies[1]. The majority of the ruthenium complexes reported to date show absorption in the visible region at around 535 nm. Essential for efficient conversion of solar energy by DSSC is the spectral match of the sensitizer absorption to the solar radiation, and in this regard, the ruthenium complexes are inadequate.

Metal-free organic sensitizers can be simply modified and functionalised in order to obtain the desired spectroscopical properties. Currently DSCs are very effective in the visible region between 400–700 nm, but NIR dyes are interesting because of their possible applications in transparent solar cells, tandem cells and exciton QDs solar cells.

Among organic molecules, squaraine dyes have been extensively investigated for their sensitization properties since they are a class of highly stable dyes with intense absorption in the red/near-IR regions. In general, these dyes are prepared by direct condensation reaction of electron rich aromatic heterocyclic compounds with squaric acid. Since a number of heterocyclic systems with varying π-framework are available, there are miscellaneous possibilities to design tunable squaraine dyes and absorption in the far red to near infrared domain[2].

In this work a series of symmetrical and unsymmetrical squaraine indoline-based dyes with one or more anchoring groups have been designed and synthesised. The introduction of different functional groups in a specific positions was designed by the help of appropriate DFT calculations. Intermediates and dyes have been extensively characterized by means of absorption and emission UV-Visible-NIR spectroscopies (solvatochromism and alochromism), NMR and mass spectrometry. The same properties were predicted and explained by DFT calculations.

A few squaraines show an interesting large and NIR absorption band, giving a green solution and promising a good light harvesting properties. Their unique photovoltaic properties will be depicted in the presentation.

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Evaluation of modified Polyamide Amino Acids (PAAs) as HIV-1 TAR RNA ligands[1]

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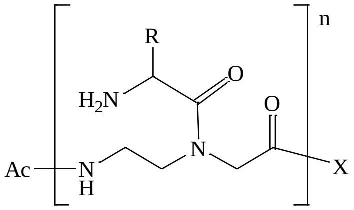
Most of the drugs currently used in anti-HIV therapy target enzymes and others viral proteins. It leads to the formation of viral strains resistant to treatment. Targeting viral RNA uncoding fragments, which are highly conserved and involved in viral replication, constitutes an interesting way for overcoming this problem.

To try to identify new specific ligands of viral RNA, we devised a new family of compounds, named "Polyamide Amino Acids" (PAAs), constituted by repetitive units of 2-(aminoethyl)glycine onto which aminoacid residues are linked [figure 1].



- figure 1 -
PAAs structure

In view of evaluating their potential as specific RNA binders, we have prepared eight tetra-PAAs *via* solid-phase synthesis as well as a small library of tri-PAAs following a combinatorial "split and mix" strategy; all compounds have been prepared starting from four different PAAs monomers deriving from Ala, Phe, Lys and Arg residues.

Interactions between these PAAs and a HIV-1 TAR RNA fragment (target model) were checked by fluorescence spectroscopy and circular dichroism. These studies showed that some PAAs have a good affinity for the target. Furthermore, some also displayed a good specificity for RNA TAR vs. dsDNA and vs. tRNA. Affinity and specificity of these PAAs for their RNA target can be modulate by changing the length or the nature of the incorporated aminoacids. Altogether, these results highlight the potential of PAAs as specific RNA ligands.

Starting from these preliminary results, a structure/activity study (modifications on aminoacids or on the backbone) have been performed to improve both affinity and specificity of PAAs. Meanwhile, the impact of a conformational strain (cyclisation) has also been assessed.

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Clean extraction of polyphenols from dried apple pomace assisted by ultrasound

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Apples (*Malus* sp.) are known to contain many types of phenolic acid derivatives and flavonoids.[1] Apple polyphenols are responsible for several properties and nutritional value of the fruit and its byproducts, as well as economic valorization due to antioxidant and free radical scavenging activities of these compounds.[2] Apple pomace (Figure 1) is a solid waste resulting from industrial processing of apple juice and cider, rich in extractable polyphenols.[3] In the search for alternative extraction procedures that overcome conventional techniques disadvantages, ultrasound plays an important role as sustainable, up-scale applicable and with a potential use in polyphenols extraction.[4] The cavitation process occurred during sonication causes rupture of cell walls allowing consequently availability of extractable cell material for the solvent contact.[5] The purpose of the present work was to evaluate the effects of ultrasound-assisted extraction (Figure 2) of polyphenols from dried apple pomace. In order to investigate the influence and relevance of operating parameters required during extractions, a response surface methodology was used, studying total polyphenol content (TPC) and extract main polyphenols as response variable. Three independent variables such as temperature (T), sonication time (t) and power (P) were studied based on a prior study of the optimal extracting conditions given by the substrate:solvent ratio. As an attempt to mimic fruit conditions, a malate buffer pH 3.8 was used as solvent in the extracton. The total phenolic content was determined using Folin–Ciocalteu reagent following the procedure described by the seller of the kit.[6] Extracted polyphenols were analyzed using HPLC-DAD. The yields from optimized ultrasound-assisted extraction were compared to conventional maceration extract yields.

Figure 1 – Apple pomace.

Figure 2 – Ultrasound apparatus.

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Anet and Rousseau revisited: Anti-inflammatory terpenoids and flavonoids from genepy

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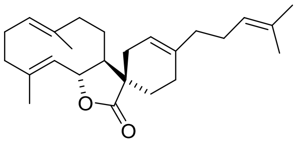
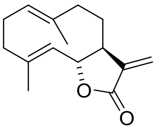
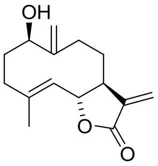
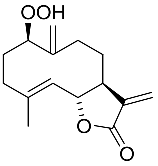
Genepy is the name given to a series of Alpine wormwoods growing at high altitude and used to prepare herbal teas and the homonymous celebrated bitter liqueur, recently granted a Geographical Indication Status by the European Union. Genepy has an interesting ethnomedicine, and has been used in folk medicine to treat cold and inflammation.[1] A remarkable testimony of this use appears in the *Les confessions* by Jean-Jacques Rousseau, where he describes the death of the gardener Claude Anet who went to the Alps to collect some genepy, but "*s'échauffa tellemantqu'il gagna une pleurésie dont le Genipi ne put le sauver, quoiq'il y soit, dit-on, spécifique*".[2]

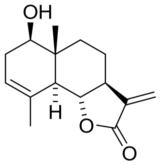
We have isolated from *Artemisia umbelliformis* Lam., the only genepy that can be cultivated, a series of sesqui- and sesterpene lactones and of flavonoids,[3] some of which show indeed potent anti-inflammatory activity *in vivo*. Results from these study, as well as a quick method, suitable also for teaching purposes, to obtain the major constituents from the plant will also be presented, as well as a remarkable transannular 1,5-photochemical sigmatropic rearrangement observed in the course of studies on the photochemical stability of the constituents of genepy.

