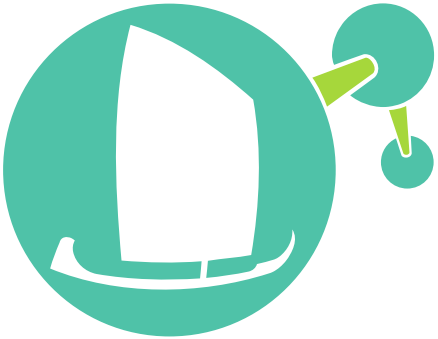


2PYCheM

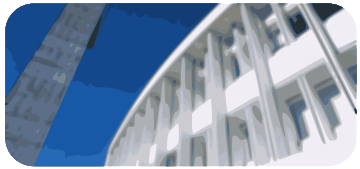
2nd Portuguese Young Chemists Meeting

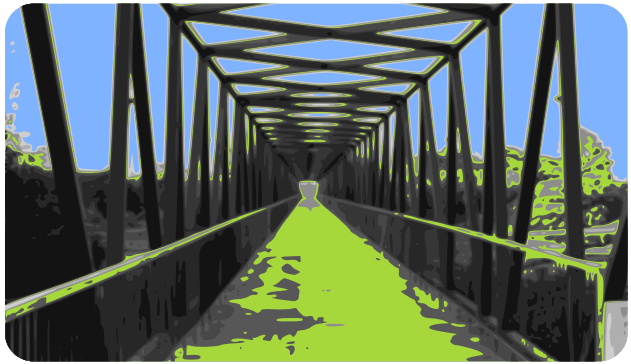
21 - 23 april 2010
universidade de aveiro, portugal

SPQ GQ universidade de aveiro

2PYCheM

2nd Portuguese Young Chemists Meeting





Contents

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Dear Colleagues,

On behalf of the Young Chemist Group - *Grupo de Químicos Jovens*, we are delighted to welcome you to the 2nd Portuguese Young Chemists Meeting (2PYCheM).

This second meeting, counting with more than 200 participants, is already one of the biggest meetings of *Sociedade Portuguesa de Química*. You are all responsible for this accomplishment and part of this community. Congratulations to all!
The outstanding program presented by the organizing committee is a reflex of the excellent work that our colleagues from Aveiro have done. Their commitment and efforts were exceptional and we would like to express our sincere gratitude.
We hope that this meeting and the forthcoming editions of PYCheM became a reference for activities organized with the contribution of all the young chemists.

We wish you a pleasant meeting and a nice time in Aveiro,

Carlos Baleizão
Frederico Ferreira
Pedro Gois

Dear Colleagues,

EYCN, the *European Young Chemists Network*, is the younger members division of the *European Association for Chemical and Molecular Science*s, EuCheMS. EYCN was founded in 2006 with the mission to bring together all young chemists within Europe and now counts with more than 20.000 members from 19 European nations – from Russia to Portugal – within the Network today.

EYCN promotes interaction among chemists in European industry, academia and professional institutions. Through networking, young chemists contribute to the promotion of chemistry and to the development of European initiatives, including scientific programs in chemistry and molecular sciences as well as scientific and technological areas.
Therefore, EYCN is happy to welcome you all to 2PYCheM, being held in Aveiro, Portugal.

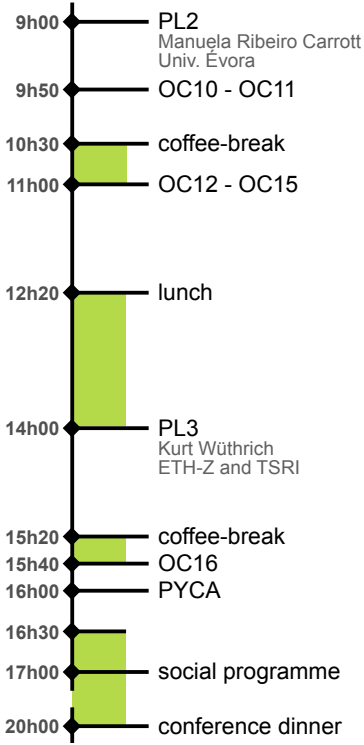
To get to know more about EYCN please visit www.EYCN.eu or contact your national representative within your chemical society.

the european
young chemists network

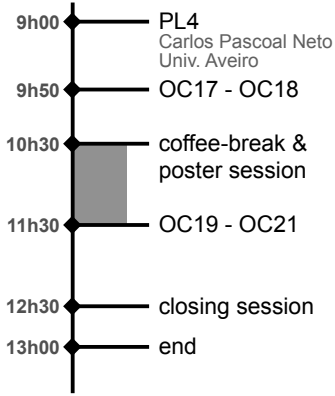
programme

21st april
wednesday

22nd april
thursday



23rd april
friday



PL - plenary lecture
OC - oral communication
PYCA - portuguese young chemists award
- free time
- poster session

summary

plenary lectures

oral communications

posters

plenary lectures

Coordination chemistry working for biology: enzymatic activity mastered by altering metal environment

José J. G. Moura | Sofia R. Pauleta | Isabel Moura

REQUIMTE, Centro de Química Fina e Biotecnologia, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

jose.moura@dq.fct.unl.pt

Metalloenzymes control enzymatic activity by changing the characteristics of the metal centers, where catalysis takes place. The conversion between inactive and active states can be tuned by altering the coordination number of the metal site, in most cases, associated with conformational changes. These processes will be illustrated using heme proteins (cytochrome c nitrite reductase, cytochrome c peroxidase and cytochrome cd_1 nitrite reductase), non-heme proteins (superoxide reductase and [NiFe]-hydrogenase), and copper proteins (nitrite and nitrous oxide reductases). These case studies catalyze electron transfer reactions that include atom transfer, abstraction and insertion.

Acknowledgments
Support from FCT-MCTES.

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Templated mesoporous materials: expectations, facts and challenges

Manuela Ribeiro Carrott

Centro de Química de Évora and Departamento de Química, Universidade de Évora, Portugal

manrc@uevora.pt

The interest in ordered mesoporous materials (OMM) had its origin in the absence of materials with pores of highly uniform width in the mesopore range (2-50 nm) as opposed to what already existed for micropores (< 2nm) with, for instance, zeolites or carbon molecular sieves. Although molecular templating was used since the 1960's for the synthesis of microporous zeolites, it was only in 1992 that the unique structural properties of OMM were disclosed for the silicas and metalosilicates of the M41S family, prepared using supramolecular templates. Starting with surfactant micelles as structure directing agents, soon the ability of self-assembly of organic and inorganic precursors in the presence of block copolymers was also reported for soft templating synthesis and later on the idea developed into hard templating preparation (nanocasting) of ordered mesoporous carbons. The variety of acronyms appearing in the literature reflects the present situation of numerous members of the OMM class, yet foreseen to be still incomplete, which is due to the high versatility of the synthesis approach. In fact, by combining the nature of the structure directing agent with careful control of the synthesis parameters, it is possible to tailor the ordering, geometry and surface chemistry of the mesopores, and in particular to fine tune their size to a target dimension. These extraordinary features, associated with the high surface areas and pore volumes, justify the intensive research dedicated to these interesting materials having potential for application in many fields of science and technology, as themselves or as host matrices for immobilisation of bulky species. This presentation will include an overview of the main types of the mesoporous structures that can be generated via template processes, addressing the role of surface chemistry on their formation and implications in their properties and applications. Some aspects to be considered will involve the introduction of catalytic functionalities, the important contributions that these model porous solids brought to the testing of fundamentals underlying gas adsorption, previously developed with common mesoporous materials having broad pore size distributions, and also their potential as molecular sieves for big molecules in the liquid phase. Together with the beautiful aspects, some challenges still to overcome, will also be mentioned.

Acknowledgments

The author thanks the research staff and chemistry students, past and present, that at the CQE have enthusiastically participated in the work with templated mesoporous materials. The work is currently financed by the Fundação para a Ciência e Tecnologia (FCT, Portugal) and the European Regional Development Fund (FEDER) (Project nº. PTDC/CTM/67314/2006).

The protein universe: structural biology in the post-genomic era

Kurt Wüthrich
(Nobel Prize in chemistry, 2002)

Institute of Molecular Biology and Biophysics - ETH-Zürich
Department of Molecular Biology and Department of Chemistry - The Scripps Research Institute

Kurt Wüthrich's research interests are in molecular structural biology and in structural genomics. His specialty is nuclear magnetic resonance (NMR) spectroscopy with biological macromolecules in solution.
The Wüthrich group started to work towards the development of an NMR method for protein structure determination in the mid-seventies with studies on NOE build-up and spin diffusion in proteins, the sequential assignment strategy for proteins and, in joint projects with Richard Ernst (Nobel Prize in Chemistry 1991), the development of twodimensional NMR with biological macromolecules. Among the three-dimensional protein structures in solution solved by the Wüthrich groups, the bull seminal proteinase inhibitor (BUSI) was the first NMR structure of a globular protein. In the further development of the method, the structure determination of the amylase inhibitor tendamistat, metallothionein, the *Antennapedia* homeodomain–BS2 operator complex and the cyclosporin A–cyclophilin A complex were of special interest.
Prion proteins (PrP) have become a major research focus of the Wüthrich laboratory since 1994. Three-dimensional structure determinations of a variety of mammalian and non-mammalian prion proteins, including those from man, cattle and chicken, now provide a framework for continued investigations of molecular aspects of the onset and the interspecies transmission of transmissible spongiform encephalopathies. Beyond three-dimensional structure determination of biological macromolecules, NMR characterization of biomacromolecular dynamics and conformational equilibra includes study of aromatic ring flips, single-site investigations of amide proton exchange, structural and kinetic characterization of hydration water of proteins in solution, studies on the role of hydration waters in protein–DNA recognition, and work on the protein folding problem.

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http://www.scripps.edu/mb/wuthrich/index.html

New materials from renewable resources

Carlos Pascoal Neto

CICECO and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

cneto@ua.pt

The foreseeable depletion of fossil resources in the forthcoming decades led to a strong research activity in the past few years, aiming to identify alternatives to petrochemistry. Biomass, being a renewable and ubiquitous resource, is one of the most promising available alternatives to oil. The biorefinery concept (Fig. 1) calls upon the using of all biomass components in a comprehensive and integrated way, as source of chemicals, materials and energy, replacing those nowadays produced by petrochemical refineries. Within, this context, many traditional forest-based industries (including pulp and paper) and food-based industries are being upgraded into modern biorefineries, generating, in addition to their main and traditional products, polysaccharides, including cellulose fibres, hemicelluloses, starch and chitin/chitosan, lignins, suberin, proteins and many high value low molecular weight products. Cellulose may be also obtained by new emerging biorefineries using bacteria (eg *acetobacter xylinum*) that transform different carbon compounds into nanofibrilated cellulose. Such biomass components may be used to produce novel materials including polymers and composites.

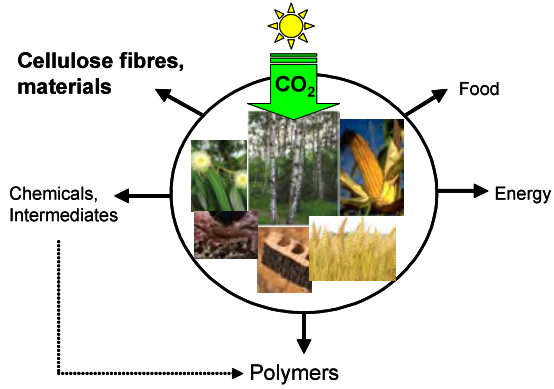


Fig. 1. The general biorefinery concept

The presentation involves a brief overview of the biorefinery concept, biomass components, followed by a review on recent advances on the development of new materials including cellulose fibre-based composites and nanocomposites, super-hydrophobic cellulose-based materials and polymers derived from biomass components. The potential applications of such novel materials are briefly discussed.

oral communications

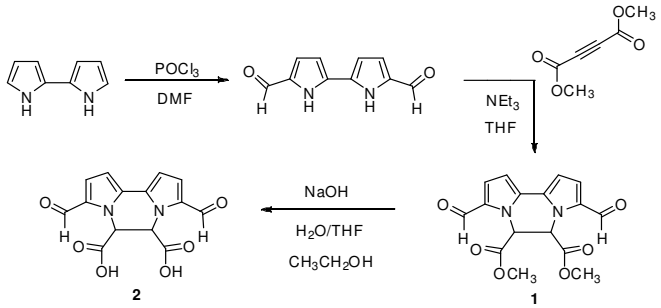
Synthesis of new bipyrrole derivatives by a double aza-Michael addition reaction

Flávio Figueira | Augusto C. Tomé | José A. S. Cavaleiro | João P. C. Tomé

QOPNA, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

ffigueira@ua.pt

Expanded porphyrins are a class of compounds with increasing interest. Most of the attention dedicated to these systems is based on their similarities to porphyrins and the hope that they could show the rich coordination chemistry found in porphyrins. Another factor leading to the study of expanded porphyrins is that they often display extensive π conjugation pathway that can be of enormous interest in several areas, such as PDT, anion binding and electronics [1]. The Michael addition reactions benefits from mild reaction conditions, large host of functional precursors, as well as high conversions and favorable reaction rates. Among the different synthetic methodologies, one of the most frequently used is the conjugate addition of amines to α,β-unsaturated ketones, esters or nitriles, which is termed as aza-Michael reaction [2]. As part of our studies on the synthesis of expanded macrocycles, in this communication we will report the synthesis and structural characterization of bipyrrole derivatives **1** and **2**. These new compounds will be used as building blocks for the construction of novel polypyrrolic macrocycles.



Acknowledgments

Thanks are due to FCT (Fundação para a Ciência e a Tecnologia) and FEDER for funding the QOPNA Unit and the project PTDC/QUI/65228/2006. F. Figueira also thanks FCT for his PhD grant (SFRH/BD/46788/2008).

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Tomato (*Lycopersicon esculentum*) seeds: new flavonoids

Marcos Taveira [1] | Federico Ferreres [2] | David M. Pereira [1] | Patrícia Valentão [1] | Paula B. Andrade [1]

[1] REQUIMTE/Department of Pharmacognosy, Faculty of Pharmacy, Porto University, R. Aníbal Cunha 164, 4050-047 Porto, Portugal
[2] CEBAS (CSIC) Research Group on Quality, Safety and Bioactivity of Plant Foods, Department of Food Science and Technology, P.O. Box 164, 30100, Campus University Espinardo, Murcia, Spain

marcos.taveira@gmail.com

Lycopersicon esculentum Mill. fruit (tomato) is widely consumed and is among the most studied vegetable species. However only a few studies were performed in their seeds. The determination of phenolic compounds in seeds has assumed increasing importance because they often constitute a source of specific compounds in high concentration.
Currently, the use of HPLC coupled with tandem mass spectrometry (MS/MS) has emerged as a simple and one of the most sensitive methods. Thus, minor or trace constituents, which are difficult to obtain by conventional means, could be detected by mass spectrometry. In this study, seeds of *L. esculentum* ("Bull's heart" cultivar) were analysed by HPLC/UV-PAD/MS^n-ESI. Fourteen flavonoids were identified, including quercetin, kaempferol and isorhamnetin derivatives, with thirteen of them being reported for the first time (Fig. 1).

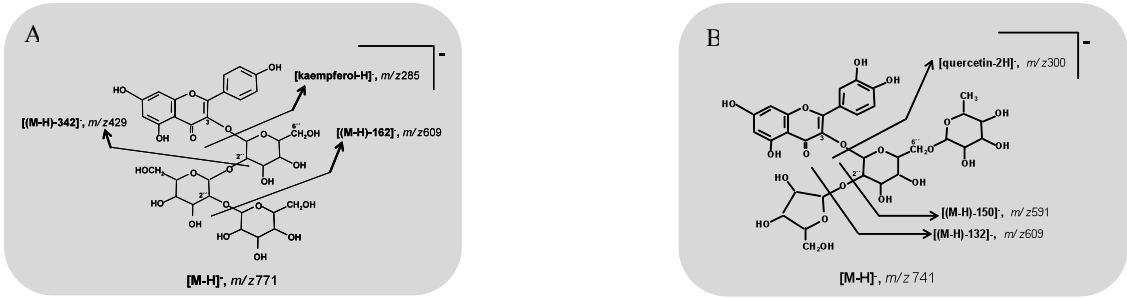

Fig. 1. Fragmentation pattern of kaempferol-3-*O*-(2-sophorosyl)glucoside or kaempferol-3-*O*-glucosyl-(1→2´´´)-glucosyl-(1→2´´)-glucoside (A) and quercetin-3-*O*-(2-pentosyl)rutinoside or quercetin-3-*O*-(2-pentosyl, 6-rhamnosyl)glucoside (B).

Acknowledgments
M. Taveira (SFRH/BD/62662/2009) and D. M. Pereira (SFRH/BD/62663/2009) are indebted to FCT for the grants.

Biomarker profiles in lung cancer by NMR-metabonomics of blood plasma and urine

C. Rocha [1] | A.S. Barros [2] | A.M. Gil [1] | B.J. Goodfellow [1] | A. Gomes [3] | V. Sousa [3] | L. Carvalho [3] | I.F. Duarte [1]

[1] CICECO, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
[2] QOPNA, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
[3] Institute of Pathological Anatomy, Faculty of Medicine, University of Coimbra, 3001-401 Coimbra, Portugal.

claudia.rocha@ua.pt, ioladuarte@ua.pt

The assessment of changes in endogenous metabolites within biological systems (metabonomics) has recognised value and multiple applications in the field of oncology [1]. In our group, we are using this approach to investigate the metabolic phenotype of lung cancer [2]. In this communication, the detection of lung cancer biomarkers in the metabolic profile of biofluids (blood plasma and urine), measured by Nuclear Magnetic Resonance (NMR) spectroscopy, is explored. Biofluid samples from lung cancer patients (n=57) and a control group of healthy volunteers (n=41) were analysed by high resolution ^{1}H NMR at 500 MHz, and their spectral profiles subjected to multivariate statistics, namely Principal Component Analysis (PCA), Partial Least Squares Discriminant Analysis (PLS-DA) and Orthogonal Projections to Latent Structures (O-PLS)-DA. In the case of blood plasma, the application of O-PLS-DA, to remove systematic variation not relevant to class separation, resulted in reasonable separation between patients and control groups, which was found to be due to increased levels of lactate, glycoproteins, LDL+VLDL and lower levels of HDL and histidine in cancer compared to healthy subjects. Urine samples from lung cancer patients could also be differentiated from controls by applying MVA methods to the ^{1}H NMR spectra. In particular, creatinine, 2-hydroxybutyric acid, citrate and some unassigned signals were elevated in tumor cases, whereas hippurate and TMAO were reduced. These results show the valuable potential of NMR-metabonomics for finding putative biomarkers of malignancy in the patients' biofluids, which may have important diagnostic/prognostic value. Correlations between the biofluids metabolic profiles and the histological type and stage of tumors are also being investigated.

Acknowledgments
Funding is acknowledged from FCT, Portugal (FCT/PTDC/QUI/68017/2006, SFRH/BD/63430/2009).

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New synthetic approaches using microwave radiation

M. Paiva | A. Gomes | S. Cravo | E. Sousa | M. Pinto

Department of Chemistry, Laboratory of Organic and Pharmaceutical Chemistry, Faculty of Pharmacy, University of Porto, Rua Aníbal Cunha, 164, 4050-047 Porto, Portugal
CEQUIMED-UP, Center of Medicinal Chemistry – University of Porto, Portugal

gpaiva.mafalda@gmail.com

Xanthones and thioxanthones have been reported to possess interesting cytotoxic activities, being a prenyl group or a basic side chain an important component for the expression of this effect [1]. Recently, the combination of microwave assisted synthesis with inorganic solid supports as catalysts, either with solvent or under solvent-free conditions, provided the synthesis of prenylated xanthones with enhanced reaction rates and high yields [2]. The aim of the present work was to compare classical routes with microwave assisted synthesis, considering some reaction parameters such as reaction temperature and time, variations in solvents, additives, and catalysts that can be used to optimize the desired chemistry. 3,4-dihydro-12-hydroxy-2,2-dimethyl-*2H,6H*pyrano[3,2-b]xanthen-6-one (XP13), and an aminated thioxanthone (TXA1) were synthesized, both by classical and microwave assisted route (Fig. 1).

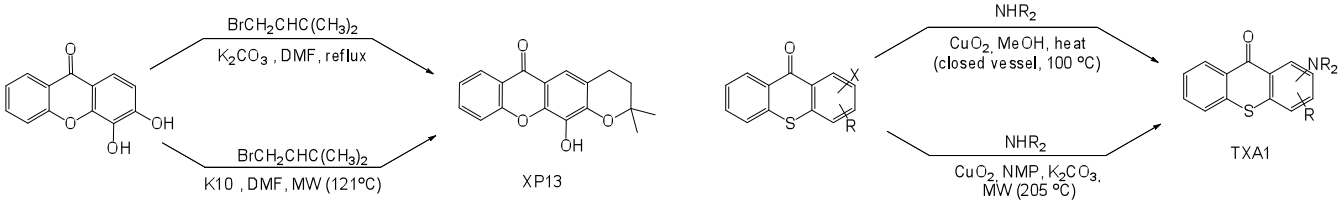

Fig. 1. Different pathways used in the synthesis of XP13 and TXA1.

Acknowledgments
To CEQUIMED-UP (I&D 4040/2007) and to U.Porto/Santander Totta for financial support.

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Use of high pressure to increase the content of xanthohumol in beer wort

Mickael da C. Santos | Fernando M. Domingues | José M. Cruz | Jorge A. Saraiva

QOPNA, Departamento de Química, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

mickael.c.santos@gmail.com

Xanthohumol (XN), a hop (*Humulus lupulus* L.) prenylflavonoid also found in beer, exhibits a large spectrum of biological activity, such as anti-carciogenic, antioxidant, anti-inflammatory and anti-infective [1]. During beer production, XN extracted from the hops through wort boiling is largely converted into its isomeric flavanone, isoxanthohumol (IXN), this being the reason why commercial beers around the world are characterized by a very low content of XN [1]. This situation leads to a great interest in the production of XN enriched beers for their enhanced health benefits.

Apart from its main commercial use in the cold pasteurization of foods, high (hydrostatic) pressure (HP), up to 500-600 MPa, has recently been suggested as a promising method to carry out faster and more efficient extraction processes at room temperature [2]. This work aimed to evaluate the possible use of HP, at room temperature, to extract XN from hop into beer wort, in order to produce worts with higher XN content for the development of XN enriched beers.

“Lager” and “dark” worts were pressurized at room temperature from 100 to 500 MPa (1000 to 5000 atm) for 5 and 15 minutes, using hop *pellets* (type 45, Czech Saaz variety) as XN source. The pressurized wort samples presented higher amounts of XN (up to 5-fold), compared to the boiled ones, while the amounts of IXN were very small. These results indicate that XN extraction occurs, under HP, with very little isomerization. For 5 min extractions, at 100 to 250 MPa, the amount of XN in wort was linearly correlated with the pressure used (R2=0,891). “Dark” wort samples present higher levels of XN than “lager” wort samples.

Acknowledgments

The authors thank Unicer Bebidas, S.A, for their support, including the supply of hop samples and wort. This work was financially supported by Instituto de Bebidas e Saúde (iBeSa), as part of the Project 11-08.

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Supercritical carbon dioxide effect on the microbiological activity of antibiotic micro/nanoparticles

K. Bettencourt | L. Pinheiro | A. Bettencourt | J. Crespo | H. A. Matos | M. A. Rodrigues | L. Padrela | A. J. Almeida | M. Castro | A. Duarte

Research Institute for Medicines and Pharmaceutical Sciences (iMed.UL), Faculty of Pharmacy, University of Lisbon, Av. Prof. Gama Pinto, 1649-003 Lisbon, Portugal

kevinbettencourt33@hotmail.com

Bacterial infection still remains an important and challenging therapeutic problem because of factors that include emerging infectious diseases and the increasing number of multi-drug resistant microbial pathogens. Delivery systems for antibacterial drugs targeting and controlled release have been developed using antibiotic micro- and nanoparticles, in an attempt to improve drug therapeutic efficacy and safety. Supercritical fluid (SCF) technology is an outcome of such research with particular emphasis in the green synthesis and particle formation. The most commonly used supercritical fluid is carbon dioxide owing to its low critical properties and safety considerations [1,2].
The study reported herein shows that the microbiological activity of minocycline, tobramycin and vancomycin micro- and nanoparticles, produced using the technology of SCF was not changed. The particles were produced by the AAS (atomization and anti-solvent) technique [3], using supercritical carbon dioxide (SC-CO_2). The morphology of the particles was evaluated using the scanning electron microscopy (SEM) and image analysis software Sigma Scan. The antimicrobial potential of the processed antibiotics was evaluated by standard microbiological assays against bacterial strains, namely a collection of reference antibiotic-susceptible and multidrug resistant isolates. The aim of the task was achieved as the results showed that the processed antibiotics have maintained their antimicrobial activity.

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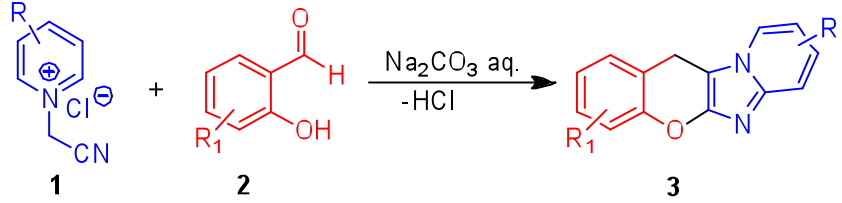
One-pot condensation-cyclization approach for the synthesis of 12*H*chromeno[2´,3´:4,5]imidazo[1,2-*a*]pyridine

Marta Costa | M. Fernanda Proença

University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

martacosta@quimica.uminho.pt

Chromene derivatives are an important class of compounds, considering their diverse biological properties and therapeutic applications. The imidazo[1,2-*a*]pyridine nucleus is also an important scaffold in the preparation of a diversity of biologically active compounds. Different synthetic pathways have been used to prepare substituted imidazo[1,2-*a*]pyridines, either from the imidazole or from the pyridine nucleus. To the best of our knowledge, the association of this moiety with the chromene unit has never been reported. The combination of these two important scaffolds may lead to new and alternative drug candidates with improved pharmacological profile.
In this work, the chromeno-imidazo[1,2-*a*]pyridine **3** scaffold was generated in an one pot condensation-cyclization reaction involving a salicylaldehyde **2** and 1-(cyanomethyl)pyridinium chloride **1**, in aqueous sodium carbonate solution (Scheme 1). These novel compounds were isolated in 47-70% yield. Different mono-substituted pyridinium chlorides were synthesized and reacted with mono-substituted salicylaldehydes and a detailed discussion of the scope of the synthetic method will be presented.



Scheme 1. Reaction of 1-(cyanomethyl)pyridinium chloride **1** with salicylaldehyde derivatives **2**.

Acknowledgments
We gratefully acknowledge the financial support from Fundação para a Ciência e a Tecnologia and a Ph.D. grant awarded to Marta Costa (SFRH/BD/31531/2006).

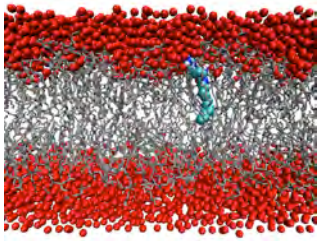
Chemical skin penetration enhancers: interaction with lipid membranes

João A. S. Almeida | Alberto A. C. C. Pais

Chemistry Department, University of Coimbra, Portugal

jasalmeida@qui.uc.pt

Transdermal drug delivery has been referred as one of the most promising routes for drug administration. Among other features, the penetration of drugs through the skin avoids the first-pass metabolism in the gastrointestinal tract and liver, provides a constant drug level in the blood and allows to easily interrupt drug input [1]. However, despite all the advantages of drug delivery through the skin over other common routes of administration, the structure [2] and the actual barrier function of the skin limit transdermal bioavailability. To overcome this difficult, some chemical compounds with ability to modify the percutaneous absorption, the so-called skin penetration enhancers, have been proposed [3].



In this work, several classes of potential skin penetration enhancers are analyzed by Molecular Dynamics (MD) simulation and their effect upon lipid membranes assessed. The interaction behavior of such molecules with a DPPC bilayer (see snapshot of Figure 1) is fully described and analyzed against experimental data. MD results further suggest new predictors for modeling the enhancing effect on skin permeation [4].

Fig. 1. MD snapshot illustrating the interaction of a skin penetration enhancer with a fully hydrated DPPC bilayer.

Acknowledgments

J. A. S. A. gratefully acknowledges PhD grant SFRH/BD/31064/2006, Fundação para a Ciência e Tecnologia, Portugal. The authors also thank the generous allocation of computational time in the Milipeia cluster, LCA, University of Coimbra, Portugal.

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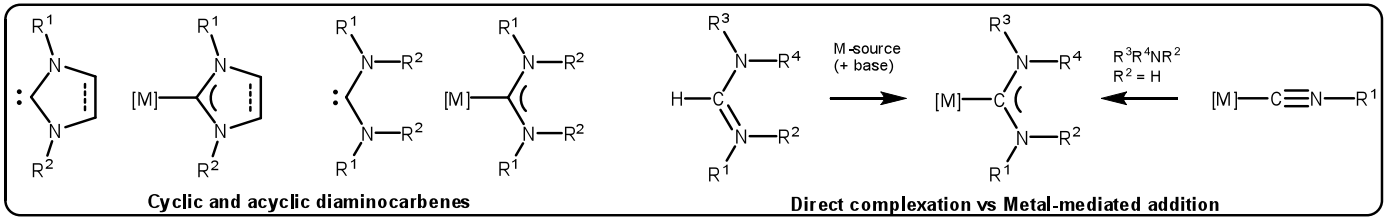
Through the history of the carbene complexes: from 1915 to our days

Konstantin V. Luzyanin [1,2] | Armando J.L. Pombeiro [1] | Vadim Yu. Kukushkin [2]

[1] Centro de Química Estrutural, Instituto Superior Técnico, TU Lisbon, 1049–001 Lisbon, Portugal Department of Chemistry
[2] St. Petersburg State University, 198504 Stary Petergof, Russian Federation

kluzyanin@ist.utl.pt

Heteroatom-stabilized carbene complexes (Scheme), in particular, those containing cyclic diaminocacarbene ligands (e.g. NHCs), have acquired a high importance in modern organometallic chemistry and catalysis [1]. The pioneering reactions leading to these compounds were performed by a world-known Russian chemist, L. A. Chugaev in early 1915 (*ca*. 50 years before Fischers works!). Two general main routes to such complexes include (*i*) the direct complexation of pre-prepared free carbenes (or typically generated *in situ* from their precursors and a base) to a metal center, and (*ii*) a metal-mediated nucleophilic addition or a dipolar cycloaddition to isonitriles.
This report provides a brief passage through the history of the organometallic chemistry of carbenes, including a comprehensive analysis of the recent developments in the field [2,3].



Acknowledgments
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Luminescent polyoxometalates encapsulated in silica nanoparticles

C. M. Granadeiro [1] | R. A. Sá Ferreira [2] | P. C. R. Soares-Santos [1] | L. D. Carlos [2] | T. Trindade [2] | H. I. S. Nogueira [1]

[1] Department of Chemistry, CICECO, University of Aveiro,3810-193 Aveiro
[2] Department of Physics, CICECO, University of Aveiro,3810-193 Aveiro

carlos.granadeiro@ua.pt

The encapsulation of polyoxometalates (POMs) in silica nanoparticles is a useful technique to increase the stability of the POM and to provide a water dispersible and non-toxic material, suitable for biological applications. The POMs used in this work are decatungstolanthanoates of the $[LnW_{10}O_{36}]^{9-}$ type (Ln(III) = Eu, Tb and Gd). The POM encapsulation was performed through a reverse microemulsion method for the hydrolysis of tetraethoxysilane (TEOS). Organic-inorganic hybrid materials based on the same type of POMs and 3-hydroxypicolinic acid [1] were prepared and encapsulated in silica by the same method. The POM/silica nanocomposites obtained are uniform spheres composed by a POM core and a silica shell (Fig. 1) with approximately 35 nm in diameter. The photoluminescence properties of the POM with and without the encapsulation in the nanosilica were evaluated and compared. The effect of the organic ligand on the luminescence [2] of the lanthanide inside the silica shell was also addressed.

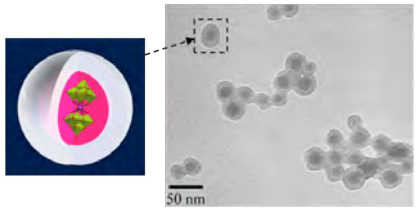

Fig. 1. Lanthanopolyoxotungstate/silica nanocomposites: TEM image and schematic representation of the obtained core-shell structure.

Acknowledgments
The authors would like to thank FCT for funding under the PTDC program and FEDER (PTDC/QUI/67712/2006), and for post graduation grants to CMG (SFRH/BD/30137/2006) and PCRSS (SFRH/BPD/14954/2004).

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Ruthenium and palladium dinuclear OPE and OTE rods for nanoelectronic applications

João Figueira [1] | José Carlos Mesquita [1] | Kari Rissanen [2] | João Rodrigues [1]

[1] Centro de Química da Madeira, LQCMM/MMRG, Universidade da Madeira, Campus da Penteada, 9000-390 Funchal, PORTUGAL
[2] Nanoscience Center, Department of Chemistry, University of Jyväskyla, P.O. Box 35, 40014 JYU, FINLAND

Highly conjugated molecules have been of great interest for their potential applications in fields such as nanoelectronics [1] or optoelectronics [2]. As such, organometallic rods with robust and redox capable metal centers can offer excellent properties and attractive advantages over their organic counterparts as well as the currently available wires by increasing energy throughput and decreasing production costs. These organic bridges, such as OPE (oligo(phenylene ethynelene)s) and OTE (oligo(thiophenylene ethynelene)s) derivatives [3] can be used to tune the electronic communication between metal centers this systems.
Using these OPEs (1,4-diethynyl-2,5-dialcoxybenzene and 4,4'-(2,5-dialcoxy-1,4-phenylene)bis(ethyne-2,1-diyl)bis(ethynyl-benzene) derivatives) and OTEs (2,5-bis(4-ethynylphenyl)thiophene derivatives) bridges, two families of rods were prepared by coordination to a Ruthenium moiety (by modified Dixneuf method [4]) and to a Palladium moiety (by typical Cu(I) catalysis). All the compounds were characterized by NMR, MS, FTIR, UV-vis and CV. The results will be discussed in terms of possible applications as molecular wires.

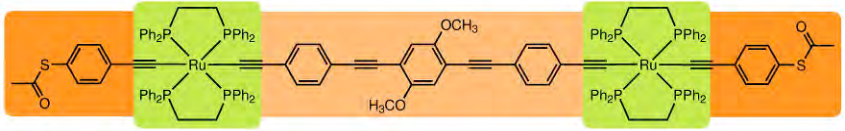

Fig. 1. Example of a dinuclear Ru OPE organometallic Wire.

Acknowledgments
JF wishes to thank the FCT for the Ph.D. grant (SFRH/BD/29325/2006). We gratefully acknowledge the NMR and MS Portuguese Networks (REDE/1517/RMN/2005, REDE/1508/REM/2005). The support from CS Madeira is also gratefully acknowledged..

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Bischlorocopper(II) modified mesoporous materials: synthesis, characterization and catalytic oxidation of ethylbenzene

Sofia M. Bruno | Diogo Queirós | Sandra Gago | Anabela A. Valente | Isabel S. Gonçalves | Martyn Pillinger

CICECO, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

sbruno@ua.pt

There is considerable interest in finding reusable solid catalysts for the selective oxidation of ethylbenzene to acetophenone, especially since the latter product is an important intermediate for perfume, drugs and pharmaceuticals. Some of us recently described the application of a novel type of bischlorocopper(II) catalyst immobilized in a pillared layered double hydroxide containing 2,2'-bipyridine-5,5'-dicarboxylate anions (LDH-BDC/Cu) in the liquid-phase oxidation of ethylbenzene using H_2O_2 or *tert*-butyl hydroperoxide (*t*- BuOOH) at room temperature. The oxidation reactions are generally faster using the homogeneous catalyst, [Cu(bipy)Cl_2] (bipy = 2,2'- bipyridine), but LDH-BDC/Cu was more efficient in terms of the "productive" consumption of the oxidant, albeit the catalytic reaction was slower [1].
In the present work, we have studied the immobilization of $CuCl_2$ in MCM-41-type mesoporous silica functionalized with a pyridylethanimine ligand, MCM-41-L1 {L1 = N-(n-propyl)1-(2-pyridyl)ethanimine(ethoxysilane)} (**1**), originating MCM-41-L1.$CuCl_2$ (**2**). The postsynthesis trimethylsilylation of **1** was also carried out to remove the residual surface silanol groups, giving silylated MCM- 41-L1 (**3**) and, after the immobilization of $CuCl_2$, silylated MCM-41-L1.$CuCl_2$ (**4**). The model complex $CuCl_2$L2 {L2 = N-(n-propyl)1- (2-pyridyl) ethanimine} was also synthesized. The supported mesoporous materials were characterized by elemental and thermogravimetric analyses, X-ray powder diffraction, $^{13}C/^{29}Si$ (CP) MAS NMR and vibrational spectroscopies. The catalytic performance of these materials was studied in the oxidation of ethylbenzene using aqueous *t*-BuOOH (70%) as the oxidant, at room temperature.

Acknowledgments
We are grateful to the FCT, POCI 2010, OE and FEDER (project PTDC/QUI/71198/2006).S. B. and S. G. are grateful for grants.

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Behavior of ruthenium amine complexes and their interactions with DNA purines within nanoporous silica matrices

Luís M. F. Lopes | Ana R. Garcia | P. Brogueira | Laura M. Ilharco

CQFM - Centro de Química-Física Molecular and IN - Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal

luis.f.lopes@ist.utl.pt

Ruthenium coordination complexes have been receiving great attention due to their promising performance in the medical field, in particular as alternative to platinum tumor-inhibiting agents. In an attempt to elucidate their biochemical mechanisms and understand the role of the metal centre in nucleic acids metabolism, several studies on the interactions of these complexes with DNA and their constituents have been conducted in solution [1]. Since the influence that a restricted environment has over the structure and reactivity of these molecules has been overlooked, in the present work we analyze the interactions between two ruthenium ammine complexes ([Ru$(NH_3)_6]Cl_2$ and $[Ru(NH_3)_6]Cl_3$) and DNA purines (adenine (Ade) and guanine (Gua)), in the confined environment created by nanostructured sol-gel silica matrices.Complementary results by diffuse reflectance UV-Vis and infrared spectroscopies showed that the sol- gel medium is not an inert support, and the matrix synthesis procedure, in particular the temperature, may be used to control the degree of decomposition of the Ru-complexes. This may be an alternative approach to prepare Ru-based supported catalysts (Fig. 1). When coencapsulation is carried out at 60 ºC, specific H bonding interactions are established between the amine group of Ade and the ammine groups of the complex or the hydroxo group of an early decomposition product (Fig. 2), thus inhibiting further decomposition of the Ru(II) and Ru(III) complexes. In contrast, Gua establishes preferential H bonds with the matrix (mainly due to the carbonyl group), leading to higher yields in the final oxidation products of the Ru complexes. Direct covalent bonding of either purine to the metal was not observed.

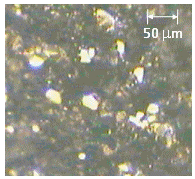

Fig. 1: Optical microscopy image of the sample dopped with Ru(II) complex, showing the metal clusters formed.

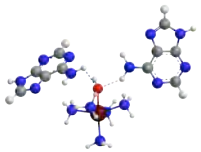

Fig. 2: Schematic representation of possible hydrogen bonds between Ade and the intermediate $[Ru(NH_3)_5OH]^{2+}$.

Acknowledgments
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Synthesis and coordination chemistry of the sterically hindered scorpionate ligand Li[Tpms^{Ph}] towards Ni^{II}, Zn^{II} and Cu^{II} metal centres

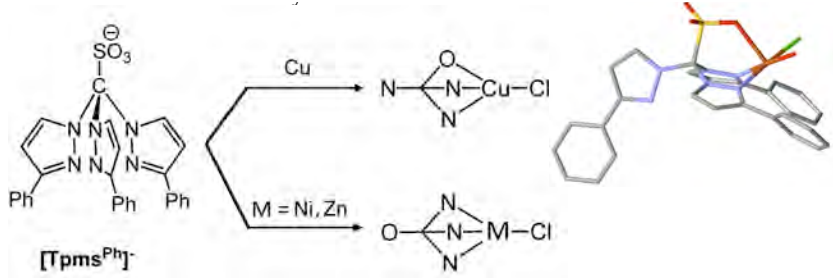
Bruno G.M. Rocha | Riccardo Wanke | M. Fátima C. Guedes da Silva | Luísa M.D.R.S. Martins | Armando J.L. Pombeiro

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

bruno_goncalo@hotmail.com

Originally introduced by Trofimenko in 1967 [1], the tris(pyrazolyl)borate (Tp) ligands and their metal complexes became one of the most widely studied class of compounds in inorganic, organometallic, and bioinorganic chemistries. Recently, we have initiated the study of the coordination chemistry of their carbon analogues, the tris(pyrazolyl)methane (Tpm) ligands, as well as the synthesis of new Tpm derivatives. For instance, we found that pyrazolyl rings containing bulky substituents at the 3-position can tune the coordination behaviour towards different metal centres and that the carbon functionalised sulfonate derivative confers higher stability and hydrosolubility to the corresponding complexes and exhibits a coordination flexibility [2].

In this work the synthesis of the sterically hindered and water soluble tris(3-phenylpyrazolyl)methane sulfonate (Tpms^{Ph})$^-$ has been optimized and its reactivity towards Ni^{II}, Zn^{II} and Cu^{II} led to the corresponding complexes of general formula [M(Tpms^{Ph})Cl] (M = Zn, Ni or Cu). All the complexes have been characterised by IR, ^{1}H and ^{13}C-NMR, MS and E.A. X-ray structure of [Cu(Tpms^{Ph})Cl]H_2O shows that the scorpionate coordinates in a N_2O mode involving the sulfonate moiety in the coordination to the copper centre.



Acknowledgments
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Synthesis and film formation of hybrid silica-polymer nanoparticles for imaging and advanced coatings

Tânia Ribeiro | Carlos Baleizão | José Paulo S. Farinha

Centro de Química-Física Molecular, Instituto Superior Técnico, Avenida Rovisco Pais, 1049-001 Lisboa, Portugall

taniaraquel19@gmail.com

We synthesized core-shell nanoparticles with a silica fluorescent core and a butyl methacrylate shell for application in imaging and high performance coating materials. Silica core particles with diameters between 270 and 440 nm and low polydispersity were labeled with a perylenediimide derivate with two terminal alkoxysilyl groups. Pure silica nanoparticles with equivalent diameters were also synthesized and surface modified with a second perylenediimide derivative. The photophysical properties of both sets of nanoparticles were studied to characterize the dependence of emission on the polarity of the environment and dye aggregation [1]. The fluorescent silica nanoparticles were surface modified with 3-(trimethoxysilyl)propyl methacrylate and used as seeds in the emulsion polymerization of a butyl methacrylate shell labeled with either a phenanthrene derivate (PheBMA) or a benzophenone derivate (NBen).

Fluorescence correlation spectroscopy (FCS) and elemental analysis was used to characterize the diameter of the core-shell nanoparticles. Films cast from water dispersions of clean core-shell nanoparticles are flexible, transparent, and exhibit fluorescence under appropriate excitation. The formation and proprieties of the films were studied by laser scanning confocal microscopy and Förster resonance energy transfer (FRET) from PheBMA to NBen to follow the interdiffusion between the particle polymer shells during film formation.

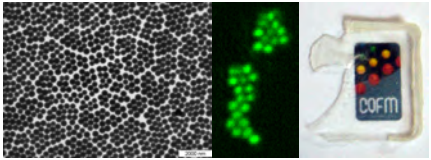

Fig. 1. TEM and confocal images of the hybrid nanoparticles, with a highly transparent hybrid film casted from the nanoparticles.

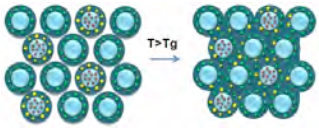

Fig. 2. Cartoon of film formation by deformation and interdiffusion of the polymer shell.

Acknowledgments

We acknowledged Prof. Carlos Afonso for the preparation of PheBMA, Leila Moura and Prof. Carlos Afonso for the preparation of NBen and Dr. Aleksander Fedorov for the fluorescence resolved in time measurements.

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Creating bases for future investigation: the e-lab generation

Sérgio C. Leal | João P. Leal | Horácio Fernandes

Departamento de Química e Bioquímica, FCUL, 1749-016 Lisboa, Portugal

sergioleal20@gmail.com

Nowadays students show a lack of motivation when learning science (for instance Physics and Chemistry) that is accentuated through their academic path. This situation suggests the predominance of a classical approach and a missing contextualization of scientific concepts [1,2]. Our work is focused in the development of an e-learning platform called e-lab. This platform is actually a virtual laboratory and thus has a great potential, as it may be used by students and teachers to collect real data of several experiments, anywhere and anytime, using a simple computer with an Internet connection, a player like VLC media player or QuickTime player and Java Web Start.
e-lab is a tool which aims to promote e-learning as a normal part of teaching over time, complementing traditional teaching methods [1,2]. It intends to support students in science learning, stimulating a scientific culture that will probably have an important impact not only in their cognitive skills but also in their future as science professionals. This motivational effect was already seen in preliminary studies performed with students from primary, secondary and higher education. With the help of e-lab we want to bring up the students' investigation bug.

Acknowledgments
S. C. Leal want to thanks the Portuguese Foundation for Science and Technology a PhD grant (SFRH/BD/44889/2008) and Instituto Superior Técnico, the Portuguese University Institute that lodge the e-lab platform.

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Olive stone as a renewable source of biopolyols

Marina Matos | Filomena Barreiro | Alessandro Gandini

CICECO and Chemistry Department, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal
LSRE, Bragança Polytechnic Institute, Campus de Santa Apolónia Ap. 1134, 5301-857 Bragança, Portugall

marina.matos@ua.pt

The development of polyols from abundant and renewable biomass resources constitute attractive choices for polyurethane and other industrial sectors where green chemistry and sustainable processes are in focus. By means of oxypropylation, the solid biomass can be converted into liquid polyols thanks to the introduction of oligo(propylene oxide) grafts [1].
Chitosan, chitin, different types of lignins, cork and more complex structures like sugar beet pulp are among the documented examples. The promising results obtained with the ensuing polyols and their subsequent incorporation into polyurethane formulations corroborate the interest to exploit these biomass resources [2-5].
The purpose of this communication was to establish the feasibility of converting the olive stone (OS) residue by means of both total and partial oxypropylation. In the first case, the oxypropylation reaction conditions are chosen in order to promote extensive grafting, and in the second case, partial oxypropylation would limit the reaction to the outer shell in view of the preparation of all-"olive stone" composites. This approach involves a straightforward transformation of the OS particles outer layer, giving rise to a thermoplastic matrix around its unreacted reinforcing inner structure, as already applied to cellulose and starch [1]. The main goal of this communication was achieved, in the attempt that was possible to convert OS by oxypropylation, partial and total, proving that this biomass residue has great potential for the production of polyols. The characterization of these new materials involved FTIR and NMR spectroscopy, as well as morphological observation through SEM. The results of the initial experiments will be presented and discussed.