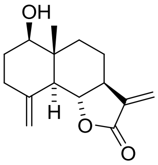


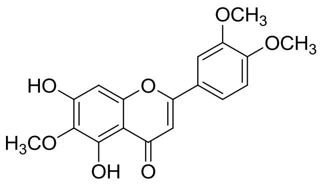












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Enantioselective Enzymatic Desymmetrization of Highly Substituted *Meso* Tetrahydropyranyl Diols. Application to the Total Synthesis of (+)-Crocacin C.

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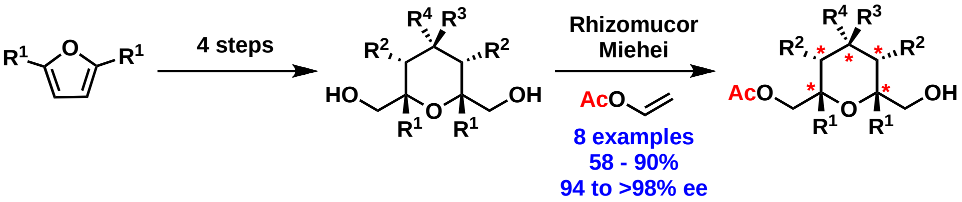
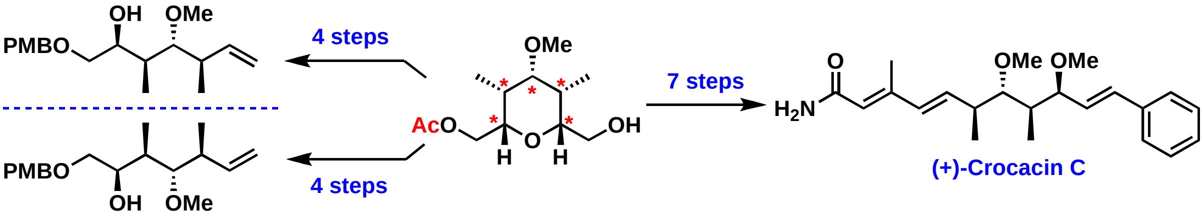
Many biologically active natural products bear a tetrahydropyran moiety. We recently developed an original approach to poly-functionalized tetrahydropyrans based on an enantioselective enzymatic desymmetrization of *meso* diols, easily obtained from furans. In this strategy, a single enantioselective step « reveals » up to five contiguous stereogenic centers.[1]

Moreover, from the same desymmetrized building block, we managed to prepare both enantiomers of a valuable fragment bearing a *syn-anti-anti* stereotetrad. Finally this strategy was successfully applied to the total synthesis of (+)-Crocacin C in which the four stereogenic centers of the natural product were revealed in a single operation.[2]





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Learning spectroscopies with computers:
a NICE approach...

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Teaching chemistry students to deduce chemical structures from the results of spectroscopic methods suffers severe practical problems. Often the theoretical basis of the method lies beyond the student's comprehension. Although theoretical models allow the prediction of spectra of simple compounds from their structures, the models have limited utility for the inverse operation of determining structures from spectra. This later operation is primarily empirical and does not lend itself to a systematic teaching approach.The ability to elucidate chemical structures is built largely on implicit heuristics and informal experience accumulated by solving numerous examples.

From the cognitive point of view, this experience spans several levels of knowledge:

- factual knowledge of existing correlations between spectral characteristics and structural features;
- procedural knowledge of methods to be applied generically;
- heuristic knowledge providing guidance to build and evaluate structural hypotheses;
- and theoretical knowledge linking the above mentioned knowledge levels and facilitating progression to new spectroscopic techniques.

Our experience with teaching the analysis of spectra[1] lead us to identify the following learning goals for the students:

- to be able to extract and describe the most significant data from the bulk of information contained in the spectrum ;
- to develop skills in recognizing typical spectral patterns associated with particular structural features ;
- to state hypothesis and make logical deductions from the presence or absence of peaks and combination of peaks ;
- to combine structural features to obtain as much information as possible about the structure of a compound ;
- to recognize the limits of each spectroscopic technique and identify what kind of information could be gained using other analytical methods.

To encourage self-formation of approaches using spectroscopic methods for structure elucidation, we designed and set up a learning environment allowing trainees to gain experience. In this poster we present the approach adopted for building such an environment for learning multi spectroscopy.

The main goal is to deduce the formula of the compound from all datas founded in the Infra Red, ^{1}H NMR, ^{13}C NMR and Mass spectra.

This collection of 100 exercises is carefully designed to cover most of the typical cases of structure-spectra relationships. Each exercice presents the four spectra : Infra Red, ^{1}H NMR, ^{13}C NMR and Mass spectra obtained for the compound. No more data is given to the student execpt the atomic percentage composition which is only available when it's not possible to deduce the molar mass from the Mass spectrum.

Each spectrum can be displayed full screen by clicking on the zoom button. In this mode, many ressources are available to help students. For each spectroscopy, we offer resources similar to those available in a reference books containing information about spectral interpretation.