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Evaluation of thin mercury film rotating disc electrode to perform Absence of Gradients and Nernstian Equilibrium Stripping (AGNES) measurements

Luciana S. Rocha | E. Companys | J. Galceran | H. M. Carapuça | J. P. Pinheiro

Department of Chemistry/CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

lrocha@ua.pt

This work is dedicated to the memory of Professor Helena Maria Carapuça.

The free metal determination with Absence of Gradients and Nernstian Equilibrium Stripping (AGNES) technique [1,2] using a thin mercury film on a rotating disk electrode (TMF-RDE) has been implemented. The thickness of the mercury film and several AGNES parameters, have been optimized. A nominal 16 nm film is chosen due to the higher faradaic current relative to the value of the capacitive current. The selected time for the AGNES measurement in the second stage (t_2) is within 1-3 ms. A specific mathematical treatment is developed in order to subtract a corrected blank taking into account the degradation of the thin film (presumably, falling down of drops).
Lower LOD, in comparison with the conventional dropping mercury electrode or the Ir-Hg microelectrode, can be attained with this electrode for comparable times. Special care has to be taken to avoid anomalous stripping currents for higher metal concentrations which lead to a loss of linearity in the calibration plot. Good results have also been obtained with TMF-RDE when performing speciation determinations. The free metal concentration, and, thus, the conditional stability constants, determined with AGNES for the two systems considered (the complexation of Pb(II) with monodisperse carboxylated latex nanospheres and the complexation of Pb(II) with iminodiacetic acid (IDA), are in reasonable agreement with values reported in the literature [3].

Acknowledgments
Thanks are due to University of Aveiro and Fundacão para a Ciência e a Tecnologia (FCT) project POCI/AMB/55939/2004. Luciana Rocha acknowledges FCT, for a PhD grant. Financial support by the Spanish Ministry of Education and Science (Projects CTQ2006-14385) and from the "Comissionat per a Universitats i Recerca del Departament d'Innovació, Universitats i Empresa de la Generalitat de Catalunya" is acknowledged.

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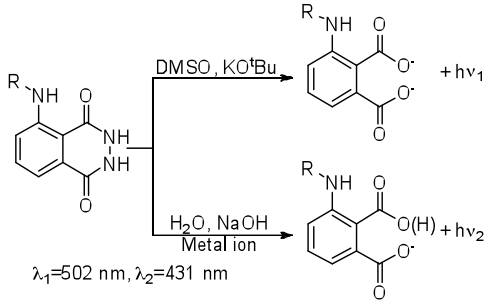
Synthesis and properties of new luminol derivatives. Study of the oxidation mechanism

Filipe M. C. Menezes | Carlos A. M. Afonso | Carlos M. Baleizão | Mário N. Berberan-Santos | Luís F. C. Veiros

CQFM – Centro Química-Física Molecular and IN – Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, Complexo I, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

filipemmenezes@gmail.com



Luminol (hydrazide, R=H) is a well-known chemiluminescent compound, with a strong blue emission. Owing to its visible emission, chemiluminescence mechanism and high quantum yield it has been used in several applications like biosensors, sensitive metal ion detection and *in vivo* analytical chemistry [1].

Several luminol derivatives have been obtained in order to enhance the chemiluminescence quantum yield and to change the emission wavelength [2]. It is known that the chemiluminescence quantum yield follows an Hammett relation but the rationale for the emission wavelength dependence is not so simple.

In this work, we report the synthesis and properties of some new derivatives of luminol in our search for green chemiluminescence. We also present DFT and *ab initio* studies of the oxidation reaction, whose mechanism is still incompletely understood [3].

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Assessment of the energetic effect of the oxygen by sulfur substitution in hetero(poly)cyclic compounds

Vera L. S. Freitas [1] | José R. B. Gomes [2] | Maria das Dores M. C. Ribeiro da Silva [1]

[1] CIQ - Centro de Investigação em Química, Faculty of Science - University of Oporto, Rua do Campo Alegre 687, P-4169-007 Porto, Portugal
[2] CICECO, Departamento de Química, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

vera.freitas@fc.up.pt

Oxygen and sulfur are elements of the same group of the periodic table, with similar outer shell configurations; as a result, the structures of many organic derivatives containing oxygen are analogues of the correspondent organosulfur compounds. The assessment and understanding of the energetic effects introduced when these two atoms are replaced one by another in heteropolycyclic compounds is the aim of this work. For these purposes, we have considered the standard molar enthalpies of formation in the gaseous phase, at *T*=298.15 K, for the oxygen and sulfur compounds determined from experimental measurements in the Thermochemical laboratory and complemented with additional computational studies. Other objectives include also the comparison and interpretation of the stability of the compounds in terms of their chemical vicinity and molecular structure. The heteropolycyclic compounds considered are cyclic compounds with two benzenic rings "fused" to a hexagonal or pentagonal central ring containing oxygen or sulfur heteroatoms. Heteromonocyclic compounds with similar structures were also considered in this work for comparison purposes.
Experimentally, the standard molar enthalpies of formation in the gaseous phase were derived from the standard molar enthalpies of formation in the condensed phase and from the standard molar enthalpies of phase transition (condensed to gaseous phase), both at *T*=298.15 K, using the combustion calorimetry and Calvet microcalorimetry techniques, respectively. In the computational studies, calculations were performed with the composite G3(MP2)//B3LYP approach, based on the Gaussian-*N* theory, which enables the optimization of the structures of the compounds and computation of their vibrational frequencies, of their energies at *T*=0 K and absolute enthalpies at *T*=298.15 K. The later were combined with the calculated absolute enthalpies of other compounds appearing in selected working reactions, and, subsequently, were used to calculate the gas-phase standard molar enthalpies of formation of the oxygen or sulfur containing compounds at *T*=298.15 K.
Herewith, the experimental and computational enthalpies of formation in the gaseous phase for the heteropolycyclic compounds will be compared and discussed in terms of the S by O substitution.

Acknowledgments
V.L.S.F. thanks FCT (Portugal) and FEDER for the award of a Ph.D. grant (SFRH/BD/41672/2007).

A photoacid for the longest reversible pH jump

Rui M.D. Nunes | Marta Pineiro | Luis G. Arnaut

Chemistry Department, University of Coimbra, 3000 Coimbra, Portugall

rnunes@qui.uc.pt

The ability to change the pH of an aqueous solution within the laser pulse duration and the usage of the excess protons to study acid-base equilibrium or to induce catalytic reactions in the irradiated volume opens new ways of time and space control of several processes. Existing reversible photoacids allow the acidification of the solution but the duration of the pH jump is quite limited [1], restricting the applicability. Using the most recent Interacting State Model framework, we envisaged a new class of molecules that possess the characteristics of reversible photoacids, like aromatic alcohols, and are capable of extending the pH jump duration into the hundreds of milliseconds time scale, through a non adiabatic intramolecular proton transfer from an active carbon acid. A persistent reversible photoacid was synthesise and, the ground and excited state acid-base equilibrium, the dynamics of the adiabatic proton transfer from the photoacid excited state to the solvent and the nonadiabatic intramolecular proton transfer from the carbon acid to the naphthol anion were determined [2]. The mechanism of the intramolecular nonadiabatic proton transfer was established with deuteration experiments. This photoacid was used in the study of a model system, allowing the evaluation of the protonation and deprotonation rate constants of Bromocresol Green.

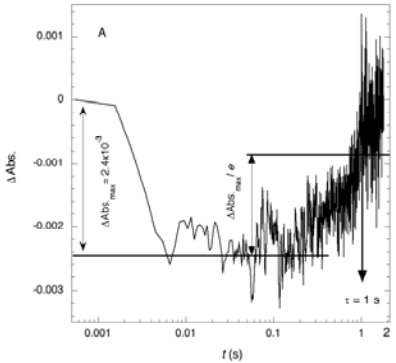

Fig. 1. Transient absorption of the anionic form of Bromocresol Green after excitation of the photoacid.

Acknowledgments
This work was supported by FCT and FEDER (project no. PTDC/QUI/70637/2006). RMDN thanks FCT for the grant SFRH/BD/24005/2005.

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Prémio Químicos Jovens / Gradiva 2010

Grupo de Químicos Jovens

Sociedade Portuguesa de Química, Av. da República 45 - 3oEsq, 1050-187 Lisboa, Portugal

gqj@spq.pt

Caros Jovens Químicos (JQ),
É com muito gosto que o Grupo de Químicos Jovens (GQJ) apresenta a primeira edição do *Prémio Químicos Jovens / Portuguese Young Chemists Award (PYCA)* que este ano conta com o inestimável patrocínio da Gradiva. Num tempo em que a produção e divulgação de resultados científicos centra as atenções de todos os cientistas nacionais, o PYCA tem como objectivo consciencializar os JQ para a necessidade de divulgar o seu trabalho junto de todos aqueles que não lêem artigos da *Nature ao pequeno-almoço*. Divulgar ciência junto da sociedade é um imperativo para quem a produz, mas descodificar os fundamentos, resultados e impacto do trabalho realizado no laboratório, sem recorrer à gíria académica/tecnológica constituí um verdadeiro esforço para a maioria dos cientistas. Assim, o PYCA reflecte um desafio lançado à comunidade de JQ para que partilhe ciência com a sociedade, no formato de um artigo de divulgação científica, tendo por base o trabalho desenvolvido no seu doutoramento.
Neste primeiro ano responderam a este repto 15 recém-doutorados, tendo as candidaturas sido avaliadas pelo Júri constituído por:

- Professor Jorge Morgado, Boletim da Sociedade Portuguesa de Química (SPQ);
- Dr. Guilherme Valente, Gradiva; - Doutora Mónica Bettencourt Dias, Instituto Gulbenkian de Ciência;
- Professor Eurico Cabrita, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa.

O candidato vencedor, para além de ver o seu artigo publicado no Boletim da SPQ, receberá a oferta de um ano de quotas da SPQ e 1000 Euros. O candidato distinguido irá hoje apresentar uma comunicação oral resultante do artigo submetido ao prémio.
O GQJ felicita o vencedor fazendo votos que o PYCA se torne um prémio motivante e incontornável para a comunidade de JQ nacionais.

Carlos Baleizão, Frederico Ferreira, Pedro Gois

posters

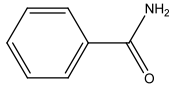
Phasic study of benzamide, *N*-methylbenzamide and *N,N*-dimethylbenzamide

Ana R. R. P. Almeida | Manuel J. S. Monte

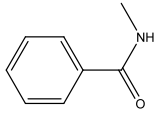
Centro de Investigação em Química, CIQ – UP, Department of Chemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal

ana.figueira@fc.up.pt

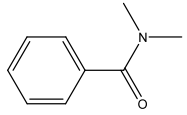
Vapour pressures of crystalline and liquid phases of benzamide, *N*-methylbenzamide and *N,N*-dimethylbenzamide were measured in the temperature range (345 to 438) K, (323 to 388) K and (297 to 362) K, respectively, using a static method [1]. The vapour pressures of the crystalline phase of benzamide were also measured in the pressure range (0.11 to 1.2) Pa using the Knudsen effusion method. From the experimental results, the standard molar Gibbs energies and enthalpies of sublimation and of vaporization, at T = 298.15 K, and triple points p,T coordinates of the three compounds were derived. The temperatures and molar enthalpies of fusion were also determined using *d.s.c.* and were compared with those calculated indirectly from the vapour pressure measurements. The phase diagrams of the studied compounds will be presented.



Benzamide



N-methylbenzamide



N,*N*-dimethylbenzamide

Acknowledgments
Thanks are due to Fundação para a Ciência e Tecnologia (FCT) Lisbon, Portugal, for financial support given to Centro de Investigação em Química of University of Porto. A.R.R.P.A, thanks F.C.T. and the European Social Fund (ESF) under the Community Support Framework (CSF) for the award of a PhD Research Grant (SFRH/BD/39210/2007).

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Cyclopentadienyl functionalized N-heterocyclic carbenes: synthesis, coordination and catalytic applications

André Pontes da Costa [1] | Eduardo Peris [2,*] | Beatriz Royo [1,*]

[1] Instituto de Tecnología Química e Biológica, Universidade Nova de Lisboa, Av. da República, EAN, 2780-157 Oeiras, Portugal
[2] Departamento de Química Inorgánica y Orgánica, Universitat Jaume I, Avenida Vicente Sos Baynat s/n. 12071 Castellón, Spain

acosta@itqb.unl.pt

The easy access to N-heterocyclic carbenes (NHCs) and their potential application in a large number of homogeneously-catalyzed processes, has led to a rapid development in the design of an almost unlimited number of NHC-containing architectures [1].
We envisioned that the functionalization of NHCs with cyclopentadienyl rings might have interesting consequences favouring stability, rigidity and catalytic activity in their metal complexes [2].
Herein, we report the coordination of cyclopentadienyl functionalized NHCs to Iridum, Rhodium and Ruthenium, along with catalytic activity of the resulting complexes in C-H activation reactions. Recent results on the preparation of chiral-at-metal cyclopentadienyl functionalized NHCs of Ruthenium will also be presented [3].

Acknowledgments
We gratefully acknowledge financial support from FCT of Portugal, POCI 2010, and FEDER through project PTDC/QUI/64458/2006. From the Spanish side we gratefully acknowledge financial support from the MEC of Spain (CTQ2007-31175) and Bancaixa (P1.1B2007-04). A. Pontes da Costa thanks the FCT for a grant (SFRH/BD/28490/2006).

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Preparation of highly bi-phobic cellulose fibers by a straightforward gas-solid reaction

Ana Gisela Cunha | Carmen Freire | Armando Silvestre | Carlos Pascoal Neto | Alessandro Gandini | M. Naceur Belgacem | Didier Chaussy | Davide Beneventi

CICECO/Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

gcunha@ua.pt

Cellulose is the most abundant biopolymer on earth and a source of many industrial derivatives and products [1]. Highly hydrophobic cellulose-based materials have several potential applications in such important areas as the papermaking, textile and packaging industries [2]. Furthermore, this strategy is also inspired and motivated by the exploitation of environmental friendly renewable resources, as opposed to fossil-based counterparts [3]. It appeared essential to us to seek simpler and greener methods to convert such a highly hydrophilic substrate into a correspondingly hydrophobic homologue, compared with previously published strategies [3].
This work describes a very simple, rapid, and efficient approach to the hydrophobization and lipophobization of cellulose fibers through their reaction with gaseous trichloromethylsilane (TCMS). The characterization of the modified surface involved FTIR-ATR and solid-state ^{29}Si NMR spectroscopy, scanning electron microscopy (SEM) and contact angles measurements with different liquids. The modification generated an inorganic coating around the fibers, associated with the construction of a three-dimensional network of Si-O-Si bridges partly bound to the polysaccharide macromolecules. This coating conferred both high hydrophobicity and lipophobicity to the samples, even when the treatments implied modest TCMS quantities and reaction times as short as 30 seconds. The details of the preparation and the characterization of these cellulose-TCMS derivatives will be discussed.

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Design of superoxide dismutase mimics

Ana Fragoso | Patrick Groves | Olga Iranzo

Instituto de Tecnologia Química e Biológica- UNL –Avenida da República, Estação Agronómica Nacional, 2780-157 Oeiras Portugal

afpf26@itqb.unl.pt

Superoxide Dismutases (SOD) are metalloenzymes that catalyze the dismutation of superoxide radicals ($O_2^{\cdot-}$) to H_2O_2 and O_2 [1].Thus, they are critical for protecting cells against these toxic radicals often associated with many age-related degenerative diseases. They have also been known to induce apoptosis of cells [2].

Our group is particularly interested on the design, synthesis and characterization of synthetic peptides capable of binding manganese and/or iron and act as a SOD mimics. These kind of systems have been drawing attention not only because their potential applications as therapeutic agents but also because they can give us a better understanding of how the native enzyme controls the metal ion properties to achieve a specific functionality.

Peptidic scaffolds were design to contain the amino acids of the metal binding site from the native SOD (three Histidines and one Aspartic Acid, Fig. 1 [3]). They were obtained either by solid phase peptide synthesis or by *E. coli* expression. The characterization of these synthetic peptides and their coordination to iron and manganese are now being studied using different spectroscopic techniques (UV-Vis, CD and NMR). These results will be presented along with their SOD-like activity.

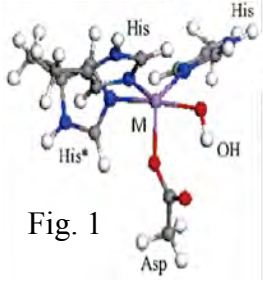

Fig. 1

Acknowledgments

The authors would like to thank the Fundação para a Ciência e a Tecnologia for a Ciência 2007 Grant to OI, the European Commission for a Marie Curie IRG fellowship to OI and to Dr. Malgorzata Palczewska (Molecular Interactions and NMR Laboratory, ITQB) for the help provided in E. coli expression.

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Comparative study of the composition of pears dried under different methods

Andreia Loureiro | Raquel Guiné | Maria João Lima | Dulcineia Ferreira

Escola Superior Agrária de Viseu / CI&DETS, Instituto Politécnico de Viseu, Quinta da Alagoa, Estrada de Nelas, 3500-606 Viseu

raquelguine@esav.ipv.pt

Drying of agricultural products under direct sunlight is the traditional way of preserving many fruits and vegetables. The use of the sun to dry foods has the advantage of being cheap. However there are some disadvantages, such as intensive labor and slowness of the process. Moreover, several factors make solar drying less attractive, such as: climatic conditions, product pollution from dust or from animal contamination, and other types of infestation and microbial or mould contamination in humid environments [1].

In Portugal, pears of the variety S. Bartolomeu (*Pyrus communis L.*) have been used to produce a traditional product named "*pêra passa de Viseu*". These pears are dried at direct open air sun exposure, following a multi-step procedure. However, this procedure does not comply with modern quality standards, and therefore in the last years some investigation around this product and the production method has been carried out to better understand it and establish alternative production techniques [2,3]. Among these alternatives, a solar stove with forced convection and a solar stove with natural convection were developed.

In the present work pears of the variety S. Bartolomeu were dried following the traditional method at direct solar exposure and also inside the two stoves developed. The chemical properties were analyzed and quantified in the pears dried by the 3 systems, having in mind to find out which system allows the obtaining of a product more similar to the traditional pears.

From the results obtained is possible to see that the drying carried out inside the solar stoves dos not produce fruits much different than those dried by the traditional method.

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Direct polycondensation of aromatic hydroxy acid simulating lignosulphonate fragments

A. P. Marques | A. Gandini

CICECO/Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

apsm@ua.pt

The main goal of the present investigation is to contribute to the development of the area of macromolecular materials derived from renewable resources [1]. Lignin is the second most abundant natural polymer and the major biomass constituent based on aromatic units. Lignin is available essentially as a by-product of the paper industry, which involves the chemical separation of cellulosic fibres from wood or other plant materials. Lignosulfonates are inexpensive and extremely versatile products of acid sulphite pulping. Lignosulphonates have found applications in numerous industrial areas because of their dispersing, binding and emulsifying properties. Recent work in our laboratory showed that lignosulphonates can be depolymerised, by oxidation with molecular oxygen in an alkaline medium, into various aromatic units which could be viable monomeric precursors for novel polymers from renewable resources. The present communication deals with the polymerization of vanillic acid and syringic acid as model monomers simulating the lignin fragments mentioned above. The polymerization of aromatic hydroxy acid is a relevant issue since polyesters are extremely important as industrial materials for fibres and films[2].

The homopolymers were prepared by direct polycondensation in pyridine using *p*-toluenesulfonyl chloride and N,N-dimethylformamide as condensing agents. The structure of the ensuing reprecipitated materials was confirmed by FTIR spectroscopy. Both homopolymers were insoluble in common organic solvents and partially soluble in 1,1,1,3,3,3-hexafluoro-2-propanol. Therefore, further structural characterization was carried out using solid state ^{13}C NMR spectroscopy, but DP could not be determined by conventional methods such as GPC. The methoxy substitution in the benzene ring decreased the thermal stability determined by TGA in inert atmosphere. The two homopolymers did not show any distinct transition in their DSC thermograms because of their high cohesive energy, which induces thermal decomposition of their crystalline structure before they reach their melting temperature.

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Luminescent epitaxial heterostructures

Angela S. Pereira | Tito Trindade | Sérgio Pereira

CICECO, University of Aveiro, 3810-193 Aveiro

aspereira@ua.pt

Group III-nitrides are attracting growing interest as a substrate material for biosensing applications. It has recently been shown that they are nontoxic, exhibit long-term chemical stability under physiological conditions, and can serve as a substrate material for living cells [1]. The application of these devices for electronic detection of specific biomolecular processes is a promising approach for novel biosensors based on molecular recognition, such as specific antibody detection or label-free detection of DNA hybridization. For this purpose, the covalent attachment of specific molecules with controlled structural order and composition on group III-nitride devices is a basic requirement.

Covalent derivitazation of GaN/InGaN thin film surfaces with organosilanes was a primary step to proceed to chemically-bonded Gold nanoparticles (Au NPs) on the thin films' surface. In this work we present a step-by-step approach of the chemical surface modification of group-III nitrides and its properties.

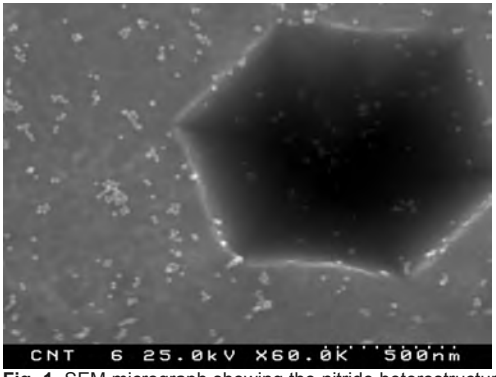

Fig. 1. SEM micrograph showing the nitride heterostructure with chemically bonded Au NPs on its surface.

Acknowledgments

ASP acknowledges Fundação para a Ciência e Tecnologia for her post-doctoral fellowship. This work was funded by FCT (PTDC/CTM/101453/2008).

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Optimization of ABS performance against UV radiation: antioxidants consumption

R.M. Santos [1] | **A. Pimenta** [2] | A.V. Machado [1] | G. Botelho [2]

[1] Departamento de Engenharia de Polímeros, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal.
[2] Departamento de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal.

ana_pimenta_020@hotmail.com

Acrylonitrile-butadiene-styrene (ABS) is widely used in technological applications due to its outstanding properties and low cost for an engineering polymer. However, it is known to present a high instability when exposed to UV radiation in the presence of oxygen, leading to degradation of the material and consequently, to properties loss [1].

Nowadays, ABS stabilization continues to be a serious problem for the manufacturers and suppliers because long-term applications are impossible without well selected additives. Light stabilizers and antioxidants are commonly added to polymeric materials in order to protect chemical structure and extend copolymer lifetime.

Stabilized samples with antioxidants were submitted to accelerated weathering during 300 h according to standard methods [2], removed periodically and characterized by several analytical techniques. The main purpose of this work is to evaluate the effect of antioxidants (Irgafos® and Irganox®) during photo-oxidative degradation to protect ABS chemical structure and physical properties.

Antioxidants consumption was evaluated by HPLC using a reversed-phase column waters Spherisorb 5.0µm ODS 2 (4,6 mm x 250 m) and a UV detector at 280 nm.