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Evaluation of cytotoxicity, cell proliferation and lipid peroxidation in 3T3 fibroblasts exposed to selected methoxyphenols produced during wood smoke exposure

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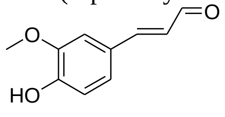
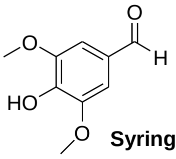
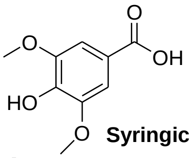
Many studies have reported that woodsmoke constitutes a major source of air pollution when produced from non intentional wildfires, open agricultural fires, cookstoves or as a source of household heating, wood being a renewable resource of energy. Woodburning emits significant quantities of health-damaging species, including gaseous pollutants (CO, No_x or O_3), inhalable particulate matter (PM_{10}), fine ($PM_{2.5}$) or ultrafine particles carrying various inorganic or organic compounds which are susceptible to induce pathophysiological inflammatory and allergenic processes in the respiratory tract.[1] In addition biomass combustion emits other toxic compounds which can be transported and reactive over long distances including many volatile organic compounds such as acrolein, formaldehyde, benzene together with semiquinonic free radicals, that can react with O_2 to yield even more reactive oxidants such as superoxide, peroxynitrite or hydroxyl radicals. Taking into account that wood is constituted by cellulose (more than 60%) and lignins (30%), the major products of combustion are considered to be derived from the pyrolysis of these two polymers. Pyrolysis of wood lignins (such as polymeric syringyl or guaiacyl propane) has been shown to produce methoxyphenols as volatile emissions which are mainly alkyl- or acetyl- substituted derivatives of guaiacol or seringol. Interestingly, because of their reliable GC-MS assay in urine samples collected from subjects submitted to woodsmoke inhalation, this class of chemicals is now used as biomarkers for exposure assessment.[2] However despite their high concentrations upon biomass combustion and their rapid urinary excretion rate, only little is known about their cytotoxicity and/or their protective cellular effects which could conversely be expected from the electron transfer or H-donor properties displayed by many other phenolic structures. In this respect, phenolic compounds, such as vanillyl derivatives where shown in our laboratory and others to be very efficient protective and antioxidant agents. On another hand, in many in vitro and in vivo studies, oxygen- carbon- or nitrogen centered radicals have been identified as key mediators of various pathological conditions such as ischemia/reperfusion injury, carcinogenesis, inflammation, or upon exposure to combustion mixtures: cigarette,[3] diesel or wood smoke,[4] leading to DNA or proteins damage and lipid peroxidation. Again, to our knowledge the exact role of the methoxyphenols (separately or in a mixture containing PM) from woodsmoke was never studied.


Coniferyl aldehyde


Syringaldehyde


Syringic acid

Taken together, the aim of the present study was to evaluate the cytotoxicity (or the innocuity) of 10 methoxyphenols produced in woodsmoke including coniferyl aldehyde, syringaldehyde and syringic acid, and to investigate their ability to cause (or inhibit) free radical-induced cellular damages. For this purpose, the in vitro DPPH radical scavenging and the ORAC assays were used and test compounds were compared to a large set of standard antioxidants or toxics. In a second step, methoxyphenols were incubated up to 12 h (0.1 to 50 µM) in the medium of murine fibroblasts (3T3) cells. Cytotoxicity and cell proliferation were evaluated by MTT test, LDH release and lipid peroxidation by MDA-TBA. In a third step, cells were maintained in an exposure chamber to mimick in vivo situation.[5] The data showed that woodsmoke methoxyphenols having no antioxidant properties display a significant cytotoxic effect and enhance oxygen-triggered free radical processes in cells.

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Thermal curing of proton-conducting ionomers based on SPEEK and SPPSU

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We show that thermal treatments of SAP membranes performed above 120 °C in presence of residual DMSO can significantly modify the mechanical and water uptake behavior of the membranes. Thermogravimetry, elemental analysis, acid-base titration, and FTIR spectra consistently indicate that the SAP microstructure stabilization is related to cross-linking of the polymer chains by SO2 bridges, which is promoted by temperature and the residual high dielectric constant DMSO facilitating the formation of electrophilic SO2 in the activated complex. The cross-linking leads to loss of sulfonic acid groups; it is therefore important to perform it on ionomers with high initial degree of sulfonation. In fact, SPPSU presenting a particularly high DS appears as a very promising candidate ionomer for the future. The performed annealing treatments are of important practical relevance, because the water budget is central for the technological viability of membranes either at higher temperature or at low relative humidity. SPEEK membranes treated at 160 °C can resist liquid water at high temperature (100-145 °C). The analysis of proton-conducting SAP membranes by stress–strain tests and DMA show a very important effect of thermal treatments, with a large increase of glass transition temperature and mechanical strength. Removal of residual casting solvent, which acts as plasticizer, leads in all cases to an increase of storage modulus.

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Importance of Slow Photons and Bragg Mirrors in the Photocatalytic Activity of Titania Microfilms

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Titania inverse opals (TIO) contain ordered arrays of holes in hcp or fcc geometry. TIOs display a complete photonic band-gap and high surface area and porosity, therefore, they could play an important role in photocatalysis[1]. TIOs have shown higher photocatalytic activity compared to the classical nanocrystalline titania[2]. In the present work we synthesized two macroporous titania powders: the first with ordered arrays of macropores, an inverse opal, the second with a disordered pores distribution. Raman spectroscopy studies showed the presence of anatase in both samples as TiO2 crystalline form, while UV-Vis reflectance spectroscopy confirmed the presence of a photonic band gap in the TIO at 330 nm in water. The TIO synthesized shows higher intrinsic photocatalytic activity toward the photodegradation of phenol than the disordered macroporous titania, and a comparable activity with respect to the commercial P25 TiO2 by Degussa (standard material in the photocatalytic field). This result confirms the importance of slow photons at the edge of the band-gap, while downsizes the role of other possible variables, such as the larger photoabsorption and mass transfer of the species owing to the porosity of inverse opals. To demonstrate that photonic crystals as Bragg mirrors can increase the optical efficiency of photocatalytic films we synthesized four different samples: a) a monolayer film of nanocrystalline titania, b) a monolayer film of TIO, c) a bilayer film with TIO as back-reflector and an active layer of nanocrystalline titania and d) a bilayer film with TIO as back-reflector and an active layer of titania with a disordered distribution of macropores. The photocatalytic activity of the films was in the order $a < b < c \approx d$, suggesting: i) a huge role of slow photons during the photocatalytic process ($a < b$), ii) the importance of photonic crystals as Bragg mirrors ($a,b < c$), iii) a secondary role of porosity and specific surface area in the photocatalytic activity of the produced films.