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Design, synthesis and biological evaluation of cysteine protease inhibitors

Alexandre Pinto | Maria M. M. Santos | Pedro M. P. Gois

Pharmacy Faculty – UL,iMed - Institute for Medicines and Pharmaceutical Sciences, Av. Prof. Gama Pinto 1649-003 Lisbon

amgpinto@ff.ul.pt

Cysteine proteases are proteolytic enzymes involved in the degradation of proteins. Considering their sequence homology three structurally different groups are formed: papain-like (clan CA), ICE-like (clan CD) and picornain-like (clan PA(C)) [1]. The great majority of cysteine proteases belong to the first two clans, being of particular interest for this work, parasite cysteine proteases which belong to clan CA. Cysteine proteases are implicated in several disease processes, such as inflammatory and immunological disorders [2], playing also a key role in some parasites life cycle, like falcipain from the parasite, *Plasmodium falciparum*, the causative agent of malaria [3]. *Plasmodium falciparum*, expresses four cysteine proteases from clan CA, known as falcipains, being falcipain-2 and 3 of particular interest as therapeutic targets given their importance to the parasite life cycle [3]. Several cysteine proteases inhibitors have been developed, taking in consideration the recognition sequence of peptide substrates and different warheads have been tested, like, diazo ketones. This class is very interesting since it inhibits irreversibly, cysteine proteases, by alkylation of the active site thiol group. Besides the irreversible inhibition mechanism , these compounds also present a very high specificity for cysteine proteases, although they are also able to inhibit serine proteases but in a much slower pace [4]. Bearing these facts in mind, several compounds carrying the diazo moiety were synthesized (Figure 1) [5,6], and their activity against falcipain-2 was evaluated by Prof. Philip Rosenthal in the USA.

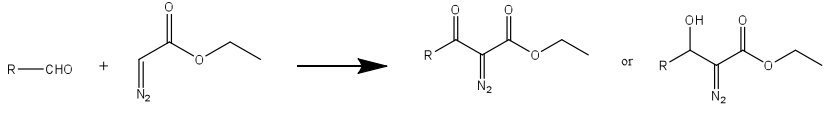

Fig. 1. Generic scheme for the synthesis of diazo moiety bearing compounds (R = alkyl, aryl, peptidyl)

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Investigating a new case of polymorphism in cyclodextrin inclusion compounds

Ana I. Ramos | José A. Fernandes | Susana S. Braga | Filipe A. Almeida Paz

CICECO, Campus Universitário de Santiago, 3810-193, Aveiro, Portugal

ana.ramos@ua.pt

A novel cyclodextrin (CD) inclusion compound was synthesized by the use of 4-phenylpyridine N-oxide (PPNO) as organic guest. βCD·PPNO was characterized by a myriad of techniques which allowed the determination of a 1:1 stoichiometry and an association constant of 164 M^{-1}. Powder X-ray diffraction indicated the attainment of two distinct crystal phases (confirmed by single-crystal X-ray diffraction) with distinct kinetics of formation: over time, the two crystal types evolved to show the same diffraction pattern. Polymorphism arises as a plausible explanation for the two initial phases [1, 2], which subsequently converge to a same, more stable, compound [3]. Kinetic studies were performed to monitor all stages of this transformation.

Acknowledgments
CICECO and FCT (PTDC/QUI/69302/2006)

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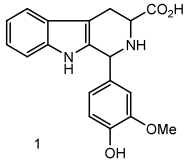
Synthesis of β-carbolines and optical studies of their sol-gel films

António M. P. Ribeiro | Ana M. F. Oliveira-Campos | Lígia M. Rodrigues | Luís F.F.F. Gonçalves | Carlos J.R. Silva

Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga

chimyster@gmail.com

Compounds of the β-carboline type either from natural sources or from synthesis have shown biological properties of different types including antitumor [1]. Due to the presence of indole in their structure they present strong absorption and fluorescence characteristics. Our first objective was the preparation and characterization of tetrahydrocarbolines and carbolines. The second one, which is still underway, consists on preparing films by the sol-gel method [2], containing compound 3 and studying their optical (UV-visible absorption and luminescence) properties. Tetrahydrocarbolines 1 and 2a were synthesised in low yields by the Pictet –Spengler reaction, starting from tryptophan and the aromatic aldehyde, using acetic acid, H_2SO_4 or toluene. The mixture of tetrahydrocarbolines 2a was treated with thionyl chloride and methanol and the product was oxidised with $KMnO_4$ to the carboline 3 in 9% overall yield. Compound 3 was also prepared, in 25% yield, by heating tryptophan methyl ester and dimethoxybenzaldehyde in toluene, and later refluxing after addition of Pd/C. The compounds were characterised by ^1H and ^{13}C NMR and mass spectrometry.



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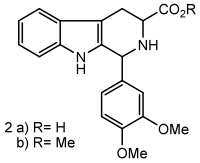
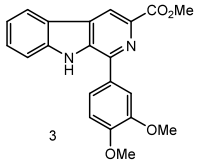


2 a) R= H
b) R= Me



3

Acknowledgments

We acknowledge the financial support from FCT and FEDER, for National NMR Network (Bruker Avance II 400) and REEQ/630/QUI/2005 (LC/MS instrument). We thank Ms. E.Pinto for obtaining NMR spectra and Ms. N.Nunes for LC/MS determinations.

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More sustainable approach for the *trans*-1,2-dihydroxylation of olefins

Andreia A. Rosatella | Carlos A. M. Afonso

CQFM – Centro de Química-Física Molecular and IN – Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

andreia.rosatella@ist.utl.pt

Considerable efforts have been devoted to finding of more environmental-friendly chemical processes such as reduction of emissions of volatile organic compounds (VOCs). The use of non-traditional solvents in chemical synthesis, such as water, provides an approach to prevent pollution. 1,2-Diols are a important building blocks, not only for the syntheses of pharmaceuticals, agrochemicals, pheromones, and liquid crystals, but also as chiral auxiliaries or ligands for asymmetric synthesis [1]. The synthesis of *trans*-1,2-diols is usually made by the oxidation of alkenes. Several methods for this transformation have been reported [1], but only a few use nonorganic solvents as reaction medium. Adkins and Roebuck [2] established in 1948 the use of formic acid as solvent for the *trans*-dihydroxylation of olefins, with an aqueous solution of hydrogen peroxide as oxidant. Sato *et al.* [3] reported the dihydroxylation of olefins in an aqueous medium with H_2O_2 as oxidant and NAFION® as a catalyst. A different method for the dihydroxylation of olefins uses OXONE® as oxidant [4].
In this work is described the synthesis of *trans*-1,2-diols in a aqueous medium [5]. Several sulfonic acids were tested as potential catalysts being *p*-toluenesulfonic acid the best catalyst. The oxidant of this reaction was also studied, being the hydrogen peroxide the greener and most efficient oxidant for this reaction. With the optimized reaction conditions (95% yield with cyclohexene as substrate), several others olefins were tested, with yields of 60-95%, including catalyst reuse. In a different approach of this reaction was possible to synthesize and isolate *trans*-1,2-cyclohexanodiol in an aqueous medium where the reaction and further work-up were made without the use of organic solvents.

Acknowledgments
We would like to acknowledge Fundação para a Ciência e Tecnologia (POCI 2010) and FEDER (POCI/QUI/66695/2006, SFRH/BD/28242/2006) for financial support.

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Experimental and computational energetic study of 2-trichloroacetylpyrrole and 2-trifluoroacetylpyrrole

Ana Filipa L. O. M. Santos | Manuel A. V. Ribeiro da Silva

CIQ - Centro de Investigação em Química, Faculty of Science - University of Oporto, Rua do Campo Alegre 687, P-4169-007 Porto, Portugal

ana.santos@fc.up.pt

Pyrrole ring is the basic chemical structure of many pharmacologically active molecules and biologically relevant natural products. Thus, a widely range of synthetic drugs with high therapeutical potential incorporates such heterocyclic moiety.

The values of the standard (p° = 0.1 MPa) molar enthalpies of formation, in the crystalline phase, of 2-trichloroacetylpyrrole and 2-trifluoroacetylpyrrole, which were derived from the standard molar energies of combustion, in oxygen, to yield HCl·600 H2O (l) and $HF \cdot 10H_2O$ (l), respectively as well as CO_2 (g) and N_2(g), at T = 298.15 K, measured by rotating bomb combustion calorimetry are reported. The values of the standard molar enthalpies of sublimation, at T = 298.15 K, derived from the Knudsen mass-loss effusion technique are also presented. From the above mentioned experimental quantities, the standard molar enthalpies of formation, in the gaseous phase, were obtained. The experimental values will be compared with estimates based on high-level ab initio molecular orbital calculations at the G3(MP2)//B3LYP level, which have also been extended to the calculation of other thermodynamic properties namely N!H bond dissociation enthalpies, gas-phase acidities and basicities, proton affinities and adiabatic ionization enthalpies.

Acknowledgments
A.F.L.O.M.S. thanks FCT (Portugal) and FEDER for the award of the post-doctoral fellowship (SFRH/BPD/41601/2007).

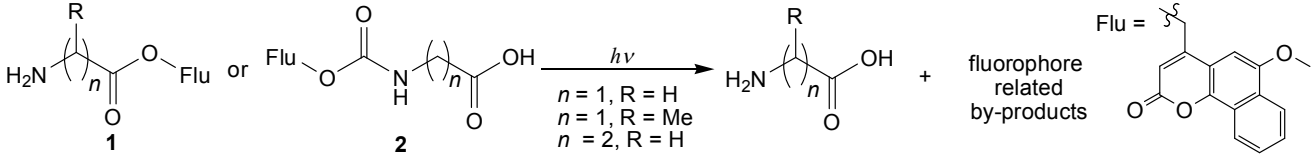
Light-induced release of neuroactive amino acids from 2-oxo-2*H*-benzo[*h*]benzopyran conjugates

Ana M. S. Soares | Susana P. G. Costa | M. Sameiro T. Gonçalves

Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

msameiro@quimica.uminho.pt

The study of the chemical mechanisms and the kinetics of synaptic transmission in neurological sciences have prompted a great interest in photo-induced cleavage applications in recent years [1]. Among the neurotransmitter molecules involved in neuronal communication at the central nervous system (CNS), neuroactive amino acids play an important role with inhibitory and excitatory functions.
Taking these facts into consideration in connection with our research interests in the development of new fluorescent heterocyclic compounds and their application as photoreleasable protecting groups [2-4], a 2-oxo-2*H*-benzo[*h*]benzopyran was evaluated as a photolabile group for the amino and carboxylic acid terminals of glycine, alanine and β-alanine. The behaviour towards photocleavage of the corresponding ester **1** and urethane **2** bioconjugates was studied by irradiation in MeOH/HEPES buffer solution (80:20), in a photochemical reactor at different wavelengths (254, 300, 350 and 419 nm), followed by HPLC/UV and ^{1}H NMR monitoring.



1 **2**

Acknowledgments
Thanks are due to the Foundation for Science and Technology (Portugal) for financial support through project PTDC/QUI/69607/2006. The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased in the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT.

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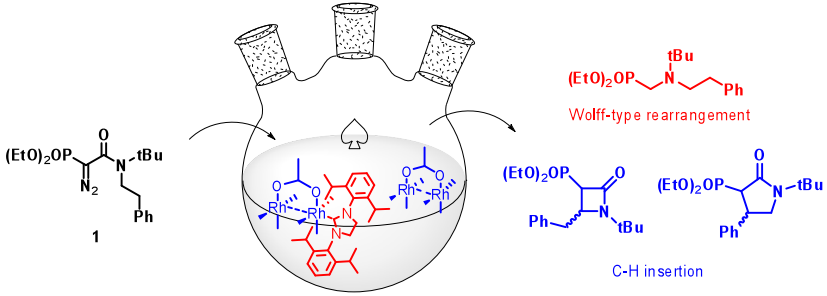
NHC effect: tuning rhodium(II) catalysis in C-H insertion reactions

Alexandre F. Trindade | Nuno R. Candeias | Luis F. Veiros | Pedro P.M. Gois | Carlos A.M. Afonso

CQFM, IN -Instituto Superior Técnico,1049-001 Lisboa, Portugal. Fax: + 351 21 846 4455/7

alexandre.trindade@ist.utl.pt

Di-rhodium(II) complexes have remarkable efficiency in the generation of metalo-carbenoids from diazo compounds. The presence of axial ligands coordinated in the rhodium can considerably alter the selectivity in C-H insertion reactions of α-phosphoryl diazoacetamides [1]. In this work, the C-H insertion reaction of diazo **1** with two Rh(II) catalysts was studied by DFT calculations in order to rationalize the NHC effect in the catalysis. The theoretical results obtained are in good correlation with the experimental data [2].



Acknowledgments

We thank Fundação para a Ciência e Tecnologia (POCI 2010) and FEDER (PTDC/QUI/66015/2006, PTDC/QUI/66695/2006 and SFRH/BD/30619/2006) for the financial support.

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Influence of drying on the texture of solar dried pears

Bruno Marques | Raquel Guiné | Pedro Cunha | Lisete Silva | Maria João Lima | Dulcineia Ferreira

Escola Superior Agrária de Viseu / CI&DETS, Instituto Politécnico de Viseu, Quinta da Alagoa, Estrada de Nelas, 3500-606 Viseu

raquelguine@esav.ipv.pt

Texture is the result of complex interactions among food components, and the changes in texture occurring during the processing of plant materials or certain physiological events have been related to tissue and cell microstructural changes [1].
The texture parameter, together with appearance and flavour, are the organoleptic quality attributes which determine the acceptability of a food by the consumer. Hence, there has been a great interest in the development of methods to predict and control the texture of plant-based foods, particularly in relation to processing treatments. Instrumental texture profile analysis (TPA) is one of the methods to determine the texture by simulating or imitating the repeated biting or chewing of a food.
The pears used in the present study are of the Portuguese variety S. Bartolomeu, which is traditionally dried, and they were dried peeled but uncut. However, unlike in the traditional method the pears were not dried under open-air sun exposure, and, alternatively, were dried in two different systems: solar stove with forced convection (STFC) and solar stove with natural convection (STNC). The drying was carried out until the pears reached a desirable moisture content of about 20 % (wet basis). Before drying, along the process and at the end, samples were used from both drying systems to evaluate their textural properties. The texture profile analysis to all the samples was performed using a Texture Analyser, and the textural properties: hardness, springiness, cohesiveness, and chewiness were then calculated after standard equations.
The objective of the present work is, on one hand, to evaluate how the textural attributes change along time during the drying operation and, on the other hand, to compare the two drying methods used.
From the results obtained is possible to see that the drying operation greatly affects the textural properties of the pears, so that the hardness diminishes very much along drying, for both the drying systems tested.

Acknowledgments
The authors thank FCT for financial support through project PTDC/AGR-ALI/74587/2006.

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New routes to the synthesis of 1-aryl-9*H*-xanthen-9-ones

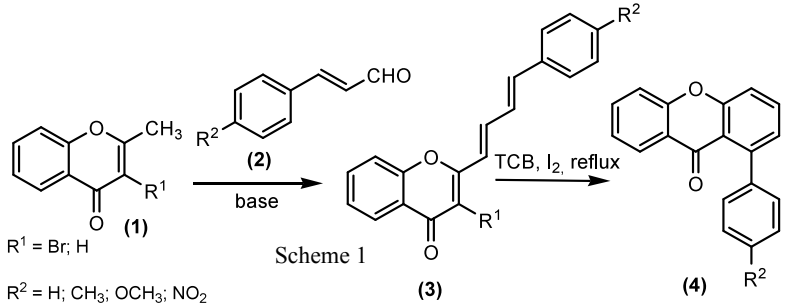
Cristela M. Brito | Artur M. S. Silva | José A. S. Cavaleiro

QOPNA, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

cristela@ua.pt

Xanthones or 9*H*-xanthen-9-one (dibenzo-γ-pirone) are an important class of oxygenated heterocycles [1]. Both natural and synthetic derivatives of this class of compounds have engendered a great deal of interest due to their wide range of biological and pharmacological activities, e.g., antibacterial, anti-inflammatory, antioxidant, antiulcer, and antitumor[2].

In this communication we report the total synthesis of 1-aryl-9*H*-xanthen-9-ones (Scheme 1) starting with the condensation of 2-methyl-4*H*-chromen-4- ones **(1)** with cinnamaldehydes **(2)** to produce (*E,E*)-2-(4-arylbuta-1,3-dien-1-yl)-4*H*-chromen-4-ones **(3)**. Chromones **(3)** were then subjected to electrocyclization and oxidation reactions in refluxing 1,2,4-trichlorobenzene giving the corresponding xanthones **(4)**. 1-Aryl-1,4-dihydro-9*H*-xanthen-9-ones have also been obtained as by-products in this transformation.



Scheme 1

Experimental procedures and spectroscopic characterization of all new compounds will be presented and discussed.

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Salvia sclareoides extracts for Alzheimer's disease: antioxidant activity, toxicity and phytochemical studies

Catarina Dias [1] | Carla Jerónimo [1] | I. Branco [1] | A. Martins [1] | A.P. Rauter [1] | F.V.M. Silva [2] | M. Goulart [2] | N. Gaspar [2] | J. Justino [2]

[1] Grupo da Química dos Glúcidos, Centro de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, 1749- 016 Lisboa, Portugal
[2] Escola Superior Agrária de Santarém, Instituto Politécnico de Santarém, Apartado 279, 2001-904 Santarém, Portugal

catarinaa_dias@hotmail.com

Preliminary studies performed by our research group suggested that *Salvia sclareoides* extracts are potent inhibitors of acetylcholinesterase and butyrylcholinesterase, two enzymes involved in the Alzheimer's disease [1]. Pursuing our studies on this plant we present now the antioxidant activity of various *Salvia sclareoides* extracts (acetone, butanol, ethanol, methanol and water). Their radical scavenging properties were evaluated using the DPPH (2,2-diphenyl-1-picrylhydrazyl hydrate) and the β-carotene-linoleic acid bleaching assays. The DPPH method revealed that butanol extract exhibited the highest antioxidant activity, while the acetone extract was the more potent one with the !-carotene-linoleic acid bleaching assay. Butanol extract also exhibited the highest total phenolics content when compared to the other extracts tested, a result that can be correlated with its higher antioxidant capacity. Determination of acute and delayed cytotoxicity and genotoxicity towards human primary and immortalized cell lines were assessed by the mitotic index evaluation techniques. The extracts were not cytotoxic to human lymphocytes at concentrations up to 4.0 mg/mL and showed no evidence for associated genotoxic risk. Given the relevant antioxidant properties observed and the absence of toxicity in human cells at higher concentrations, *Salvia sclareoides* is a promising plant regarding its application for therapeutics and nutrition purposes. Phytochemical studies of the bioactive extracts are being carried out and will also be presented.

Acknowledgments
Fundação para a Ciência e a Tecnologia (FCT) is gratefully acknowledged for the Post-Doc research grant of Alice Martins and for the research grant (BI) of Carla Jerónimo.

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New cyclen derivatives with pendant arms for possible medical applications

Catarina V. Esteves [1] | Luís M. P. Lima [1] | Nicolas Bernier [1] | Jorge Santos [1] | Rita Delgado [1,2]

[1] Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. da República (EAN), 2780-157 Oeiras, Portugal
[2] Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

cvesteves@itqb.unl.pt

In recent decades, a large number of acyclic and macrocyclic compounds have been evaluated as chelators for medical applications. Tetraazamacrocycles functionalized with additional donor groups are very efficient ligands for these applications [1]. More recently, new macrobicycles, especially cross-bridged ones, were found to be powerful chelators due to the remarkable thermodynamic and kinetic stability of their metal complexes, with potential applications in the field of medical diagnosis and therapy [2].
In this work two different cyclen derivatives were synthesized, both containing two pendant arms with donor atoms on opposite amines and one of them an additional cross-bridge (*vide* Fig. 1), in order to understand the effect of the increased rigidity of the ligand framework on the stability of the metal complexes. For such purpose the protonation constants of both compounds and the thermodynamic stability constants of a series of their metal ions have been determined. The properties of some of the metal complexes were also studied by additional spectroscopic techniques in order to have structural information.

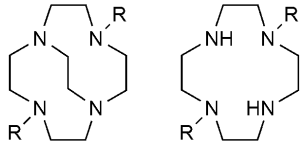

Fig. 1.

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The authors acknowledge the financial support from FCT (Project PTDC/QUI/67175/2006).

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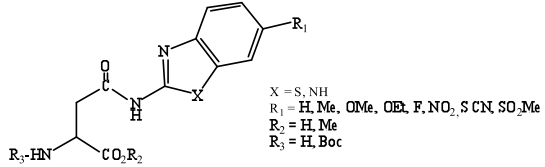
Synthesis and interaction studies of novel heterocyclic asparagines with metal cations

Cátia I. C. Esteves | M. Manuela M. Raposo | Susana P. G. Costa

Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

spc@quimica.uminho.pt

Unnatural amino acids bearing fluorescent heterocyclic moieties have been described as fluorescent and/or colorimetric chemosensors for anions and metal cations and biomarkers [1]. These applications can result from synthetic manipulation at the side chain of coded amino acids, that generate altered physicochemical or photophysical properties. Recently, our research group has been involved in the development and application of benz-X-azole-containing amino acids with application as fluorescent probes and metal ion chemosensors, namely benzoxazolyl-alanines [2,3], benzothiazolyl- and benzimidazolyl-asparagines [4]. We now report the synthesis and photophysical characterization of novel deprotected asparagine derivatives (Figure) and the interaction study with biologically important metallic cations such as Cu(II), Zn(II), Co(II) and Ni(II), through spectrophotometric and spectrofluorimetric titrations.



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Tailoring confined space for enantioselective oxidation catalysis

Cristina I. Fernandes [1] | Marta S. Saraiva [1] | Teresa G. Nunes [2] | Pedro D. Vaz [1] | Carla D. Nunes [1]

[1] CQB, Departmento de Química e Bioquímica, FCUL, Campo Grande, Ed. C8, 1749-016 Lisboa, Portugal
[2] Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

csilvafernandes@gmail.com

Chiral mesoporous materials synthesis was accomplished using ammonia as co-surfactant [1]. The material thus prepared retains the basic structure of the silicon based matrices, but with a confined environment tailored in a spiral manner, as evidenced in Fig. 1. The inner surface is able to accept building blocks (the ligands) which will confer further application to the host material. Functionalization by reaction with ligands bearing a pendant arm with a silylated chain allows binding to the walls of the material. Such ligands contain two donor atoms (N, O or P) to accomplish metal coordination. Ligands will react with proper complex precursors, giving rise to potential heterogeneous catalysts [2]. Homogeneous counterparts are also prepared for benchmarking. All these (homo- and heterogeneous entities) will be tested in oxidation catalysis, namely the enantioselective epoxidation of olefins, with hydrogen peroxide or *t*- butylhydroperoxide, and their performance compared. All synthesized complexes and materials are characterized by means of adequate spectroscopic (such as NMR, UV/Vis and FTIR) or other (XRD, TGA, SEM/TEM and sorption measurements) techniques.

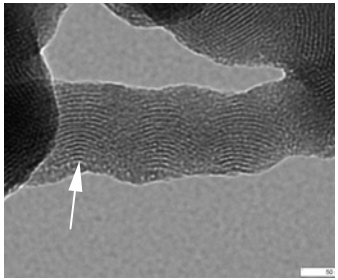

Fig. 1 – TEM image of a chiral MCM-41 like mesoporous material (please notice de curved channels).

Acknowledgments
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Application of polysaccharide-based stationary phases in the separation of chiral xanthone derivatives

C. Fernandes | P. Brandão | M. E. Tiritan | C. Afonso | Q. Cass | M. Pinto

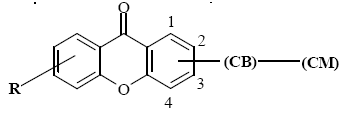
Department of Chemistry, Laboratory of Organic and Pharmaceutical Chemistry, Faculty of Pharmacy, University of Porto, Rua Aníbal Cunha, 164, 4050-047 Porto, Portugal.

cfernandes@ff.up.pt

Over the last 20 years, derivatives of polysaccharides such as amylose and cellulose coated onto functionalised silica have been used as chiral stationary phases (CSP) for High-Performance Liquid Chromatography (HPLC) [1]. About 95% of racemates can be successfully resolved by their use [2]. HPLC is a crucial analytical tool for the resolution of racemates, evaluation of the enantiomeric purity, control of asymmetric reactions and pharmacokinetics studies [3]. Chiral xanthone derivatives (CXD) are of great interest since can be associated with important pharmacological activities such as anticonvulsant, antidepressant, anti-inflammatory and antitumor, with mechanisms of action many times associated with enantioselectivity [4].

This work describes the resolution of a small library of CXD (Fig. 1) on polysaccharide-based columns, under normal, reversed-phase, and polar organic conditions.

The polysaccharide-based CSP have proved to be successful to separate this class of compounds, showing excellent enantioselectivity and resolution.



R: Functional Group
PQ: Chemical Bridge
CM: Chiral Moiety

Fig. 1. Schematic representation of a CXD.

Acknowledgments
CEQUIMED-UP (I&D 4040/2007), U.Porto/Santander Totta and FCT-GRICES/CAPES 00770 29/05/08 for financial support.

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A study of diflunisal co-crystal formation with pyridine-carboxamide isomers

Carina A. D. Forte [1] | Teresa M. R. Maria [1] | Mário T. S. Rosado [1] | Ricardo A. E. Castro [2] | M. Ramos Silva [3] | A. Matos Beja [3] | João Canotilho [2] | M. Ermelinda S. Eusébio [1]

[1] Department of Chemistry | [2] Faculty of Pharmacy | [3] Department of Physics, University of Coimbra, 3004-535 Coimbra, Portugal

carina.forte@gmail.com

Co-crystals, containing two or more molecular components in the crystal lattice, are attracting increasing attention in the pharmaceutical community because of their desirable physicochemical and biopharmaceutical properties [1].
In this communication a combined experimental and theoretical study concerning the formation of co-crystals is presented. Differential scanning calorimetry, infrared spectroscopy, X-ray powder diffraction and density functional theory (DFT) have been used to study the phenomenon of co-crystal formation in stoichiometric mixtures of diflunisal (5-[2,4-difluorophenyl] salisylic acid), a non-steroidal anti-inflammatory drug, with two isomeric co-crystal formers, nicotinamide and picolinamide. Co-crystal screening is performed via solid-state grinding and solution crystallization.
There are striking differences in the co-crystal formation capabilities of the two isomers whose structures only differ in the ring nitrogen position. The DFT calculations (M06/cc-pVDZ) allowed to compare the relative stability of homodimers and heterodimers in order to predict and rationalize the experimental outcomes.

Acknowledgments
We are grateful to FEDER/POCI 2010 for financial support.

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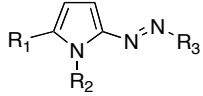
Synthesis and evaluation of the electrochemical, nonlinear optical and photochromic properties of novel pyrrole azo dyes

C. Sofia G. S. Gomes | M. Cidália R. Castro | A. Maurício C. Fonseca | M. Belsley | Luís M. Carvalho | P. Coelho | M. Manuela M. Raposo

CQ-UM, Center of Chemistry, University of Minho, Campus de Gualtar 4710-057 Braga

mfox@quimica.uminho.pt

One of the most recent approaches to the design of organic systems with strong nonlinear optical (NLO) responses is based on the presence of five-membered heterocyclic rings, (*eg* thiophene, pyrrole and thiazole) to create significant modulation of the conjugate !-electron bridge in donor-acceptor chromophores. Recently heteroaryl azo dyes have assumed an increasingly important role in the design of advanced materials and devices due to their versatile applications as conducting materials, solvatochromic probes and NLO chromophores [1-3]. The E/Z isomerizable N=N double bond within a conducting chain can work as molecular switch, making the heteroaryl azo systems promising candidates as photochromic materials [4-5]. As part of our continuing interest in heterocyclic azo dyes for optical applications we present in this communication the synthesis of compounds **1**-**2** (Figure) using as coupling components pyrroles, thienylpyrroles and aryl or thiazolyldiazonium salts. Evaluation of the electrochemical and optical properties of azo dyes bearing π-conjugated pyrrole **1** or thienylpyrrole **2** heterocyclic moieties showed that they could be used as conducting and photochromic materials and efficient NLO chromophores.



1-2

R_1 = H, thienyl
R_2 = alkyl, aryl
R_3 = Ph, 4-CNPh, 4-NO_2Ph, thiazolyl

Acknowledgments
Thanks are due to the Fundação para a Ciência e Tecnologia (Portugal) and FEDER for financial support through Centro de Química - Universidade do Minho, through Project PTDC/QUI/66251/2006.

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New cationic glycoporphyrins for the photoinactivation of microorganisms

Clara Gomes | Maria Graça Neves | José Cavaleiro | Adelaide Almeida | Ângela Cunha | João Tome

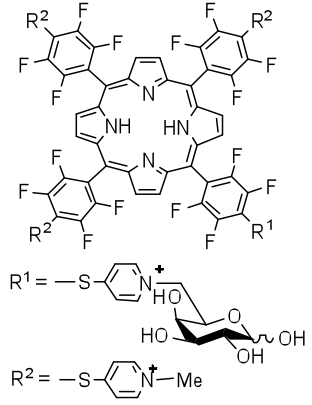
QOPNA, Department of chemistry and biology, University of Aveiro, 3810-193 Aveiro, Portugal

clara.gomes@ua.pt

Photodynamic therapy (PDT) uses three non-toxic elements: light, oxygen and a photosensitizer (PS) that when combined lead to the formation of highly cytotoxic reactive oxygen species (ROS). These species show ability to change cellular constituents resulting in lethal oxidative damage [1].

As part of our program on the development of porphyrin derivatives with potential use in medical and environmental applications, we have been preparing and characterizing new water soluble glycoporphyrins. The combination of carbohydrate moieties and positively charged groups with porphyrin derivatives results in an increased cell recognition and water solubility, which improves cell membrane penetration and accumulation in sub cellular compartments [2].

In this communication we will discuss the synthesis and characterization of a new cationic glycoporphyrin, and preliminary experiments of photoinactivation of microorganisms.



Acknowledgments

Thanks are due to University of Aveiro, FCT (Lisbon) and FEDER for funding the QOPNA unit and the project PTDC/QUI/65228/2006.C. Gomes is also grateful to FCT for a BI grant.

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Measuring folding kinetics and energetics on a nanosecond time scale

Catarina S. H. Jesus [1,2] | Sónia P. Lopes [1] | Alex Correia [1] | Rui M. D. Nunes [1] | Carlos Serpa [1] | Rui M. M. Brito [1,2] | Luis G. Arnaut [1]

[1] Chemistry Department, University of Coimbra, 3004-535 Coimbra, Portugal
[2] Center for Neuroscience and Cell Biology, University of Coimbra, 3004-517 Coimbra, Portugal

catarina.jesus@student.qui.uc.pt

One of the major challenges in the field of biophysical chemistry is the understanding of the mechanisms of protein folding, i.e. how an unstructured polypeptide chain can rapidly adopt a unique, densely packed, three dimensional structure. Erroneous folding is the molecular basis for a wide range of human disorders, such as neurodegenerative diseases like Alzheimer's and Parkinson's. Protein structure is influenced to a large extent by the charge state of ionizable groups on the side chains of several amino acids. At pH below neutrality, the amino acids mainly involved in the ionic equilibrium are glutamic acid, aspartic acid and histidine.
In the present work, we use a laser-pulsed pH-jump technique to induce protein unfolding, a methodology in which a suitable phototriggered acid generator deprotonates very quickly, resulting in extremely long-lived and reversible pH-jumps in the environment. These proton gradients protonate acid residues of the protein, producing different charged species and consequently protein conformational changes. The modification of charged groups in proteins also induces a rearrangement of the structure of the solvent molecules, in order to accommodate the charge changes. Those structural changes are accompanied by a variation in the overall solution volume, inducing a pressure wave. This allows the determination of the enthalpy, kinetics and volume changes accompanying the unfolding of the protein with a single method.
Our aim is to study the earliest conformational events related to protein folding and unfolding, such as the formation of isolated helical segments, reverse turns and β-hairpins, that occur within microseconds or less. We started by studying the isolated aminoacids involved in ionic equilibria in proteins. Additionally, we selected short peptides that fold into α-helix and β-hairpin structures, and that show pH-dependences of their conformation. As a model protein, we are studying the well characterized acid-induced conformational changes of apomyoglobin from its native state to an unfolded form near pH 4. Another important protein under study is serum albumin, the most abundant protein in the circulatory system of mammals, which plays a key role in the transport of a large number of metabolites, hormones, anesthetics, and commonly used drugs.

Acknowledgments
We thank FCT for financial support trough project POCI/QUI/55505/2004 and PhD grants SFRH/BD/43896/2008 (C.S.H.J.) and SFRH/BD/24005/2005 (R.M.D.N.).

Intramolecular aromatic π-π interactions in diarylnaphthalenes: a NMR, thermodynamic and quantum chemical approach

Carlos F. R. A. C. Lima | Luís M. N. B. F. Santos | Lígia R. Gomes

Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, R. Campo Alegre, 687 4169-007 Porto

carlos.chemistry@gmail.com

Aromatic π-π interactions are weak non-covalent interactions (5 to 15 kJ mol-1) between aromatic moieties with great significance on chemistry and biochemistry [1]. In this work, an experimental and theoretical approach regarding the relation between molecular structure and energetics in 1-arylnaphthalenes and the corresponding 1,8-diarylnaphthalenes (illustrated in Fig. 1) was used to evaluate the intramolecular π-π interactions between the two aryl groups and the influence of substituents on those interactions.

The compounds were synthesized by the Suzuki-Miyaura cross-coupling reaction and were structurally characterized by X-ray crystallography. A ^{1}H-NMR study, comprising the rationalization of the aryl protons' chemical shifts and the determination of internal rotational barriers, was employed in order to elucidate the effect of substituents. Combustion calorimetry and vapour pressure measurements were carried out for the mentioned compounds. The experimental results obtained were supported and complemented by a theoretical (DFT and MP2) structural and energetic analysis.

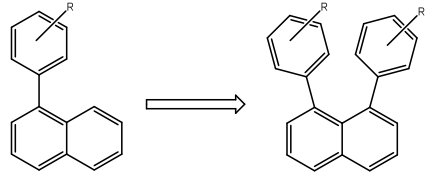

Fig. 1. General structure of the compounds studied in this work.

Acknowledgments

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Effect of high pressure on the enzymatic hydrolysis of carboxymethyl cellulose

Cátia Martins | Jorge A. Saraiva

QOPNA, Departamento de Química, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

catiamartins@ua.pt

In the last years, research has focused on the possible feasible use of cellulose, the most abundant renewable bioresource, for the production of fermentable sugars that can be converted to fuels such as ethanol, due to the limited reserves of fossil fuels [1]. However, enzymatic hydrolysis of cellulose to fermentable sugars is difficult due to the tight packing of cellulose chains in microfibrils. Firstly used in the fields of chemistry and physics, the use of the so called high (hydrostatic) pressure (HP), up to 1000 MPa (~10000 atm), is now viewed also with great potential to improve enzymatic reactions [2,3]. Under HP, due to water volume decrease and compaction, several physical events can occur, like increase of interactions between water and other molecules, due to the so called "*electrostriction*" occurrence [4]. This can be of interest to improve interaction of water with macromolecules, particularly those more tightly packed, by promotion of water (and solutes dissolved in it) "*infusion*" throughout the macromolecule.

With this background reasoning in mind, we decided to study the effect of HP treatments (from 50 to 500 MPa, during 1, 3, 5 and 15 minutes) on the subsequent enzymatic hydrolysis of carboxymethyl cellulose (CMC) at atmospheric pressure. The results showed an increased amount of reducing sugars resulting from CMC enzymatic hydrolysis, when the reactional system (CMC/buffer/cellulase) was submitted to HP at the beginning of the reaction. As an example, when 100 MPa was applied for 1 minute, production of reduction sugars increased by 160-fold after 5 min of reaction time. The amount of reducing sugars resulting from CMC hydrolysis correlated linearly with the pressure level, for the same time under HP. The results of this first study are promising to further develop new processes leading to more efficient cellulose enzymatic hydrolysis. Experiments are under way to obtain evidences for the hypothesized water infusion through cellulose.

Acknowledgments
Author C. Martins acknowledges Fundação para a Ciência e Tecnologia (FCT) for the scholarship Bolsa de Integração na Investigação (BII).

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Simple method for the enzymatic resolution and separation of Sulcatol employing a biodiesel component

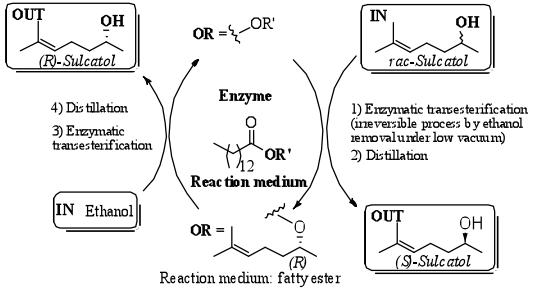
Carlos M. Monteiro | Nuno M. T. Lourenço | Carlos A. M. Afonso

CQFM, IN, Instituto Superior Técnico, 1049-001 Lisboa, Portugal. Fax: + 351 218464455/7; Tel: +35218419785

carlosmmonteiro@ist.utl.pt

Sulcatol is a pheromone in which the active form for pest control *to Gnathotrichus sulcatus* needs both enantiomers enriched in the (*S*)-enantiomer in a ratio of 65:35 (*S*)/(*R*) and only the (*S*)-enantiomer for *Gnathotrichus retusus* [1]. Some reported methods for the synthesis of enantiomeric pure Sulcatol are based on enzymatic resolution of a racemic mixture, the use of active building blocks with the suitable configuration such as ethyl (*R,S*)-lactate (through chiral methyloxirane), (*R,S*)-glutamic acid or (*R*,*S*)-γ-trityloxymethyl-γ-butylrolactone, or desoxydgenation of *L,D*-fucose, or enzymatic reduction of ethyl acetoacetate or 2-acetyl-5-methythex-4-enoate [2].

A simple, robust, reusable and more environmental friendly process [3,4] is described for the resolution and separation of Sulcatol (6-methylhept-5-en-2-ol) by using just a biodiesel component (ethyl tetradecanoate) in the presence of enzyme. The simple isolation of each enantiomer by distillation is based on the combination of efficient enzymatic resolution through anchor of one enantiomer as an ester and distillation of the free (*S*)-Sulcatol enantiomer. In a consecutive enzymatic transesterification the (*R*)-Sulcatol can be de-attach and isolated by second distillation [4].



Acknowledgments

FCT (POCI 2010) and FEDER (SFRH/BPD/41175/ 2007 and SFRH/BD/48395/2008) and ACS Green Chemistry Institute (Ref. GCI-PRF#49150-GCI) for their financial support, Novozymes and Amano enzymes for their generous enzyme supply.

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Oxazolones as possible multiphoton absorbing molecules

Catarina A. B. Rodrigues | Ermelinda M. S. Maçôas | José M. G. Martinho | Carlos A. M. Afonso

CQFM – Centro de Química-Físsica Molecular and IN – Institute of Nanoscience and Nanotechonology, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

catarina.b.rodrigues@ist.utl.pt

Multiphoton absorbing chromophores are molecules that absorb two or more photons, accompanied by the transition of an electron from a lower energy level to a higher level, and release half of the absorbed photons with twice of energy. These types of compounds have attracted high interest in the last few years due to their photochemical properties and subsequent wide range of applications such as microfabrication, data storage, photodynamic therapy, optical power limiting and sensors [1].
Oxazolones may have potential two photon absorbing properties [2] and can be synthesized by two different methods (Fig. 1) [3,4]. Herein, we wish to present the synthesis and to evaluate the multiphoton absorbing properties of oxazolones.

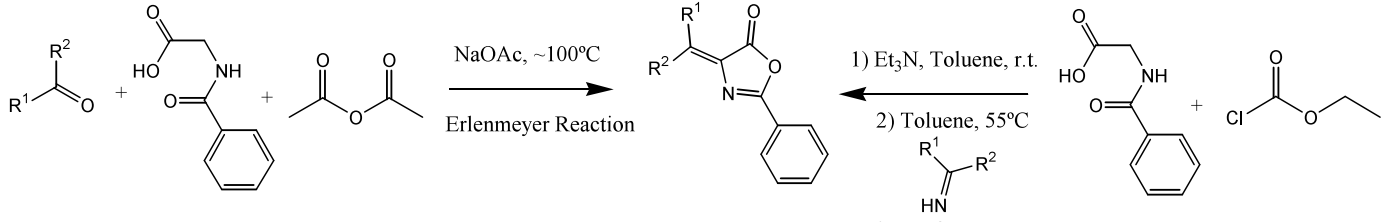

Fig. 1. Different methods for the synthesis of oxazolones, R^1=Ar, R^2=Ar or H

Acknowledgments
We would like to acknowledge Fundação para Ciência e Tecnologia (SFRH/BD/48145/2008) for financial support.

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Studying the metabolome of highly mistranslating *Saccharomyces cerevisiae* by NMR

Claudio H. Santos | João Paredes | Manuel Santos | Brian J. Goodfellow

CICECO, Chemistry Department, Universidade de Aveiro, 3810-193 Aveiro, Portugal

claudiosantos@ua.pt

High mRNA translation fidelity is critical for the production of stable and functional proteomes and, therefore, mRNA mistranslation events that produce aberrant proteins are often linked to disease. In order to understand this phenotype at the molecular level, we have induced constitutive mRNA mistranslation in *Saccharomyces cerevisiae*, using tRNA engineering methodologies [1] and optimized the extraction methods compatible with high- throughput, reproducible nuclear magnetic resonance spectroscopy (NMR).

This work focused on the optimization of an experimental method for obtaining global metabolic profiles by NMR and on the identification of the maximum number of intracellular metabolites present in yeast, particularly *Saccharomyces cerevisiae* with high levels of mistranslation. Optimization of experimental methods used for the extraction of intracellular metabolites in eukaryotic cells using NMR, must meet fundamental requirements like high yield, reproducibility, simplicity and it should also be straightforward. Optimization of an experimental process is not always easy to optimize, since many factors can affect it. In order to achieve our objectives, the experimental variables were minimized by studying: the growth media; the growth curves, in order to recognize when to collect the cells; and the metabolite extraction procedures. After obtaining the metabolic extracts (<5 kDa) using different methods, 1D spectra were acquired and, for selected samples, 2D ^{1}H-^{13}CHSQC spectra were also acquired. Using unsupervised PCA analysis, important variables were identified and, subsequently, controlled in order to reduce the variability between samples and optimise an efficient process to obtain metabolic extracts. The final optimised experimental method, similar to that of Lewis *et al.* [2], consists in two stages of lyophilisation. After the first lyophilisation, glass beads (5 mm) were added to the lyophilised extracts and then submitted to vigorous dried vortex. After dissolved in a buffer, the extracts were filtered (<5 kDa) and again lyophilized. As previously said, this work also consisted in the identification of a maximum number of characteristic metabolites present in yeast. The maximum number of identified metabolites was *ca.* 40, as showed in previous studies. However, in our work, we were able to clearly identify *ca.* 60 compounds using NMR.

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Spin trapping of glycated 1-palmitoyl-2-lineloyl-phosphatidylethanolamine free radicals generated under oxidative stress, using DEPMPO, DMPO and mass spectrometry

Cláudia Simões | M. Rosário M. Domingues | Ana Reis | Pedro Domingues

Mass spectrometry Centre, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

claudiasimoes@ua.pt

Glycation of phosphatidylethanolamines (PEs) occurs in diabetic patients as a consequence of hyperglycemia. Glycated PEs boosts oxidative stress effects and diabetic complications, such as atherosclerosis and cardiovascular diseases. Recently it was found that oxidation of glycated PEs occurs either in unsaturated fatty acyl chains or in glycated polar head, in contrast with non glycated phospholipids, for which oxidation only occurs in fatty acyl chains [1]. This finding suggests that the presence of glucose promotes the abstraction of a hydrogen in the vicinity of the imine bond of glycated derivative. Mass spectrometry (MS) combined with spin trapping is being used for the detection of carbon and oxygen centered radical adducts of phospholipids, peptides and proteins, allowing the identification of the radical's and it specific location.

In order to understand the oxidation mechanism of these glycated biomolecules, oxidation of glycated 1-palmitoyl-2-lineloyl-phosphatidylethanolamine (PLPE) induced by the hydroxyl radical (Fenton reaction) and in the presence of the spin traps DEPMPO and DMPO was monitored by MS. The results showed the formation DMPO and DEPMPO adducts of both carbon and oxygen (hydroxyl and peroxyl) centered radicals in glycated PLPE. The adducts observed in ESI-MS spectra as $[M+Na]^+$ ions, corresponded to the insertion of one DMPO or DEPMPO molecules combined with insertion of oxygen atoms. Also, adducts resultant from insertion of two DMPO/DEPMPO molecules combined with insertion of oxygen atoms were found, confirming the formation of two radicals in the same molecule. MS/MS analysis allowed identifying several targets of radical formation, including at glycated polar head.

Acknowledgments

The authors thank the financial support provided to Cláudia Simões (PhD grant, SFRH/BD/46293/2008), project PTDC/QUI- p BIOQ/104968/2008 and RNEM by the Foundation for Science and Technology (FCT).

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Synthesis of 2-(methacryloyloxy)ethyl palmitate by transesterification of tripalmitin with HEMA

Carla Vilela | Armando Silvestre | Alessandro Gandini

CICECO/Chemistry Department, University of Aveiro, Aveiro, Portugal

cvilela@ua.pt

The vital issue regarding the preservation of natural resources has refurbished the interest in developing novel materials from the use of renewable sources, whose ubiquitous character offers civilization valuable elements of sustainability [1]. Vegetable oils, predominantly formed by mixed triglycerides with fatty acid moieties, have become an emergent field of research due to their remarkable potential as starting materials for the production of original polymers. However, the rather low reactivity of the saturated or unsaturated aliphatic chains of fatty acids makes them ineffective monomers for direct polymerization. This drawback can be overcome by functionalizing the fatty acids with polymerizable moieties. The transesterification with monohydric alcohols (mostly methanol) yields fatty acid alkyl esters, which are promising substitutes for diesel fuel [2,3], but which do acquire the monomer status because the transformation does not incorporate reactive functions.

The present communication reports the synthesis of a fatty acid-based monomer bearing acrylic moieties via the transesterification of tripalmitin with 2-hydroxyethyl methacrylate (HEMA). A systematic study was performed in order to optimize reaction conditions, yields and purity of the ensuing monomer. Results related to a preliminary investigation of its polymerization will also be reported.

Acknowledgments

The authors wish to thank the Portuguese Foundation for Science and Technology for the financial support of this work (SFRH/BD/44884/2008).