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Quinolizidinyl derivatives as antiarrhythmic agents

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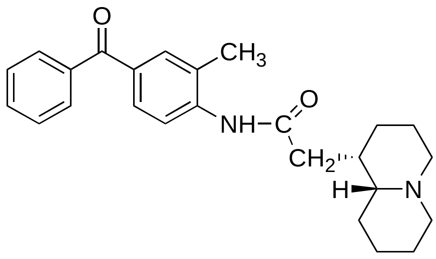
Arrhythmia is a complex abnormality of cardiac rhythm, affecting an increasing percent of the population with the increase of age. Despite the availability of a large number of drugs able to suppress dysrhythmic cardiac activity through different mechanisms, a satisfactory pharmacological therapy has not yet been developed.

Therefore, the search of new antiarrhythmic agents is largely pursued, particularly with the aim to obtain compounds with multiple mechanisms of action.

Pursuing our research on antiarrhythmic agents[1,2] we now describe fifteen compounds characterized by the presence of the rigid and cumbersome quinolizidine ring to replace the usual aminoalkyl chain of classic drugs as lidocaine, procainamide, amiodarone, etc.

The relevant compounds have been tested for antiarrhythmic, inotropic and chronotropic effects on isolated guinea pig (gp) heart tissues and to assess calcium antagonist activity. All compounds exhibited from moderate to high antiarrhythmic activity and five of them were more active and potent than the reference drugs (amiodarone, lidocaine, procainamide and quinidine) with EC_{50} in the range 0.15-0.59 μM. These compounds were studied on Langendorff-retrogradly perfused gp heart; even at concentration 17-67 times higher than the corresponding EC_{50} for antiarrhythmic activity they prolonged the QT intervals only moderately, comparing favourably with amiodarone and quinidine. Compounds **3** and **15** deserve further investigation due to their interesting cardiovascular profiles.



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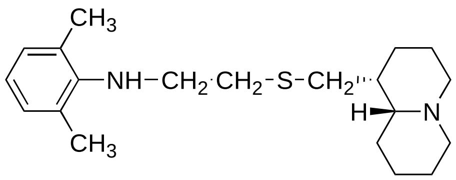

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Quinolizidinyl derivatives as potent inhibitors of acetyl- and butyryl-cholinesterase (AChE and BuChE) of potential interest for the treatment of Alzheimer's disease.

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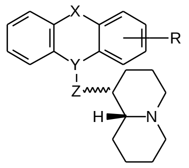
Alzheimer's disease (AD) is a progressive, neurodegenerative disorder characterized by a gradual decline of cognitive processes. The multifactorial pathogenesis of AD includes accumulation of aggregates of β-amyloid and loss of cholinergic neurons, with consequent deficit of the neurotransmitter acetylcholine (ACh).

The inhibition of AChE, that is responsible for the breakdown of ACh, has proven useful to relieve some cognitive and behavioral symptoms of AD.

In advancing AD, AChE levels in the brain are declining, but a progressive increase (up to 90%) of BuChE is observed , which too is able, even if at lower rate, to hydrolize ACh.

Selective BuChE inhibitors have already been reported to increase ACh levels in the brain, and, interestingly, to also reduce the formation of abnormal amyloid. Potent and selective BuChE inhibitors are represented by some physostigmine derivatives as phenethylnorcymserine, and by ethopropazine[1], whose high activity, with respect to other phenothiazine-derived drugs, is related to its particular basic chain. Therefore, in order to achieve novel cholinesterase inhibitors, either dual or , even better, selective for BuChE, we have prepared and tested a number of derivatives of phenothiazine and other tricyclic systems bearing a peculiar basic moiety, as the bulky quinolizidine ring, linked through different kind of spacers.

All tested compounds exhibited activity against both cholinesterases, but inhibition of BuChE was generally stronger, with submicromolar IC_{50} values for most of them.



R = H, CF_3, OCH_3
X = -, O, S, Se, CH_2, CH_2-CH_2, CH=CH
Y = N, CH, C=
Z = CH_2, SCH_2, =CH− $(CH_2)_n$-S−CH_2
$CO-CH_2$, $CO-(CH_2)_n$-S−CH_2

Molecular modeling studies provide valuable insights to interpret structure-affinity relationships and suggest appropriate structural modifications to improve the binding affinities of either one of the two enzymes.

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Preparation of flavour compounds by catalytic "ene" reaction

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The "ene" reaction, rearrangement of an alkene bearing an allylic hydrogen with a double or triple bond, accompanied by migration of the double bond and a 1,5-hydrogen shift is potentially 100% atom efficient[1].

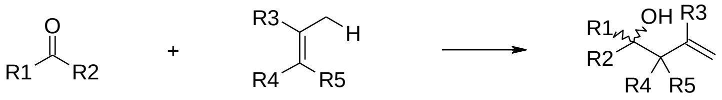
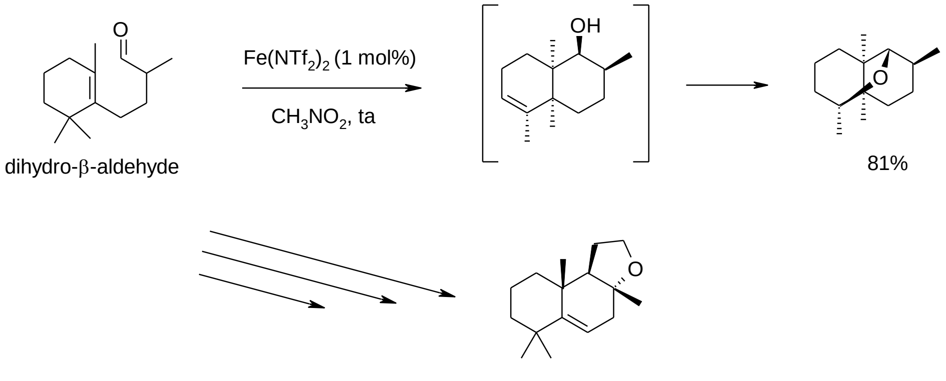


Figure 1 : General scheme representing carbonyl-ene reaction

This reaction generally uses Lewis acid such as $AlMe_2Cl$ in stoichiometric amounts. More recently, Lewis superacids such as $Sc(OTf)_3$[2], $Yb(OTf)_3$[3] and $Bi(OTf)_3$[4] were reported in catalytic amounts. We were interested in developing this intramolecular cyclization catalytically, in particular with a precursor of "superambrox" which is a highly appreciated compound in flavour and fragrance industry.