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Development of an ELISA procedure to follow sorption of atrazine onto a soil sample

Diana L. D. Lima | Carla Patrícia Silva | Rudolf J. Schneider | Valdemar I. Esteves

CESAM & Department of Chemistry, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal
Department of Complementary Sciences, Superior School of Health Technology of Coimbra, Apartado 7006, 3040 - 854 Coimbra, Portugal

diana.lima@ua.pt

Without pesticides is practically impossible to produce the enormous quantities of food required to feed the world's growing population. Between herbicides, one of the most frequently used groups is the triazines, which include atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) a weak-base, with a pK_a of 1.7, low solubility in water (28 mg L^{-1}) and widely used to control annual grasses and broadleaf weeds. Since the behaviour of herbicides in soils greatly depends on sorption-desorption phenomena, a fundamental understanding of these mechanisms is critical for accurate predictions of their geochemical mobility and potential runoff to natural groundwaters [1]. Enzyme-linked immunosorbent assay (ELISA) offers a way to quantitatively determine residual pesticide concentrations in water and soil samples with much less effort, higher sensitivity, portability, simplicity and no need of samples' cleanup or concentration step [2,3]. The aim of this study was to develop an ELISA technique that could be useful in the determination of atrazine in soil samples in order to follow the sorption behaviour of this pesticide onto a soil sample. The Freundlich parameters (K_F and N) were calculated from the fitting, of non-linear regression of the equation $Qe = K_F \times Ce^N$, to the experimental data, where Q_e is the total sorbed concentration (mg kg^{-1}), Ce is the solution-phase concentration (mg l^{-1}), K_F (mg kg^{-1})(mg l^{-1})$^{-N}$ is the Freundlich distribution coefficient, and N is the isotherm nonlinearity factor. The *t*-test, for 4 degrees of freedom at 95 % confidence level, was applied to compare the results obtained for K_F and N, using ELISA and MEKC, and no significantly differences were observed.

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Evaluation of phospholipids profile of dendritic cells using lipidomic approach

Diane Marques | Elisabete Maciel | Cláudia Simões | M. Teresa Cruz | M. Rosário M. Domingues

Mass Spectrometry Centre, Department of Chemistry , University of Aveiro, 3810-193 Aveiro, Portugal

dianemarques@ua.pt

Phospholipids (PLs) are the main components of cell membranes and play important structural and signalling roles in biological systems. They have been also associated with the pathogenesis of various diseases, such as cancer, inflammation, Alzheimer's and toxic manifestations of infectious diseases. The biological importance of PLs has led to an increased focus on analytical methods for the characterization of their individual molecular species. Lipidomics is a methodology based on mass spectrometry that is very popular, nowadays, to obtain information about lipid profile on cells or tissues. It allows the identification of the constituents of different classes of phospholipids [1].

Dendritic cells (DC) are immune cells, able to capture, process and present antigens to T lymphocytes, thus playing a crucial role in initiation and modulation of immune response. Recognition of antigens, such as allergens and pathogen-associated molecular patterns, by dendritic cells (DCs) leads to DC maturation. It is being considered that besides cytokines/chemokines, lipid mediators may also have effects on the immunogenicity of DCs. Alterations in particular lipid levels are the result of the metabolic activity and the environment and affect cellular signaling and behavior. Therefore it will be interesting to understand the influence of PLs in the process of DC cell signalling, maturation, membrane architecture, cell-cell and cell-protein interactions and responses to environmental changes [2].

The aim of this study is to identify the profile of phospholipids in dendritic cells and evaluate the changes that occur in PL profile of DC induced by the presence of skin allergens that trigger DC maturation, and irritants, which are not able to mature DC. Moreover, this strategy could disclose a specific PLs profile activated only by allergens and not by irritants and that could be useful to distinguish skin sensitizers from nonspecific chemical irritants. As a DC model we used a fetal skin-derived dendritic cell line. The PLs profile will be evaluated by mass spectrometry, using a lipidomic approach. Briefly, the different PL classes were initially separated by TLC and further analysed by ESI-MS and by tandem mass spectrometry (ESI-MS/MS), allowing to identify the detailed structural, namely PL polar head and fatty acyl composition. Main PLs identified in DC extracts included phosphatidylcholines (PC), phosphatidylethanolamines (PE), phosphatidylinositols (PI), phosphatidylserines (PS), cardiolipins (CL), phosphatidylglycerol (PG) and small amounts of sphingomyelin (SM).

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HPLC-PAD-APCI-MS analysis of carotenoids: a case study with the marine equinoderm *Marthasterias glacialis*

David M. Pereira | Federico Ferreres | Angel Gil-Izquierdo | Patrícia Valentão | Teresa Mouga | Paula B. Andrade

REQUIMTE/Serviço de Farmacognosia, Faculdade de Farmácia, Universidade do Porto, R. Aníbal Cunha 164, 4050-047 Porto, Portugal

david.ffup@gmail.com

Carotenoids are a class of hydrocarbons (carotenes) and their oxygenated derivatives (xanthophylls). Their basic structure reflects their biosynthetic pathway and consists of eight isoprenoid units. A series of conjugated double bonds constitute the characteristic chromophore. Carotenoids are quite widespread in Nature and marine organisms are no exception. Due to the heat lability of carotenoids, GC-MS is not suitable for their analysis, the most convenient method being high performance liquid chromatography (HPLC) with UV-Vis detection or, if possible, mass spectrometry (MS) detection.

Xanthophylls and carotenes form both molecular ions and protonated molecules during positive-ion atmospheric pressure chemical ionization (APCI). APCI is an ideal method of ionization for low to medium-polar compounds, which include also carotenoids and related compounds. Since their molecular mass does not excess 2000 u even in the case of glycosides or esters, this method is suitable for their analysis

In this work, a HPLC-PAD-APCI-MS metabolite profiling analysis of the marine equinoderm *M. glacialis* was carried. Two different extraction solvents were used, methanol and acetone, and lutein, zeaxanthin and astaxanthin revealed to be major compounds, among the high number of compounds found.

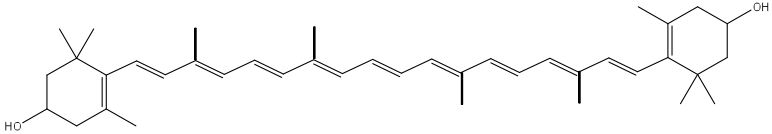


Fig. 1. *Marthasterias glacialis* and the chemical structure of the main carotenoid (zeaxanthin).

Acknowledgments
David M. Pereira is indebted to FCt for the grant (SFRH/BD/62663/2009)

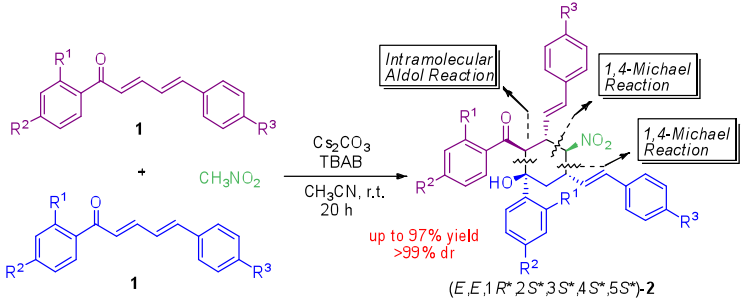
Domino multicomponent Michael/Michael/Aldol reactions under phase transfer catalysis: diastereoselective synthesis of *penta*-substituted cyclohexanes

Diana I. S. P. Resende [1] | Cristina G. Oliva [1] | Artur M. S. Silva [1] | Filipe A. Almeida Paz [2] | José A. S. Cavaleiro [1]

[1] QOPNA, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal
[2] CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

dianaresende@ua.pt

A simple, efficient and environmental-friendly domino multicomponent reaction to construct new cyclohexane derivatives with five new stereocenters, one of them quaternary, under phase-transfer catalysis is reported. This novel one-pot reaction allows the transformation of very simple starting materials into *penta*-substituted cyclohexane derivatives bearing hydroxy, nitro and ketone moieties and involving the formation of three new C—C bonds. All compounds have been formed in a complete diastereoselective way and have been isolated in high yields [1].



Acknowledgments
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New synthesis of 3-styrylflavones

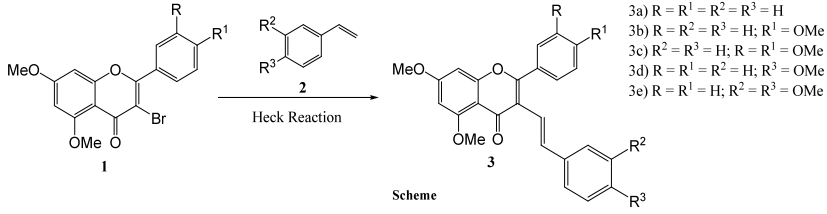
Djenisa H. A. Rocha [1] | Diana C. G. A. Pinto [1] | Artur M. S. Silva [1] | Tamás Patonay [2] | José A. S. Cavaleiro [1]

[1] Department of Chemistry & QOPNA, University of Aveiro, 3810-193 Aveiro, Portugal
[2] Department of Organic Chemistry, University of Debrecen, 4010 Debrecen, Hungary

djenisa@ua.pt

Styrylchromones constitute a small group of oxygen heterocyclic compounds which have shown significant biological activities. Synthetic approaches to 2- and 3-styrylchromones are relatively well documented and some of their biological activities have been evaluated [1]. Only a few synthetic methods are available for the preparation of 3-styrylflavones. The first report belong to Parthasarathy's group in the early 90's and consists on the transformation of 3-methylflavone to 3-styrylflavone by Wittig reaction [2]. More than a decade later 3-styrylflavones were obtained from the treatment of 3-acylflavones with $MeSO_3H$ [3].

This work presents a new and easier procedure for the synthesis of 3-styrylflavones (**3**), from the Heck reaction of 3-bromoflavones (**1**) with styrenes (**2**). Our purpose is to establish a new synthetic method and to prepare new compounds having antioxidant activity, reasons to focus our study on the synthesis of polymethoxy-3-styrylflavones (**3**) (Scheme), and develop alternative, economic, efficient, safety and cleaner methods, by using microwave irradiation conditions. The synthetic procedures and structural characterization of the obtained compounds will be presented and discussed.



Scheme

Acknowledgments
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Synthesis and high ranked NLT properties of new sulfonamide-substituted indium phthalocyanines

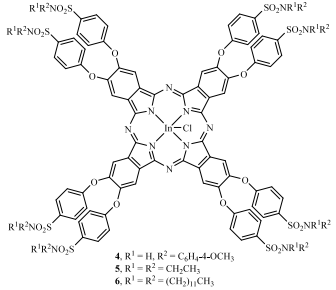
Eliana F. A. Carvalho | Mário J. F. Calvete | José A. S. Cavaleiro | Danilo Dini | Moreno Meneghetti | Augusto C. Tomé

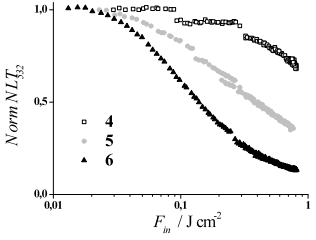
Department of Chemistry/QOPNA, University of Aveiro, 3810-193 Aveiro, Portugal

elianacarvalho@ua.pt

Peripheral modulation of macrocyclic compounds is a challenging and attractive pathway in the search for new materials. In this respect, peripheral modification of phthalocyanines is still a rewarding route to new materials suitable for diverse applications, namely those related with their nonlinear transmission (NLT) properties, for instance the limiting of laser radiation intensity. It is known that electron-withdrawing substituents produce an enhancement on the NLT properties of phthalocyanines [1,2].

Taking this into consideration, we idealized a synthetic route, that involves the chlorosulfonation of a phthalonitrile precursor, reaction with amines to yield the sulfonamide groups, and then tetramerization to form the symmetrical phthalocyanines (Scheme. 1) [3]. The optical power limiting was evaluated in order to assess the effect of such groups on their NLT properties (Fig. 1). All three phthalocyanines behave as reverse saturable absorbers with increasing efficiency of optical limiting in the order $MPAP_8PcInCl$ (**4**) < $DEAP_8PcInCl$ (**5**) < $DDAP_8PcInCl$ (**6**).





Acknowledgments

Thanks are due to FCT/FEDER for funding the Organic Chemistry Research Unit and the Project PTDC/QUI/74150/2006. M. Calvete also thanks FCT for his post-doc grant (SFRH/BPD/26775/2006).

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Oxidation of cardiolipin by the hydroxyl radical generated under Fenton conditions: identification of short chain products by LC-MS/MS

Elisabete Maciel | Diane Marques | Cláudia Simões | Ana Reis | Pedro Domingues | M. Rosário M. Domingues

Mass Spectrometry Centre, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

elisabete.maciel@ua.pt

Cardiolipin (CL) is an important phospholipid found almost exclusively in the inner mitochondrial membrane where it plays an important role in mitochondrial energetic metabolism. CL is associated with different complexes of the respiratory chain, which are involved in the transduction of electrons and the production of ATP in the mitochondrial inner membrane. The CL is also involved in different stages of the mitochondrial apoptotic process and in mitochondrial membrane dynamics. Alteration of CL namely by oxidative modifications has been related with various pathological conditions, particularly in neurodegenerative diseases [1].

CL structure bearing four chains of fatty acids that can diversify in length and degree of unsaturation, is susceptible to oxidative damage by reactive oxygen species (ROS), due to the presence of the double bonds in fatty acyl chains, similarly to other phospholipids, CL. Their location, in the mitochondria, makes them even more likely to be oxidized, since that there is a considerable production of ROS in the inner mitochondrial membrane [2]. ROS, and mainly $^{\bullet}OH$, are involved in oxidative stress modification of different biomolecules, namely lipids, leading to changes in their structure and in consequence, loss of their function. In spite of the importance of CL oxidation and it biological consequence, there is a limited knowledge of the oxidation products of CL.

In this study, mass spectrometry coupled with liquid chromatography (LC-MS) was used to identify the specific oxidative modifications of tetra-linoleoyl CL induced by the $^{\bullet}OH$ generated under Fenton reaction conditions (H_2O_2 and Fe^{2+}). Short-chain products (with fatty acyl chains shortened) formed during CL oxidation were identified for the first time and were further characterized by LC-ESI-MS/MS. The short-chain products identified resulted from β-cleavage of oxygen-centered radicals and comprised aldehydes, hydroxyaldehydes and dicarboxylic acids, yielding abundant $[M-H]^-$ and $[M-2H]^{2-}$ ions. Detailed identification of the fragmentation of the precursor ions allowed the identification of specific product ions that allow their unequivocal assignment, which may be useful for their detection in biological samples.

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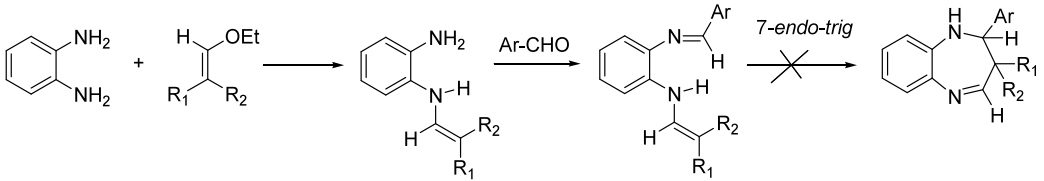
The reaction of *o*-phenylenediamine with ethoxymethylene compounds and aromatic aldehydes

Elina R. Marinho | Fernanda P. Proença

Centro de Química, Universidade do Minho, Campos de Gualtar, 4710-057 Braga, Portugal.

elinamarinho@sapo.pt

The treatment of psychiatric disorders is still an unsolved problem of our society and results, in part, from the diversity of receptors associated to this type of pathologies [1]. Schizophrenia is among the most serious mental illnesses; with a considerable social and economic impact and globally affects approximately 1% of the world population [2]. The present work is part of a project aiming at the synthesis of flexible analogs of clozapine, a golden standard for the treatment of schizophrenia, used when other medications fail due to severe adverse side effects, in particular agranulocytosis. Synthetic efforts were centred on the use of *o*-phenylenediamine as a precursor of disubstitued compounds, where different moieties were incorporated in each aromatic amino group. The basic synthetic approach, represented in the scheme, will be discussed in detail.



All the compounds were fully characterized by spectroscopic techniques and elemental analysis and were submitted for testing their antipsychotic activity and also to be used as ligands for the preparation of metal complex catalysts.

Acknowledgments

Thanks are due to Universidade do Minho and Fundação para a Ciência e Tecnologia (PPCDT/QUI/59356/2004) for financial suport.

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Influence of drying method on the colour of dried pears

Fatima Carrilha | Raquel Guiné | Maria João Lima | Dulcineia Ferreira

Escola Superior Agrária de Viseu / CI&DETS, Instituto Politécnico de Viseu, Quinta da Alagoa, Estrada de Nelas, 3500-606 Viseu

raquelguine@esav.ipv.pt

Colour is considered a fundamental property of foods, since it has been widely demonstrated that it correlates well with other physical, chemical and sensorial indicators of product quality [1]. In fact, colour plays a major role in the assessment of external quality in food industries and food engineering research. The measure of the standard colour of fruits and vegetables can be done by a wide range of colour spaces. However, the L*a*b* system is suggested as the best colour space for quantification in foods with curved surfaces [2]. Drying is one of the methods used for preserving foods, based on the removal of water to a level that minimizes microbial spoilage and deterioration reactions [3]. Pears of the variety S. Bartolomeu are traditionally dried in Portugal by a direct sun-exposure method. However, because of the disadvantages associated with this procedure, including not guarantying the sanitary quality and safety of the final product, in the past years alternative drying methodologies have been developed, such as solar stoves with natural or forced convection) and drying tunnel.

In the present work pears of the variety S. Bartolomeu were dried under different systems and their colour was evaluated using a colorimeter in the L*a*b* mode, as recommended by the Commission Internationale de l'Eclairage (CIE). The objective of this study was to compare the colour of the fruits produced by the different systems to find out which one allows the obtaining of a product as much as possible with the same colour of the traditional pears.

From the results obtained was possible to see that the drying carried out in the drying tunnel is the one that differs more from the traditional fruits.

Acknowledgments

The authors thank FCT for financial support through project PTDC/AGR-ALI/74587/2006.

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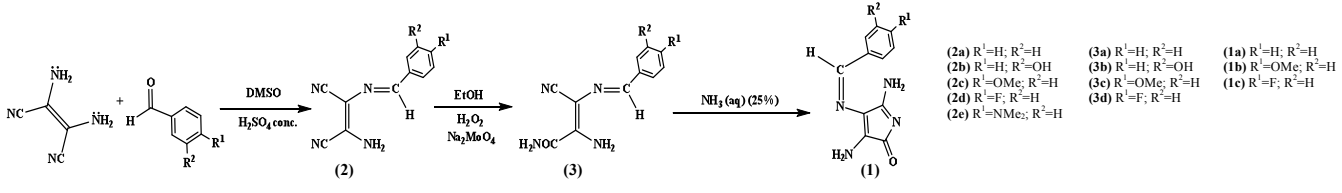
Synthesis and evaluation of antioxidant capacity of 2-oxopyrroles by cyclic voltammetry

F. O. Gomes | A. P. Bettencourt | M. A. Carvalho

Departamento de Química, Universidade do Minho, 4710-057, Braga, Portugal

figs8@hotmail.com

The aerobic organisms are exposed to reactive oxygen species (ROS), which potentiate redox reactions that can cause several diseases. Thus, there is a great interest in understanding and studying the control of oxidative stress by antioxidants. Phenolic antioxidants react with free radicals by a process that involves the transfer of the hydrogen atom. The pyrroles also contain an active hydrogen atom (NH), and by analogy, it is expected that this hydrogen atom can be transferred (HAT) to a free radical [1]. Numerous methods are used to measure the ability of a compound to act as an antioxidant, including chemical and electrochemical methods. The chemical methods rely on redox reactions with specific reagents (e.g.: DPPH·) while the electrochemical methods, namely cyclic voltammetry allow the evaluation of this activity, without the addition of reactants, acting the electrode as the specific reagent [2].
The work presented here describes the synthesis of novel pyrrole compounds of structure 1, and their precursors derived from combinations of diaminomaleonitrile (DAMN) with aldehydes and the assess to the antioxidant activity of each family using cyclic voltammetry. The voltammetric data will also be discussed considering the effect of the substituent groups.



(2a) R^1=H; R^2=H
(2b) R^1=H; R^2=OH
(2c) R^1=OMe; R^2=H
(2d) R^1=F; R^2=H
(2e) R^1=NMe$_2$; R^2=H

(3a) R^1=H; R^2=H
(3b) R^1=H; R^2=OH
(3c) R^1=OMe; R^2=H
(3d) R^1=F; R^2=H

(1a) R^1=H; R^2=H
(1b) R^1=OMe; R^2=H
(1c) R^1=F; R^2=H

Acknowledgments
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Extraction of biorefinery platform materials using ionic liquids

Filipe S. Oliveira [1,2] | João M. M. Araújo [2] | Mara G. Freire [1,2] | Rui Ferreira [2] | Luís P. N. Rebelo [2] | João A. P. Coutinho [1] | Isabel M. Marrucho [1,2]

[1] CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal
[2] Instituto de Tecnologia Química e Biológica, ITQB, Universidade Nova de Lisboa, Av. República, Apartado 127, 2780-901 Oeiras, Portugal

Sustainable economical growth requires safe resources of raw materials for the industrial production. Today's most frequently used industrial raw material, petroleum, is neither sustainable, because limited nor environmentally friendly.
While the economy of energy can be based on various alternative raw materials, such as wind, sun, water, biomass, the economy of substances is fundamentally depending on biomass, in particularly on biomass of plants. The development of biorrefineries represents the key for the access to an integrated production of food, feed, chemicals, materials, goods and fuels of the future.
Special requirements are placed to both, the substantial converting industry as well as research and development regarding the efficiency of the bio based product line as well as sustainability. The objective of this work is to evaluate the extraction capacity of Ionic Liquids regarding biorefinery platform materials, focusing on organic acids such as lactic, glutamic, succinic and malic acids. Several strategies were developed and will be presented.

Effect of high hydrostatic pressure on flavonoids extraction from hops (*Humulus lupulus*)

Fátima L. Sousa | Mickael C. Santos | Jorge A. Saraiva

QOPNA, Departamento de Química, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

fatima.sousa@ua.pt

Hop (*Humulus lupulus*) is an essential ingredient in beer production, imparting beer with several organoleptic and sensorial properties. Moreover, some hop constituents are now known to have important health promoting properties and is the case of flavonoids, a group of phenolic compounds. Particularly important is the case of xanthohumol, the main flavonoid of hop that has been shown to inhibit the development of tumors in the early stages, to reduce the proliferation of pre-adipocytic cells, to have sedative and anti-inflammatory activities among several others [2,3]. At least some of these flavonoids are passed to wort beer during wort boiling and in smaller amounts appear on beer, contributing to increase the health benefits of beer consumption [1]. Currently, for the sake of easier preservation and easiness of use, the beer industry uses hop extracts instead of hop itself. These extracts are usually produced by ethanol extraction, in a process that takes time and involves the use of temperature, what causes degradation of some of the flavonoid compounds showing health promoting characteristics.

This work aimed at evaluate the effect of High (Hydrostatic) Pressure (HP) at room temperature on extraction of flavonoids from hop, by quantifying total flavonoids. Various experimental conditions were tested, such as concentration of ethanol (10-90%, v/v), time of extraction under pressure of (1 and 5 min) as well as the ratio of hop to extraction solvent (from 5:1 to 200:1) and pressure level (200 or 400 MPa). Generally, extraction under pressure resulted in higher amounts of flavonoids. For instance, use of 30 and 50% of ethanol under pressure yielded similar results, compared to 90% ethanol at atmospheric pressure. Additionally, in the former case, much less extraction of chlorophylls was verified, resulting in an extract with a yellow color, while in the latter case a green colour was observed. This is an important advantage since chlorophylls presence in hop extracts for beer production is undesirable.