Superambrox

Figure 2 : Cyclization of the dihydro-β-aldehyde

We tested different catalytic systems and iron triflimidate $Fe(NTf_2)_2$ was the best for this reaction. We extended this methodology to a series of compounds such as geranyl acetone, citronellal and gerano-nitrile.

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The Dechromatation Step in Wastewater Treatment Plants, Optimization of the Process

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Among the various metals, chrome, with its wide range of oxidation states and particular characteristics, represents a strong chemical agent, necessary in many industrial processes such as surface-treatment industries. Unfortunately, it is a great pollutant for the aquatic environment and, along with the different species, Cr(VI) is the most dangerous one. For this reason, it requires a preliminary reduction in wastewater treatment plants to be transformed in the less toxic and more insoluble Cr(III) form. A strong oxidant, as bisulfite, is generally employed, at acidic pH, in excess to make the reaction complete.

The aim of this work was to optimize the industrial process in order to consume fewer amount of reagent, which could interfere during further steps, like neutralization and coagulation treatments. Moreover, this optimization also produces less final sludge, reduces the salinity and also allows to economize the whole process. In fact, the reactant injection is determined by a redox sensor immersed into the reactor, generally fixed in the range 220-260mV. In our studies, we proved that, at the pH generally used at industrial scale (i.e. 1.8-2.5), Cr(VI) is already reduced to Cr(III) for rH values equal to 290mV, as can be easily seen in Figure 1.

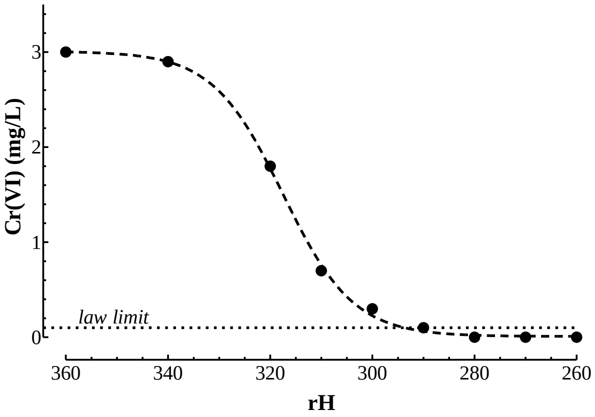

Figure 1. Correlation between Cr(VI) and the rH.

The excess of bisulfite can further reduce some other species, like organic compounds, making them even more difficult to be separated from treated water. In addition, there is a higher amount of sulfate ions in the industrial effluent, which can also form insoluble salts, so increasing the amount of produced sludge. Moreover, if hydrated lime ($Ca(OH)_2$) is used both to adjust pH and to precipitate fluoride ions as CaF_2, sulfate ions subtract Ca^{2+} ions to the desired reaction, precipitating as $CaSO_4$. Then, it is evident the strong interest to improve the dechromatation step to optimize the entire wastewater process, saving the reactant, too. In this communication, the results will be presented and discussed.

Ultrasounds assisted maceration: An original procedure for direct aromatisation of olive oil with basil

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The use of ultrasound and its applications to the food industry has been widely studied and it is still one of the most studied research area. It was preliminarily used as a control system in the food industry by using high frequency ultrasounds (also called diagnostic ultrasounds) but more and more interest has been given to high power (or low frequency) ultrasounds as a food processing alternative. In fact low frequency ultrasounds have been found to give greater yields in extraction processes, or same yields at lower temperature or even decreasing the processing time. The effect of ultrasound on extraction yields is attributed to the microstreaming and enhanced mass transfer produced by cavitational bubbles collapse resulting in cell destruction and greater solvent penetration into the plant material [11].

Essential oils of aromatic plants are well known for showing high antioxidant activities which constitute an interesting product on a nutritional point of view. In fact the protective effect of the Mediterranean diet against risk of cancer and cardiovascular diseases has been attributed to high intake of antioxidants. Essential oil glands are usually located on the external part of the plant so are directly exposed to the cavitating bubbles which explains why ultrasonic power is a very interesting alternative system for essential oil extraction.

Olive oil aromatisation is a new trend in the Mediterranean area, both for sensory and for nutritional improvement. The aim of this work was to develop a green enrichment of an olive oil with basil. Basil leaves are directly put in the olive oil and ultrasounds are applied to the mixture in order to accelerate diffusion of the basil aromas in the olive oil. The processing time is reduced from days to few minutes when comparing traditional maceration and ultrasound assisted aromatisation. Sensory profiles are similar between macerated and ultrasounds assisted oils and the news aromatised oil is well accepted by potential consumers.

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Docking analisys on 1-substitued-2-[(benzotriazol-1/2-yl)methyl] benzimidazoles as inhibitors of RSV F-protein.

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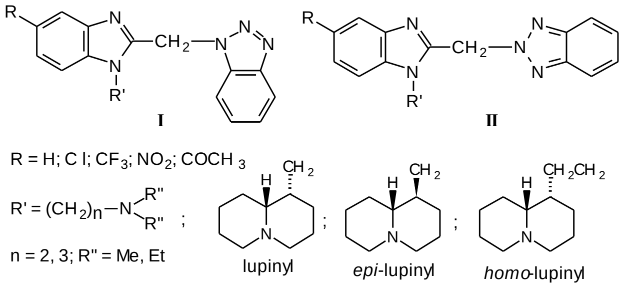
Respiratory syncitial virus (RSV) is a major cause of severe respiratory tract infections in pediatric, elderly and immunocompromised patients. Currently no vaccine has been approved and therapy is restricted to ribavirin, while humanized monoclonal antibody palivizumab is used for the prevention in high-risk infants. RSV genome encodes ten major species of mRNAs and ten major viral proteins: the F (fusion) and G (attachment) glycoproteins are the main antigenic determinats, expressed on virion surface, and play an important role in viral entry into host cells, so that they represent an interesting targets for designing small molecule inhibitors. Recently, we studied a series of 1-substituted-2-[(benzotriazol-1/2-yl)methyl]benzimidazoles[1] of general structure **I** and **II** against a large panel of RNA and DNA viruses, confirming, in particular, a potent anti-RSV activity, previously described by other authors,[2] and attributed to the inhibition of viral fusion process.[3,4] With the aim to propose a molecular rationale for the mechanism of action of our compounds, in particular those 5-substituted and bearing in position 1 the bulky quinolizidinyl residue, docking studies have been carried out within the fusion-protein hairpin structure.



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Lead discovery and synthesis of selective T-type calcium channel blockers

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T-type calcium channels belong to the family of voltage-gated calcium channels (VGCCs). The electrophysiological features of the T-channels are well established: low-voltage activated calcium current, fast inactivation kinetics and low unitary conductance. Calcium enters through T-channels and mediates membrane depolarisation and increases intracellular calcium concentration that are thought to contribute significantly to pacemaker activities in the heart and in neurons, hormone secretion, epilepsy and pain.

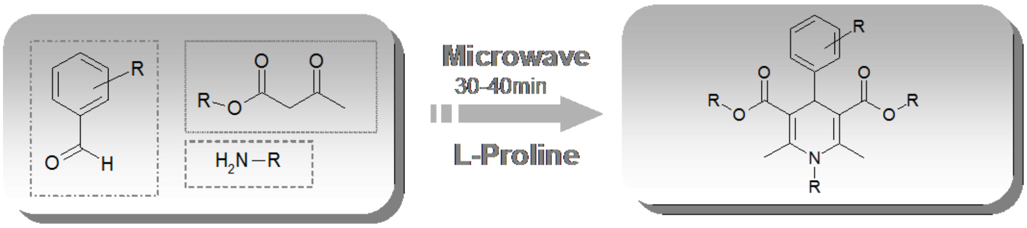
Though their presence in many tissues and their potential implication in various disease states, low-voltage activated T-type calcium channels have only recently become targets of interest. Unfortunately, the lack of selective T-channel blockers has hampered further characterisation of these channels. Selective inhibition of T-channels may have clinical importance in cardiovascular diseases and some forms of epilepsy and pain.[1]

This work focuses on novel research approaches to discover potent and selective T-channel modulators. These molecules may be potential drugs for treating human diseases, as well as important tools to understand the physiological role of these channels.

A 1,4-dihydropyridine scaffold with a potential selective inhibition activity of T-type calcium channels was drawn using molecular modeling techniques. In particular computing alignment-free molecular descriptors, also called GRid-INdependent descriptors or GRIND, were used to obtain a model able to predict T-type calcium channel activity and to test potential hERG toxicity based on a model developed in our laboratory.[2]

The N-substituted 1,4-dihydropyridines were synthetised by a microwave assisted multi-component reaction catalyzed by L-Proline.

Microwave assisted Multicomponent Organocatalysed Reaction



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MedChem-Decision: a medicinal chemistry oriented tool for ligand de novo design

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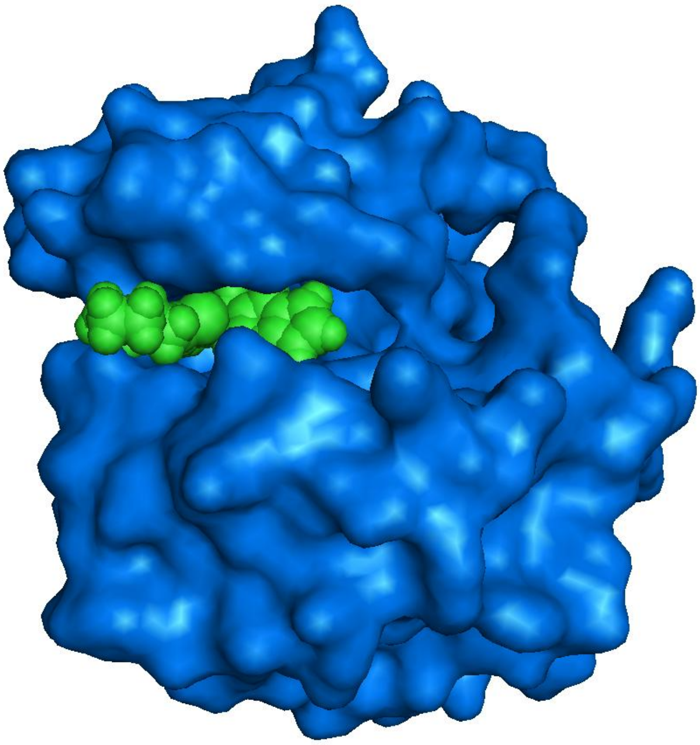
Nowadays, we cannot talk about drug discovery without mentioning the crucial role of chemoinformatics. Indeed, chemoinformatics has become a valuable tool for computational and medicinal chemists for speeding up the process of lead identification and optimization as well as decision making processes. In this context, we assessed the potential of the software platform developed by Nova Decision in drug design. Two main cheminformatics platforms has been dealt with: (1) MedChem-Decision® for assessment of docking and chemical feasibility of new compounds, and (2) EZ-Design® for the virtual library design and profiling.

The target of interest in this study is EGFR (Epidermal Growth Factor Receptor), a pharmaceutically validated target. EGFR is a cell-surface receptor, member of the tyrosine kinase super family. It has been clearly demonstrated that over-expression of this kinase results in many cancers, including lung cancer. Existing treatments such as Iressa® or Tarceva® are less and less efficient due to the rise of a mutation in EGFR. This mutation (T790M) is located in the active site of the kinase and prevents actual ligands to bind with a good affinity, leading to resistant cell lines.

The docking part of this work is intended to evaluate new designed molecules and selection of lead compounds for chemistry synthesis. The aim of the present work is to show the methodology used to reproduce crystallographic experimental data and selection of compounds to be synthesized for the discovery of new original ligands of EGFR mutant T790M.