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Enhancing sensitizer delivery through skin for photodynamic treatments

Gonçalo F. F. Sá | João Mariani | Carlos Serpa | Luis G. Arnaut

Chemistry Department, University of Coimbra, 3004-535 Coimbra, Portugal

gsa@qui.uc.pt

The development of an efficient passive delivery of a sensitizer through skin requires strong manipulation of the parameters that control the interaction between the delivery formulation, the skin and the physical-chemistry characteristics of the drug. The widespread use of the transdermal pathway in Medicine is limited by the major obstacle that the *stratum corneum* represents to drugs in excess of 500 Da. The performance of chemical enhancers as adjuvant in passive delivery transforms this paradigm and opens up new frontiers [1]. In this work we explore the use of several chemical enhancers to efficiently deliver a porphyrin (>1000 Dalton) through the *stratum corneum*.

The delivery of the porphyrin into *ex vivo* minipig skin was tested with formulations containing three distinct chemical enhancers: oleic acid, *Azone*® and dimethylsulfoxide (DMSO). Their physic-chemistry proprieties differ widely, principally the 1-octanol-water partition coefficient, which is known to limit the flux of molecules from the formulation to the skin. Oleic acid is a lipophilic enhancer, *Azone*® neutral and DMSO a hydrophilic one.

It is shown that formulation stability and passive delivery of porphyrins is enhanced when a neutral absorption promoter is used.

Acknowledgments
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The effect of spacer chain length of 12-s-12 Gemini surfactants in the host-guest association with β-cyclodextrin: ^{1}H NMR and ROESY study

Hugo A. Correia [1] | Rui A. Carvalho [1] | Olle Soderman [2] | Artur J.M. Valente [3]

[1] Department of Life Sciences and Center of Neurosciences, University of Coimbra, 3001-401 Coimbra, Portugal
[2] Physical Chemistry 1, Lund University, P.O. Box 124, Se 22100 Lund, Sweden
[3] Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal

haragog@gmail.com

Cyclodextrins (CD) are macrocycles with the shape of a hollow truncated cone. Its hydrophilic exterior and hydrophobic interior enables it to form complexes with a wide range of molecules. This ability is explored in multiple applications. In this study we investigated the host-guest association between β-CD and a gemini surfactant (GS). GS are molecules with two amphiphilic moieties in which the hydrophilic head groups are connected by a spacer of varying length and therefore flexibility. GS have low CMC values compared to the corresponding surfactants of equivalent chain length. We have used GS with a varying methylene spacer length from 2 to 10.
One dimensional proton NMR as well as ROESY experiments were carried out in order to investigate the inclusion mode of the gemini surfactant, especially with emphasis on the influence of spacer lengths. In this work, the association stoichiometry and the association constants for β-CD:12-*s*-12 ($2 \leq s \leq 10$) aqueous systems, at 25 ºC, is presented. It was employed the continuous variation method (Job's plot) to evaluate the association stoichiometry [1]. The analysis of chemical shifts of CDs, upon variation of the GS concentrations, shows that the interaction is predominantly 1:2 (GS:CD), being the second association cooperative. The role of the experimental method in the computation of *K* values is also evaluated [2].

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Effect of post-polymerization treatment on monomer content of an acrylic biomaterial

Helena Ferrão | Cristina Neves | Luís Pires Lopes | Matilde Castro | Ana Bettencourt

iMed.UL, Faculty of Pharmacy, University of Lisbon, Av. Prof. Gama Pinto, 1649-003 Lisbon, Portugal

asimao@ff.ul.pt

Hard chair-side reline resins are acrylic based prosthetic biomaterials used to provide a better fit of removable denture bases to oral mucosa. The composition of these biomaterials is based on polyethylmethacrylate, whereas, the liquid composition varies among materials and can contain isobutylmethacrylate (IBMA). During the polymerization reaction, the conversion of monomer into polymer is not complete and different amounts of unreacted monomers remain in the polymerized resin. These residual monomers (RM) are suspected of being a contributing factor for allergic reactions of the oral mucosa when released into the medium. Methods for decreasing RM content like immersion in hot water and microwave irradiation have been described as post-polymerization treatments [1, 2].
Objectives: 1) Optimization of a quantification method for IBMA by high performance liquid chromatography (HPLC) and 2) Evaluation of the effect of a new post-polymerization treatment based on ethanol solutions on RM content of a hard chairside reline resin (Kooliner). *Methods:* Method optimization was performed by studying linearity, precision, limits of detection and quantification and accuracy. Post-polymerization treatment consisted in incubating Kooliner specimens in water, 20%, 50% or 70% ethanol solutions at 23±2oC or 55±2°C for 10 minutes. HPLC was used for the determination of RM content (n = 60). The data was analysed by ANOVA followed by Tukey tests at α= 5%. *Results:*1) Method optimization: quantification method was linear between 5 and 160 μg mL^{-1} for IBMA. Adequate assay for intra- and inter-day precision and accuracy was observed. The limits of detection and quantification were 1,286 and 4,285 μg mL^{-1}, respectively. 2) Post-polymerization treatment: ethanol increased the leaching of RM from the polymer. The immersion of Kooliner specimens in ethanol solutions at 55±2°C had a significant reduction on RM content (Fig. 1). Overall, the immersion of relined dentures, in specific ethanol solutions at 55 ºC for 10 minutes can be considered an effective post-polymerization treatment to reduce the amount of RM of Kooliner material.

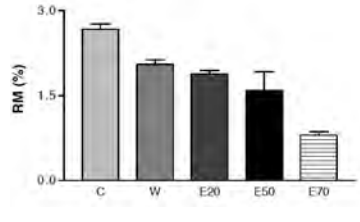

Fig.1. RM (%); 55±2ºC.

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Effect of climate on PM concentration and size distribution in two sites in the city of Lisbon

Hugo F. Silva [1] | Manuel J. Matos [1] | Cristina Oliveira [2] | A. F. Ferreira [2] | João C. Oliveira [2] | Paula Cantinho [1] | Marta Calado [1] | César Oliveira [3] | Natércia Martins [3] | Casimiro Pio [3] | M. Filomena Camões [2]

[1] DEQ-High Engineering Institute of Lisbon, Lisbon, Portugal
[2] CCMM/DQB- Faculty of Science, University of Lisbon, Portugal
[3] CESAM, Aveiro University, Aveiro, Portugal

cmoliveira@fc.ul.pt

Ambient particulate matter (PM) is a complex mixture of inorganic and organic compounds aggregated with water and present in the atmosphere in different sizes. The most important aerosol fraction, due to the hazardous health effects it causes, is the fine fraction, usually considered PM2.5. European environmental laws impose limits for air particle concentrations in cities. In Lisbon, at high traffic sites, like Avenida da Liberdade, legal limits are often exceeded, namely in summer. Several studies showed that meteorological factors affect PM concentrations within urban areas, with dispersion being more effective under high local wind speed conditions; in rainy days PM concentrations decrease. These effects depend on the particles size.
In this study we have monitorized two sites in Lisbon: Avenida da Liberdade, owing to its high car traffic and Olivais, an urban background site. Sampling campaigns were carried out in the summer of 2008 and in the winter of 2008/2009. Particulate matter was collected on nuclepore filters in a cascade impactor using a low volume sampler (coarse fraction, PM10-2.5 and fine fraction, PM2.5.
Principal Component Analysis (PCA) of the results of PM concentrations for the two sites and for both size fractions gives evidence of their dependence on meteorological conditions.

Acknowledgments
This work was performed under Project PAHLIS (PTDC/AMB/65699/2006) financed by "Fundação para a Ciência e a Tecnologia". João C. Oliveira and César Oliveira acknowledge FCT for their grants.

Comparative study of the drying kinetics of pears for different drying systems

Inês Almeida | Raquel Guiné | Maria João Lima | Dulcineia Ferreira

Escola Superior Agrária de Viseu / CI&DETS, Instituto Politécnico de Viseu, Quinta da Alagoa, Estrada de Nelas, 3500-606 Viseu

raquelguine@esav.ipv.pt

Open-air sun drying has been used since immemorial times to dry grains, vegetables, fruits and other agricultural products. This is a common method used to preserve foods and it is practiced until today in many countries where the combination of solar radiation, temperature and relative humidity is appropriate. However, despite being a cheap method, the open-air natural sun drying is not always applicable to large-scale production [1].

"Pera Passa de Viseu" denominates a traditional food product produced from pears of the variety S. Bartolomeu (*Pyrus communis L.*) using a traditional solar drying method, which is based on an open-air exposure [2]. Notwithstanding being quite a cheap drying method, making use of the sun as energy source, it has some very important disadvantages, like for example, the process is slow and very much dependent on weather conditions, and the quality of the product is not satisfactorily taking into account factors such as pollution from dust or from animal contamination or other types of infestation and microbial or mould contamination in humid environments. Therefore, the development of alternative drying methodologies assumes a pivotal role.

The pears used in the present study were dried uncut after peeling, in three different systems: solar stove with forced convection, solar stove with natural convection and drying tunnel. The moisture content of the pulp was quantified along drying with a Halogen Moisture Analyzer. The objective of the present work is to fit the kinetic data to different models found in literature to describe the drying rates of food products, in order to compare the drying rates in the different systems tested and also to find out which model is best to describe the drying kinetics of these pears.

Acknowledgments

The authors thank FCT for financial support through project PTDC/AGR-ALI/74587/2006.

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An NMR metabonomic study of the response of osteosarcoma cells to CisPlatin ($Pt(NH_3)_2Cl_2$, CDDP)

Inês Lamego [1] | Joana Marques [1] | Maria Paula M. Marques [2] | Iola F. Duarte [1] | Ana M. Gil [1]

[1] CICECO, Department of Chemistry, University of Aveiro, Aveiro, Portugal
[2] Unidade I&D Química Física Molecular, University of Coimbra, Coimbra, Portugal

ineslamego@ua.pt, agil@ua.pt

Cell metabonomics is an appealing approach in drug testing and development, especially since NMR enables the direct assessment of cells composition and follow-up of metabolome changes [1,2]. This communication describes the use of high resolution magic angle spinning (HRMAS) NMR to analyse osteosarcoma MG-63 cells which have been exposed to cisplatin (CDDP), a drug commonly employed in the treatment of this and other types of cancer.

In order to assess the time course effects of different drug doses on the cells metabolic profile, cell samples collected at different time points after treatment with 0 (control), 30 and 50 μM CDDP were mechanically lysed and analysed by HRMAS NMR. The spectral data were then interpreted using signal integration (to determine quantitative variations), and multivariate statistical tools, such as Principal Component Analysis (PCA), Partial Least Squares Discriminant Analysis (PLS-DA) and Orthogonal Projections to Latent Structures (O-PLS)-DA. The application of O-PLS-DA to the whole spectral range (δ 0.25-10) and its sub-regions resulted in the clear separation between control and CDDP-treated cells; the metabolite signals identified in the corresponding loadings to be responsible for this separation were then integrated and their quantitative variations followed over time in both control and CDDP-treated cells. It was found that, at 48 hours (last time point measured), CDDP-treated cells were characterised by increased levels of lipids, lactate, and glycerophosphocholine and decreased levels of *myo*- and *scyllo*-inositol, inosine/adenosine, alanine and other amino acids, compared to controls. These results show that the drugs metabolic impact may be studied by NMR-metabonomics, providing a tool for evaluation of drug action and efficacy.

Acknowledgments
Funding is acknowledged from FCT, Portugal (FCT/PTDC/SAU-BEB-66896/2006 and FCT-DFRH-SFRH/BD/63916/2009), the Associate Laboratory IBMC-INEB (for kindly providing the MG-63 cell line) and CRMN- Centre de RMN à Très Hauts Champs, CNRS / ENS Lyon, France (for access to 700MHz NMR spectrometer).

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Conformational changes of Dengue virus capsid protein upon lipids interaction

Ivo C. Martins [1] | Ronaldo Mohana-Borges [2] | Fábio Almeida [2] | Fabiana A. Carneiro [2] | Miguel Castanho [1] | Nuno C. Santos [1] | Andrea T. Da Poian [2]

[1] Instituto de Medicina Molecular (IMM), Faculdade de Medicina da Universidade de Lisboa (FMUL), Av. Egas Moniz, 1649-028, Lisboa, Portugal
[2] Centro de Ciências da Saúde (CCS), Universidade Federal do Rio de Janeiro (UFRJ), Ilha do Fundão, 21941590, Rio de Janeiro, Brasil

ivomartins@fm.ul.pt

Dengue virus (DV), a member of the *Flavivirus* genus, is the major causative agent of viral hemorrhagic fever, for which, after infection occurs, no specific and effective treatment is currently available [1]. This is partially due to the lack of knowledge on the basic aspects of the viral life cycle, namely the molecular mechanisms of viral assembly and encapsidation [1]. This process is mediated by the dengue virus capsid protein (DVCP) through the interaction with RNA [2, 3] and, possibly, lipid droplets [4]. The molecular details of this process are not understood yet [1, 4]. We hypothesized that DVCP interaction with lipid droplets may involve specific residues, promoting the binding to RNA and then tested this hypothesis by circular dichroism (CD), nuclear magnetic resonance (NMR) and protein sequence comparison via the BLAST algorithm. CD analysis shows a decrease in α-helical content upon interaction, suggesting that residues within the protein α-helices may play a role in the interaction. NMR analysis co-substantiates this and also implies that the interaction occurs via specific residues located in the *α2-α2* region of the protein and that upon this initial interaction, conformational changes may be transmitted to the *α4-α4* region of the protein, a postulated RNA-binding region [3]. Moreover, NMR also demonstrates that residues within the protein N-terminus (5-26) interact with lipid droplets. Consistent with this finding, the BLAST analysis of DVCP against non-redundant proteins reveals an N-terminus conserved motif among *Flavivirus* spp. (NMLKRXXXRV, residues 14-23). Taking all of the above into account, we propose that DVCP specifically interacts with lipid droplets via the N-terminus conserved region and the hydrophobic pocket formed by the *α2-α2* region, after which conformational changes that facilitate the binding of the *α4- α4* region of DVCP to RNA occur, allowing the dengue virus assembly and encapsidation to proceed.

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Energetic study of the monofluorinated benzonitriles. The influence of the fluorine atom in the CN bond

Inês M. Rocha | Ana Filipa L. O. M. Santos | Manuel A. V. Ribeiro da Silva

Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007, Porto, Portugal

inesmrocha@gmail.com

In the present work, the energetic study of the three monofluorinated benzonitrile isomers was made using two experimental techniques: rotating-bomb calorimetry [1], to determine the standard (p^o = 0.1 MPa) molar enthalpies of combustion in oxygen, from which the standard molar enthalpies of formation, in the crystalline phase, were derived, and Calvet microcalorimetry [2] from which data was possible to calculate the standard molar enthalpies of vaporization and sublimation (for 4-fluorobenzonitrile isomer), at T = 298.15 K. The combination of the values of the standard molar enthalpies of formation, in the crystalline phase, and of the standard molar enthalpies of vaporization/sublimation, allowed the calculation of the enthalpies of formation, in the gaseous phase, at T = 298.15 K.
The results are discussed based on the relationships between structural properties and the energetic of chemical bonds. Using the values of the Carbon-13 NMR and of the effective atomic charges calculated computationally, it was possible to evaluate the influence of the fluorine atom in the CN bond.

Acknowledgments
I.M.R. and A.F.L.O.M.S. thank FCT and the European Social Fund (ESF) under the Community Support Framework (CSF) for the award, respectively, of the Ph.D. research grant (SFRH/BD/61915/2009) and the post-doctoral fellowships (SFRH/BPD/41601/2007).

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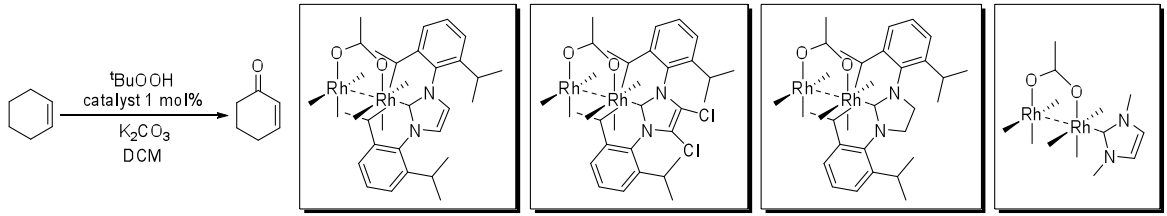
Allylic oxidation of alkenes using NHC Dirhodium(II) complexes as catalyst

Jaime A. S. Coelho | Alexandre F. Trindade | Pedro M. P. Góis | Carlos A. M. Afonso

CQFM – Centro de Química-Física Molecular and IN – Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, Complexo I, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

jaimeacoelho@gmail.com

Dirhodium(II) complexes, specifically Rh_2(caprolactam)$_4$, have been recently reported as catalysts in allylic oxidation of alkenes with *tert*-butyl hydroperoxide. The methodology was also applied to oxidation of steroids, for which was recently filled a patent [1]. On the other hand, it has been shown that a dirhodium(II) complex with acetates as bridging ligands have limited activity in this transformation. However, the coordination of N-heterocyclic carbene (NHC) in the $Rh_2(OAc)_4$ resulted in shift on the half wave oxidation potential providing an active oxidation catalyst. Herein, we wish to present our results in the optimization of the reaction. It was studied the impact on the yield and selectivity of cyclohexene oxidation to cyclohexenone of variables such as: NHC ligand, type and quantity of base, oxidant quantity, solvent, atmospheric conditions and temperature [2].



Acknowledgments
Fundação para a ciência e a Tecnologia (SFRH/BD/30619/2006 and PTDC/QUI/66695/2006)

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Thermodynamic and structural study of terthiophene isomers

José C. S. Costa | Carlos F. R. A. C. Lima | Luís M. N. B. F. Santos

Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, R. Campo Alegre, 687 4169-007 Porto

jc.costa.87@gmail.com

This work is part of a wider project dealing with the thermodynamic study of conducting polymers [1]. The thermodynamic study of the phase transitions (fusion and sublimation) of 2,2′:5′,2″-Terthiophene and 3,2′:5′,3″-Terthiophene will be presented and will be used to evaluate the structural effect in the solid-liquid and solid-gas equilibrium. The structure of the compounds studied is presented in Fig. 1.

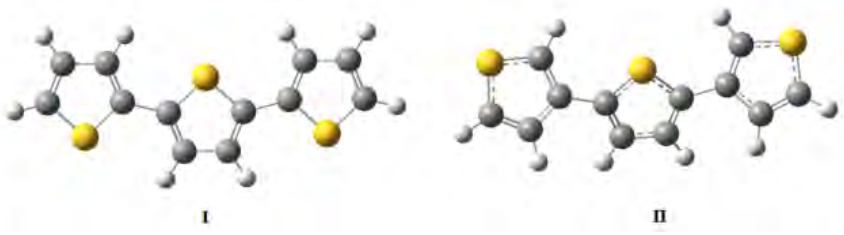

Fig. 1. I: 2,2′:5′,2″-Terthiophene; II: 3,2′:5′,3″-Terthiophene

For each of these compounds, the vapor pressures at different temperatures were measured by the Knudsen effusion method based on the vacuum quartz crystal micro balance. The temperature, molar enthalpies and entropies of fusion were measured in a power compensated differential scanning calorimetry (DSC) (SETARAM model 141). Based on the previous results, the standards molar enthalpies, entropies and Gibbs function of sublimation were derived at 298.15 K. The relationship between structure and energetics will be discussed based on the experimental energetics results and ab-initio calculations.

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Synthesis of porphyrin dyads via click chemistry

Joana I. T. Costa | Augusto C. Tomé | Maria G. P. M. S. Neves | José A. S. Cavaleiro

Departamento de Química/QOPNA, Universidade de Aveiro, 3810-193 Aveiro, Portugal

The Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of alkynes and azides, to give 1,4-disubstituted 1,2,3-triazoles, has been classified as a "click" reaction because of its high yielding, high atom efficiency and selectivity. The Cu(I)-catalyzed 1,3-dipolar cycloaddition has emerged as powerful linking reaction and found widespread applications ranging from combinatorial drug research, material science, to bioconjugate chemistry. However, the reports on application of this "click" reaction protocol to porphyrin chemistry are scarce [1-5].
In this communication we will report the synthesis of porphyrin dyads generated from the reaction of meso- tetrakis(pentafluorophenyl) porphyrin derivatives containing alkyne and azide groups via "click" chemistry. The structures of the new compounds were unambiguously established by spectroscopic data (mass spectrometry and NMR spectroscopy).

Acknowledgments
Thanks are due to FCT/FEDER for funding the Organic Chemistry Research Unit and the Project PTDC/QUI/74150/2006.

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Analysis of polyphenols in wines by LC-MS

J.C. Dias | J.M. Ribeiro | A.P. Bettencourt | M.D. Geraldo

Departamento de Química, Universidade do Minho, 4710-057, Braga, Portugal

jchris_01@hotmail.com

Phenolic compounds or polyphenols are substances widely distributed in most fruits and vegetables. They are characterized by being biologically active substances and are also classified as flavonoids, lignins and hydrolysable tannins. Interest in analysis of phenolic compounds has increased due to their antioxidant properties leading to significance in health, namely for prevention of cardiovascular diseases, cancer and other diseases related to aging [1]. These compounds act as antioxidants, not only due to its ability to donate electrons and hydrogen ions to free radicals, but also because of the stability of the formed radical intermediates, thus preventing the damage of cellular proteins and lipids or the formation of DNA adducts, which are targets of free radicals [2].

In this work a method for the analysis of two polyphenols, catechin and gallic acid, by LC-MS was developed. The optimization of the experimental parameters for both compounds were performed and the calibration curves of the peak area obtained using the mass detector (SIM-MS) and/or PDA detector versus catechin and gallic acid concentrations were obtained. The method was applied to the analysis of white wines. To validate the developed method several figures of merit such as working range, sensitivity, analytical thresholds, reproducibility, accuracy and selectivity were determined.

Acknowledgments

J.C. Dias acknowledges to FCT for the Integration into Research Grant, Centro de Química, Universidade do Minho.

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Smart magnetic core-shell nanoparticles for protein separation

Leila Moura | José Paulo S. Farinha

Centro de Quimica Fisica Molecular, Instituto Superior Técnico, 1049-001 Lisboa, PORTUGAL

leila.moura@ist.utl.pt

We synthesized and characterized polymer core-shell nanoparticles with a magnetic core and a stimuli-responsive shell constituted by a copolymer of *N*-isopropylacrylamide (NIPAM) and acrylic acid (AA) that collapses onto the core, either by increasing the temperature, decreasing the pH or increasing the ionic force (Fig. 1). The particle core is constituted by poly(methylmethacrylate) (PMMA) with "entrapped" Fe_3O_4 magnetic nanoparticles and the shell is a crosslinked copolymer of NIPAM and AA with N,N'-metilenobisacrilamide (MBA). The particles are prepared in two steps. In the first step, the magnetic nanoparticles were produced by co-precipitation from a basic Fe^{3+}/Fe^{2+} aqueous solution. These particles were coated with oleic acid, to promote their stability in organic media. In the second step, the oleic acid coated magnetic nanoparticles were first dispersed in a mixture of MMA (methylmetacrilate) (monomer) and hexadecane (hydrophobic costabiliser) to form the organic part of the emulsion. Then, water and sodium dodecyl sulphate (emulsifier) are added and the emulsion is subjected to sonication to form a miniemulsion. The polymerization is initiated at 70 ºC after the addition of potassium persulfate (KPS). At 80% conversion of the MMA, shots containing the shell constituents are added. The stimuli-responsive magnetic nanoparticles are used as cationic adsorbent and assessed for their binding capacity towards IgG. Magnetic separation, binding and eluting conditions will be optimized. The selectivity of the process will be evaluated in the separation of IgG from a protein mixture.