A new on-line SPE HPLC-MS/MS method to study the sun light photodegradation of mono-chloroanilines in river waters

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Recently the interest for water health protection greatly increased, also due to the increasing amount of pollutants introduced into the environment. Particular interest is devoted to chloroanilines (CAs) because of their recognised toxicity associated to their ubiquitous diffusion. They are therefore diffused and accumulated in surface waters, industrial effluents, sludge and soils. In addition, they are characterised by great persistence and low natural biodegradability. For all these reasons, CAs are considered by the European Water Framework Directive (WFD) 2000/60/EC[1] among the priority contaminants to be monitored. Even if in the recent past CAs have been considered as persistent pollutants, new experimental evidences show that their solutions can undergo natural photodegradation processes. This study investigates the natural photodegradation pathway of mono-chloroanilines (ortho-chloroaniline, meta-chloroaniline and para-chloroaniline) in river waters, with the aim to identify the predominant photoproducts formed. At this purpose a new sensitive on-line SPE HPLC-MS/MS method has been developed. The degradation processes of o-, m- and p-chloroaniline was investigated subjecting their solutions, prepared both in ultra pure water and in three different river waters (collected in Sesia, Tanaro and Po rivers, Piedmont, Italy), to sun light irradiation simulated by a solar box system.

The use of on-line SPE coupled with a LC-MS hybrid mass spectrometer (3200 Q Trap™) permitted to reach LOQ values lower than the legal threshold concentration levels (0.1 µg L^{-1} for o-CA and p-CA and 0.2 µg L^{-1} for m-CA)[2] of mono-chloroanilines in waters. The on-line extraction procedure employed is based on the use of a cationic extraction column (Strata X-CW) coupled with LC-MS through a two-way switching valve, which allows the loading and the injection steps. An automated LC/MS/MS workflow using Information Dependent Acquisition (IDA) was used both to automatically obtain information about the species present and to build a scheduled multiple reaction monitoring (sMRM) method with the MS/MS fragmentation pattern for the species considered.

For all the analytes linearity range, R^2, limit of detection (LOD), limit of quantification (LOQ), intra- and inter-day RSD (%), recovery yield and matrix effect were evaluated.

Finally the developed method was applied in the analysis of the three river samples.

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[2] European Directive 2455/2001/EC.

Superhydrophobic, superoleophobic surfaces: morphological signature of electrodeposited polymers

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The control of surface wettability and in particular of surface hydrophobicity is of great significance in domain of non-adhesion. Today, lot of developments and proceeds offers the possibility to realize superhydrophobic[1] surfaces but there are few reports on superoleophobic[2] surfaces. The electrochemical deposition of substituted organic conducting polymers is one method which, in comparison with other processes of surface structuration, allows a fast deposition of superhydrophobic conductive polymer films. The method is very fast (one-pot, no post-treatment) and needs soft conditions (room temperature, atmospheric pressure). Our group demonstrated first the impact of the introduction of a fluorinated moiety in the monomers structure before the electrochemical polymerization step. The obtained surfaces exhibited incomparable superhydrophobic as well as oleophobic or superoleophobic behavior. A correlation between the surface oleophobicity, which depends on the surface morphology, and the electrochemical properties, which depends on the monomer chemical structure, can be determined. Thus, in this work, for the same conditions of electrodeposition (temperature, charge, and doping) a relation between the molecular structure of monomers and morphological signature of polymer film will be illustrated. Consequently, this librarian can be use as reference to choose wettability according to applications.

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New acrylic denture resins with antifungal properties

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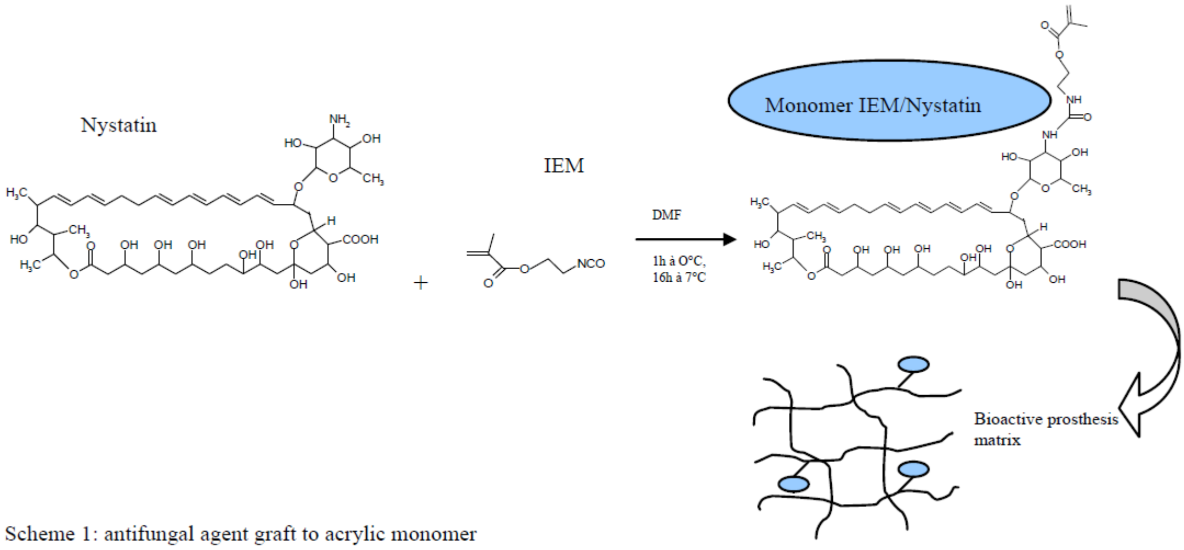
The removable denture bases are made with polymethyl methacrylate resin (PMMA). They are colonized in vivo by the endogenous oral flora but which is responsible in denture stomatitis of 65% of geriatric or institutionalized patients. Normally this biofilm must be regularly eliminated by brush and/or antiseptic solutions but it's too difficult for them.

So the aim of this work is to realise a bioactive denture resin. In order to, the adopted strategy is to graft an antifungal agent (nystatin, similar to amphotericin B, which preferentially bind to ergosterol, the primary sterol in the fungal cell membrane, with leakage of intracellular potassium and magnesium, and also disruption of oxidative enzymes in target cell) with acrylic monomer like the isocyanatoethyl methacrylate (IEM) [Scheme 1]. The modified monomer is then included in prosthesis matrix during the polymerization process.

The first results will be developed as well as specific chromatographic methods to analyze the new obtained monomer.



Scheme 1: antifungal agent graft to acrylic monomer

Elenco
Partecipanti
ed Autori

Partecipanti

ABED Charline	Nice
AGOSTINO Angelo	Torino
AINA Valentina	Torino
AL ABDULLAH Jamal	Nice
ALESSI Matteo	Genova
ANGELONI Franco	Sanremo
ANTONIOTTI Paola	Torino
ANTONIOTTI Sylvain	Nice
ARDINI Francesco	Genova
ARTINI Cristina	Genova
ASTEIAN Alice	Marseille
AVONTO Cristina	Novara
BAGNASCO Lucia	Genova
BAKIZ Bahcine	Toulon
BALBI Alessandro	Genova
BARBERO Nadia	Torino
BARICCO Marcello	Torino
BARTOLI Alexandra	Marseille
BASSO Andrea	Genova
BATTEZZATI Michele	Torino
BAZZI Stefano	Torino
BEDINI Andrea	Torino
BELLANGER Hervé	Nice
BENZI Paola	Torino
BENZI Micaela	Alessandria
BERETTA Paolo	Finale Ligure
BIALE Chiara	Genova
BIANCHI Lara	Genova
BIENVENU Céline	Nice
BIGNASCA Antonello	Genova
BOIDO Vito	Genova
BORAGNO Luca	Genova
BOTTIZZO Elena	Torino
BOUHLEL Ahlem	Marseille
BOUSBIA Nabil	Avignon
BRULLO Chiara	Genova
BRUNO Olga	Genova
CAGLIERO Stefano	Torino
CANEPA Fabio	Genova
CANU Caterina	Genova
CARLINI Riccardo	Genova
CAVALLO Dario	Genova
CELIA Elena	Nice
CEVASCO Giorgio	Genova
CHABREUIL Lucie	Marseille
CICIONE Lavinia	Novara
COLOMBINO Mario	Genova
CONSTANTIEUX Thierry	Marseille
COSULICH Maria Elisabetta	Pavia
COUTURIER Isabelle	Marseille
COZZA Erika Simona	Genova
CRAVINO Antonio	Angers
CRINI Gregorio	Besançon
DAVEZZA Manuela	Torino
DELLA GATTA Giuseppe	Torino
DEMARIA Chiara	Torino
DI CARRO Marina	Genova
DI VONA Maria Luisa	Roma
DRIOWYA Mohsine	Nice
DUNACH Elisabet	Nice
DZIUBA Dmytro	Nice
FARHAT Asma	Avignon
FIGARI Giuseppe	Genova
FINOCCHIO Elisabetta	Genova
FORINA Michele	Genova
FORNASINI Maria Luisa	Genova
GAL Jean-François	Nice
GALY Nicolas	Marseille
GARZON Cécile	Marseille
GERBALDO Michela	Cherasco
GIACOMINO Agnese	Torino
GIUNCO Francesco	Genova
GODEAU Julien	NICE
GOSETTI Fabio	Alessandria
GREINER Jacques	Nice
HANZU Ilie	Marseille
HAUVILLE Agnès	Nice
HORZIC Dunja	Avignon
IELUZZI Gianmarco	Torino
JADHAV Sushilkumar A.	Genova
JULLIARD Michel	Plan de Cuques
KHADHRAOUI Mustapha	Marseille
KHAN Muhammad Kamran	Avignon
KHOUMERI Omar	Marseille
KLEIN Laurie	Marseille
KNAUTH Philippe	Marseille

LANTERI Silvia	Genova
LEBEAU Alexandre	Valflaunes
LEKHLIFI Adil	Marseille
LUCERO Paola	Avignon
MACCAGNO Massimo	Genova
MAGI Emanuele	Genova
MAGNASCO Valerio	Genova
MAILHOL Damien	Marseille
MALNUIT Vincent	Nice
MASSI Lionel	Nice
MASSOLO Serena	Genova
MAURINO Valter	Torino
MAZZEI Mauro	Genova
MEIERHENRICH Uwe	Nice
MERLO Franco	Genova
MINASSI Alberto	Novara
MINELLA Marco	Torino
MONFARDINI Ilaria	Nice
MONTANARI Tania	Genova
MORETTI Giulia	Alba
MOSTACCI Erminio	Torino
MOSTI Luisa	Genova
MUSUMECI Francesca	Genova
NAPOLETANO Myrta	Genova
NECHAB Malek	Marseille
NOVELLI Federica	Genova
OLIVERI Paolo	Genova
OPERTI Lorenza	Torino
ORTET Risoleta	Nice
OTTONELLO Giuliana	Genova
OUMAR Mamadou	Nice
PADOAN Gennifer	Nice
PANI Marcella	Genova
PARK Jinhyung	Torino
PARRAIN Jean-Luc	Marseille
PASCALE Lise	Nice
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PETRILLO Giovanni	Genova
PIATEK Anna Maria	Genova
PIETRI Nathalie	Marseille
PINGRET Daniella	Avignon
POLLASTRO Federica	Novara
PONS Jean-Marc	Marseille
RABINE Jean-Pierre	Nice
RAHMOUNI Hidayat	Marseille
RANISE Angelo	Genova
RIANI Paola	Genova
RICQUEBOURG Emilie	Marseille
ROBOTTI Elisa	Alessandria
ROTOLO Chiara	Genova
RUIZ Karine	Avignon
SACCONE Adriana	Genova
SANCASSAN Fernando	Genova
SANCEY Bertrand	Besançon
SANCHEZ DUQUE Maria	Marseille
SANTELLI Maurice	Marseille
SCAPOLLA Carlo	Genova
SGRECCIA Emanuela	Marseille
SORDELLO Fabrizio	Robilante
SPARATORE Fabio	Genova
TASSO Bruno	Genova
THEA Sergio	Genova
TONELLI Michele	Genova
TREMEL Pascal	Nice
TRUNFIO Giuseppe	Besançon
TURCO Francesca	Torino
VAZZANA Iana	Genova
VECE Vito	Nice
VEILLET Sébastien	Avignon
VETTORETTI Gerolamo	Genova
VISENTIN Sonja	Torino
WARNAULT Pierre	Nice
ZAMPIERI Davide	Alessandria
ZANICCHI Gilda	Genova
ZAPPIA Stefania	Genova
ZENERINO Arnaud	Nice
ZERBIB Carine	Nice
ZILL-E-HUMA	Avignon
ZUNIN Paola	Genova

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