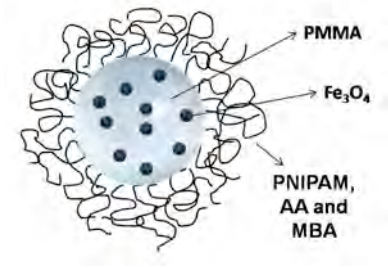


Fig. 1. Scheme of the structure of the final nanoparticles

Acknowledgments
This work was partially supported by Fundação para a Ciência e a Tecnologia (FCT, Portugal) and POCI 2010 (FEDER) within project PDCT/CTM/68451/2006.

First approach to organic secondary building units. Potassium 4,4'-biphenyldicarboxylate included in β-cyclodextrin

José Fernandes | Filipe A. Almeida Paz | Paulo J. Ribeiro-Claro | Susana S. Braga | João Rocha

CICECO, Department of Chemistry, Universidade de Aveiro, Campus de Santiago, 3810-193 Aveiro

jafernandes@ua.pt

Uni-, bi- or tridimensional coordination polymers are one new class of materials prepared in CICECO. These materials can be prepared by reacting the so-called Secondary Building Units with bridging ligands. An SBU comprises an unsaturated coordination compound with straightforward synthesis and predictable reactivity. The bridging ligands are usually ditopic, comprising simple organic compounds. Instead of these simple organic compounds we aim to use some of these included in cyclodextrins as more complex bridging ligands. These require previous synthetical work, and because they form supramolecular assemblies they represent a new type of SBUs.
The first inclusion compound to be prepared was potassium 4,4'-biphenyldicarboxylate (K_2bpdc) in β-CD. The formation of this inclusion compound was studied by preliminary theoretical calculations before synthetical work. Nuclear Magnetic Resonance studies proved that K_2bpdc@β-CD has a considerable stability in liquid state, which is a favourable factor for its use as organic SBU. Two different crystalline structures were obtained. One comprises a 1:1 inclusion with an unprecedented crystalline structure having a large water layer. The other comprises a mix of 1:1 and 2:1 compound in the same crystal, which is remarkably rare.

Acknowledgments
We are grateful to FCT for financial support to J. A. P. through the post-doc scholarship PTDC/QUI/65805/2006

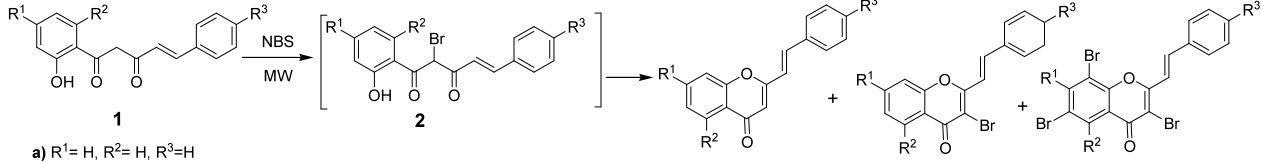
An efficient and solvent-free microwave-assisted synthesis of 3-halo-2-styrylchromones

Joana P. A. Ferreira | Vera L. M. Silva | Artur M. S. Silva | José A. S. Cavaleiro

Department of Chemistry and QOPNA, University of Aveiro, 3810-193 Aveiro, Portugal

jpferreira@ua.pt

3-Halo-2-styrylchromones are valuable intermediates to be efficiently converted into other biological interesting compounds by simple chemical transformations. However there are few reports on methods to prepare these compounds [1]. An efficient and solvent free protocol for the synthesis of 3-halo-2-styrylchromones is reported. Microwave heating of a mixture of 1,3- diketones **1** and *N*-bromosuccinimide at 800 W power resulted in high yield conversion into the corresponding 3-halo-2-styrylchromones **4**. An halogenation followed by a cyclodehydrohalogenation transformation occur in only one step and the easy set up and purification tasks of this sustainable method make it interesting for the synthesis of these valuable scaffolds. The solvent free protocol make it more ecologically desirable than the already known methods for the synthesis of 3-halo-2-styrylchromones [2].



a) R^1= H, R^2= H, R^3=H
b) R^1= H, R^2= H, R^3= OCH_3
c) R^1= H, R^2= H, R^3 = Cl
d) R^1= H, R^2= H, R^3 = NO_2
e) R^1= OCH_3, R^2= OCH_3, R^3= H

Acknowledgments
Thanks are due to Fundação para a Ciência e Tecnologia (FCT), to University of Aveiro and FEDER for funding the Organic Chemistry Research Unit (QOPNA). Joana P. A. Ferreira is also thankful to FCT for the PhD grant (SFRH/BD/45107/2009).

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Thermochemical study of three difluorinated nitrobenzenes

Juliana A. S. A. Oliveira | Ana I. M. C. Lobo Ferreira | Manuel J. S. Monte | Manuel A. V. Ribeiro da Silva

Centro de Investigação em Química, Department of Chemistry, Faculty of Science,University of Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal

oliveira.juliana@live.com.pt

It is extensively described in the literature the use of halogenated nitrobenzenes as basic chemical intermediates in the synthesis of various aromatic compounds with important pharmaceutical, industrial and agricultural applications. Despite their relevant applications, the energetics of these compounds is not yet fully documented.

As part of a broad research project on the systematic study of the energetics of halogenated organic compounds [1,2], being carried out in the University of Porto Chemical Research Center, we have studied the thermochemistry of three difluoronitrobenzene isomers: 2,4-difluoronitrobenzene; 2,5-difluoronitrobenzene and 3,4-difluoronitrobenzene.

The standard (p^o = 0.1 MPa) molar enthalpies of formation in the liquid phase, at T = 298.15 K, were derived from the respective massic energies of combustion, determined by rotating-bomb combustion calorimetry. The vapor pressure study was done on a static apparatus, equipped with a capacitance diaphragm gage [3], from which the phase diagrams of the studied compounds were elaborated and the respective triple point coordinates and the standard molar enthalpies of vaporization, at T = 298.15 K, were determined. The combination of the referred thermodynamic parameters yielded the standard (p^o = 0.1 MPa) molar enthalpies of formation in the gaseous phase, at T = 298.15 K, of the studied compounds. These experimental values were compared with the ones estimated by the Cox Scheme [4] and interpreted in terms of molecular structure.

Acknowledgments

Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal and to FEDER for financial support to Centro de Investigação em Química (CIQ), University of Porto. A. I. M. C. L. F. thanks FCT and the European Social Fund (ESF) under the Community Support Framework (CSF) for the award of the post-doctoral fellowship (SFRH/BPD/27053/2006).

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Exploratory chemistry focused on the synthesis of 6-deoxy-D-glucal

João P. Pais | João Sardinha | Alice Martins | Amélia P. Rauter

Grupo da Química dos Glúcidos, Centro de Química e Bioquímica/Departamento de Química e Bioquímica da Faculdade de Ciências da Universidade de Lisboa, Ed C8, Piso 5, Campo Grande, 1749-016 Lisboa, Portugal

jota_vs@hotmail.com

6-deoxy glycals are valuable precursors for a variety of key transformations in carbohydrate chemistry and synthons of antibiotics against *Bacillus* species, *Enterococcus faecalis and Listeria monocytogenes* [1,2]. In this work we present synthetic approaches and reactions optimization for deoxygenation of D-glucose position 6 focusing on the preparation of 6-deoxy D-glucal (IUPAC name: 1,5- anhydro-2,6-dideoxy-D-*arabino*-hex-1-enitol), which may be regarded as a key precursor of a variety of bioactive molecules. Hence, exploratory chemistry was initiated on D-glucose, an easily available and non-expensive sugar. The approaches explored are based on regioselective transformation/protection of the primary alcohol and subsequent reduction. The reactions exploited make use of triphenylphosphane/iodine/imidazole and reduction of the intermediate iodide, selective protection with TBDMS or with trityl ethers, bromination and reduction with Bu_3SnH, with additional protection/deprotection steps, when necessary. The results obtained will be presented and discussed.

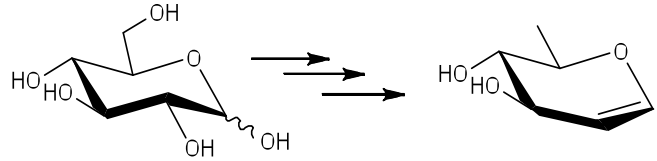

Fig. 1. D-Glucose as a starting material for the synthesis of 6-deoxy-D-glucal.

Acknowledgments
Fundação para a Ciência e a Tecnologia (FCT) is gratefully acknowledged for the Post-Doc research grant of Alice Martins and the research grant (BI) of João Pedro Pais.

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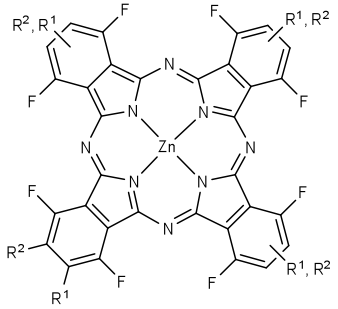
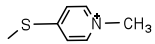
Multi-charge phthalocyanines for microorganisms photoinactivation

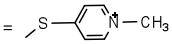
Joana Pereira | Eliana Carvalho | Graça Neves | José Cavaleiro | Ângela Cunha | Adelaide Almeida | João Tomé

QOPNA, Department of Chemistry, Department of Biology, University of Aveiro, 3810-193 Aveiro, Portugal

jbp@ua.pt



1 $R^1 = R^2 =$ 

2 $R^1 = F$ and $R^2 =$ 

Photodynamic therapy (PDT) is based on the uptake of a photosensitizing dye by target cells, which are damaged by reactive oxygen intermediates generated upon irradiation with light. This emergent therapy is being used in tumor
treatment and more recently to treat bacteria, fungi and viruses infections [1]. Phthalocyanines (Pcs) are second generation photosensitizers due to their strong absorption in the red region of the spectrum, allowing a deeper light penetration in living tissues. However, one of the main disadvantages of Pcs is the low solubility in physiological fluids, which is essential to their *in vivo* administration. So, in order to obtain water-soluble Pcs, the macrocycle periphery must contained adequate substituents. Pyridinium substituents definitively improve water solubility, and have advantages over neutral and anionic substituents, mainly by enhancing cell uptake by Gram-negative bacteria, resulting in more efficient photosensitizers [2]. In this work, we will discuss the synthesis, characterization and preliminary results of bacteria photoinactivation experiments.

Acknowledgments
Thanks are due to University of Aveiro, FCT (Lisbon) and FEDER for funding the QOPNA unit and the project PTDC/QUI/65228/2006.

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Quantification of antioxidants in foodstuff by LC-MS

J.M. Ribeiro | J.C. Dias | A.V. Ferreira | A.P. Bettencourt | M.D. Geraldo

Departamento de Química, Universidade do Minho, 4710-057 Braga, Portugal

joana-m-ribeiro@hotmail.com

Antioxidants are present in many foodstuffs such as fruits, vegetables, teas and wines [1]. Their role in the prevention of cardiovascular diseases, degenerative diseases and even cancer is well-known therefore it is crucial the development of methods for its quantification in foods [2]. The most abundant antioxidants in these foods are phenolic compound namely catechin, propyl gallate and gallic, caffeic, ferulic, vanillic and syringic acids.

In this work a method for the analysis of several phenolic compounds in foodstuffs by LC-MS was developed. The conditions of analysis, including flow and polarity of the eluent were optimized. The method validation was carried out considering the performance parameters of the method: detection and quantification limits, working range, linearity, sensitivity, reproducibility and accuracy. The method was applied to the analysis of samples of teas, strawberries, juice and wine.

Acknowledgments

Financial support from the Centro de Química, Universidade do Minho is acknowledged.

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Screening of pharmaceutical co-crystals

João D. B. Ribeiro [1] | Ricardo A. E. Castro [2] | Teresa M. R. Maria [1] | M. Ramos Silva [3] | A. Matos Beja [3] | João Canotilho [2] | M. Ermelinda S. Eusébio [1]

[1] Department of Chemistry | [2] Faculty of Pharmacy | [3] Department of Physics, University of Coimbra, 3004-535 Coimbra, Portugal

jdb.ribeiro@gmail.com

Pharmaceutical co-crystals represent an innovative strategy to successfully improve the solubility, and therefore the oral bioavailability, of an active pharmaceutical ingredient (API) by using suitable molecules as the co-crystal formers [1]. Compound A presents a functional acid group and it is a non-steroidal anti-inflammatory drug (NSAID) that belongs to Class II (high permeability, low solubility) of the Biopharmaceutics Classification System (BCS) [2].

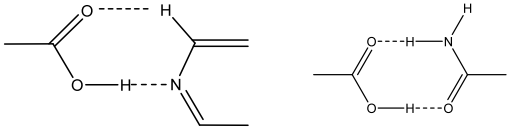

Fig. 1. Supramolecular heterosynthons

Cambridge Structural Database (CSD) analyses of pharmaceutical co-crystals indicate that the supramolecular heterosynthons presented in Fig. 1 are strongly favored over their respective COOH···HOOC supramolecular homosynthon [3]. A screening of compound A co- crystals with co-formers picolinamide, nicotinamide and isonicotinamide, is performed by mechanochemistry. The solids obtained are characterized by differential scanning calorimetry, DSC, polarized light thermomicroscopy, PLTM, infrared spectroscopy, FTIR, and X- ray powder diffraction, XRPD.

Acknowledgments
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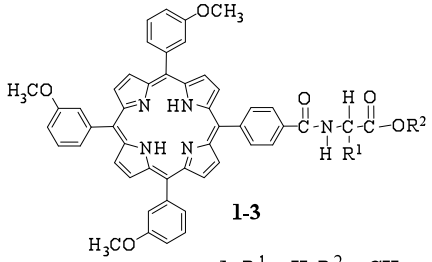
Porphyrin amino acid conjugates: photostability and singlet oxygen determination

João M. M. Rodrigues | V. Vaz Serra | M. G. P. M. S. Neves | M. A. F. Faustino | J. A. S. Cavaleiro

Departamento de Química/QOPNA, Universidade de Aveiro, 3810-193 Aveiro, Portugal

jrodrigues@ua.pt



1-3

1: $R^1 = H$; $R^2 = CH_3$;
2: $R^1 = CH_2OH$; $R^2 = CH_3$.
3: $R^1 = CH_2C_6H_4OH$; $R^2 = H$;

Porphyrins are present in several biochemical systems, which are responsible for vital processes such as transport and storage of oxygen. In the last decades, a large number of porphyrins have been extensively exploited as photosensitizers (PS) for Photodynamic Therapy (PDT) [1]. This photodynamic process uses a photosensitizer agent and light of adequate wavelength to generate cytotoxic oxygen species namely singlet oxygen, considered the principal responsible for cancer cells death. However, porphyrin derivatives can also go through photobleaching when exposed to UV-Vis light and oxygen. A fast photobleaching would cause the concentration of the drug to decrease, thus impairing the effectiveness of the treatment. So, the determination of singlet oxygen and the photostability are very important parameters to evaluate the possible application of a porphyrin as PS for PDT [2]. Following our interest on the synthesis and biological evaluation of new porphyrin derivatives, with potential application in Medicine, we will consider in this communication the photostability and singlet oxygen determination of porphyrin amino acids conjugates **1**-**3**, recently prepared in our laboratory.

Acknowledgments
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Polyoxometalate/silica nanomaterials as heterogeneous catalysts

Joana Sousa [1] | Isabel Santos [2] | Mário Simões [2] | José Cavaleiro [2] | Helena Nogueira [1] | Ana Cavaleiro [1]

[1] CICECO | [2] QOPNA, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

joanasousa@ua.pt

Polyoxometalates (POMs) already proved to be efficient catalysts for oxidative transformations, namely for the epoxidation of olefins with H_2O_2 in homogeneous conditions [1]. The immobilization of these well-known catalysts in solid supports offers some advantages for catalysis, like easier recovery and recycling or increased stability of the catalyst. In particular, the use of nanoscale materials as support for those species can originate new heterogeneous nanocatalysts, which show additional advantages when compared with other porous catalysts [2].

In the present work, an iron(III) mono-substituted POM with the Keggin structure, $[PW_{11}Fe^{III}(H_2O)O_{39}]^{4-}$ ($PW_{11}Fe$), and a sandwich-type tungstophosphate of formula $[(PW_9O_{34})_2Fe^{III}_4(H_2O)_2]^{6-}$ $[(PW_9)_2Fe_4]$, both in the potassium salt form, were supported in silica nanoparticles using a method based on water-in-oil (w/o) microemulsions [3]. It was possible to characterize the morphology of the resulting POM/SiO_2 composites by transmission electron microscopy (TEM) as nanospheres with approximately 30 nm in diameter (Fig. 1). The catalytic behaviour of these two POM/SiO_2 nanomaterials was studied in the epoxidation of some monoterpenes, namely geraniol, nerol and linalool, using H_2O_2 as the oxygen source. The experimental details and results will be presented in this communication.

Fig. 1. TEM image of the $(PW_9)_2Fe_4/SiO_2$ nanomaterial.

Acknowledgments

Thanks are due to the University of Aveiro and FCT/FEDER for funding CICECO and QOPNA. Joana Sousa thanks CICECO for her research grant (BAIC/UI89/3916/2007).

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The nature of 1,1,3,3-tetramethylguanidinium chloride in the gas phase

J. Vitorino | J. P. Leal | M. E. Minas da Piedade

Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, Edifício C8, 1149-016 Lisboa, Portugal

jmvitorino@fc.ul.pt

Ionic liquids, ILs, are a class of substances in which interest has flourished in the last decade, due to the challenges and opportunities offered in terms of fundamental research and technological applications. They are normally regarded as organic salts which, conventionally, melt below 373 K and may be considered as either protic or aprotic in character. Aprotic ionic liquids were initially considered essentially involatile, but this belief was shown to be incorrect, and it is now well established that many ILs of this type can be distilled under reduced pressure without decomposition and their vapors are composed by ion-pairs. In contrast protic ionic liquids tend to vaporize by an intrinsically different mechanism, decomposing into the two neutral acid and base precursors [1,2]:

$$[BH^+][A^-](l) \rightarrow AH(g) + B(g) \qquad (1)$$

This tendency seems, however, to significantly depend on the nature of these precursors and on the "strength" of the donor acceptor interaction [3-5]. Using Fourier transform ion cyclotron resonance mass spectrometry we previously showed that 1-methylimidazolium ethanoate, [Hmim][O_2CCH_3], immediately decomposes in vacuum, at ~298 K, to yield the parent neutral base and acid (in this case 1-methylimidazole and ethanoic acid). Here we describe experiments demonstrating that in the case of 1,1,3,3-tetramethylguanidinium chloride, [Htmg][Cl], the mechanism described by eq (1) is still the only route for vaporization.

Acknowledgments

This work was supported by FCT, Portugal (Project PTDC/QUI/66199/2006). Thanks are also due to Prof. L. P. N. Rebelo and his group at ITQB for the gift. of the [Htmg][Cl] sample used in the experiments.

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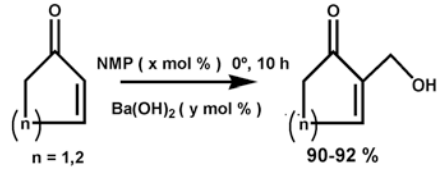
New efficient catalytic system for aqueous Baylis-Hillman reaction between cyclic enones and formaldehyde

Krassimira P. Guerra | Carlos A. M. Afonso

CQFM, Centro de Química-Fisica Molecular, IN, Instituto de Nanociência e Nanotecnologia, IST, Instituto Superior Técnico, Av. Rovisco Pais,P-1049- 001, Lisboa, Portugal

krassimira.guerrra@ist.utl.pt

The cyclic enone's structure is found on a broad range of natural products and important drugs defining theirs final vital pharmacological effectiveness [1]. The versatile and valuable synthetic intermediates, β-hydroxymethyl derivatives, could be obtained directly using the Baylis-Hillman reaction (BH) with active electrophile HCHO. The principal difficulties of this reaction are: a long reaction time and an excess of HCHO and a stoichiometric amount of promoter [2]. We were able to overcome those limitations composing and tuning by HPLC techniques, a new synergic environmentally friendly catalytic system of nucleofile N-methylpirrolidine and soft inorganic base Ba $(OH)_2$, which promotes nicely BH reaction between HCHO (1.2 mol equivalent) and cyclic enones in H_2O/MeOH solution under mild conditions for short reaction time (Scheme 1). The 2-hydroxymethyl enone derivatives were obtained in very good yield, (90-92%) being the scope of our catalytic system enlarged to the hydroxyaryl enones derivatives (Table 1).



Scheme 1. The typical BH reaction.

BH product			
Yield (%)	(73)	(65)	(83)

Table 1. Yield of BH product for some studied ArCH.

Acknowledgments
We are grateful to Fundação para a Ciência e a Tecnologia and FEDER for financial support (SFRH / BPD / 28038 / 2006 and PTDC / QUI / 66695 / 2006).

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New α-glucosidase inhibitors: synthesis, biological assays and computational studies

L. Fernandes | L.R. Guerreiro [1] | A.T. Caldeira [1] | R. Guedes [2] | R. Moreira [2] | A.J. Burke [1]

[1] Departamento de Química e Centro de Química de Evora, Universidade de Evora, Rua Romão Ramalho, 59, 7000 Evora, Portugal.
[2] Research Institute for Medicines and Pharmaceutical Sciences- iMedUL, Faculty of Pharmacy, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649- 003, Lisbon, Portugal.

nachteldar@gmail.com

The iminocyclitols are a family of important pharmacologically active compounds. The α-glucosidases are an important target for these compounds, for example, deoxinojirimicin (DNJ) is an inhibitor of endoplasmic reticulum α-glucosidases I [1], whilst 1,4-dideoxy-1,4-imino-D-arabitol (DAB-1) is a powerful inhibitor of α-glucosidases (Fig. 1) [2].
In an attempt to understand both the minimum structural and functional group requirements for optimal α-glucosidase inhibition, a range of DAB-1 analogues were synthesized and screened for α-glucosidase inhibition. The results were encouraging and prompted us to carry out computational studies to understand the mechanism of action. Our preliminary results will be discussed in this communication.

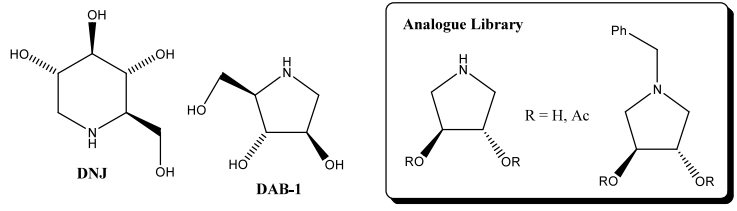

Figure. 1

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Amberlyst®: an efficient and recyclable catalyst for the regioselective dehydration of tertiary alcohols

Luís M. T. Frija | Carlos A. M. Afonso

CQFM - Centro de Química-Física Molecular and IN - Institute of Nanoscience and Nanotechnology, Departamento de Engenharia Química e Biológica, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal

luisfrija@ist.utl.pt

Conversion of alcohols to olefins is an important transformation in organic chemistry and a vast number of methods are documented in the literature for this purpose [1]. However, most of these methods include heterogeneous and homogeneous reactions with a stoichiometric amount of dehydrating agent (such as copper(II) sulfate on silica gel, ferric chloride on silica gel, $SOCl_2/NEt_3$, TsOH/PhH, BF_3/OEt_2, $Ph_3P/CCl_4/NEt_3$ or Ph_3PBiBr_2/I_2) or involve the use of strong acids, high temperatures or transformation to their ester derivatives, which, in some cases, preclude their use with sensitive molecules. More recently, the regioselective dehydration of tertiary alcohols by treatment with triphenylphosphine-iodine has been described [2]. In this communication will be presented recent and innovative results on the dehydration of tertiary alcohols, using Amberlist® as dehydrating agent. It will be shown that tertiary alcohols undergo rapid conversion to olefins under mild reaction conditions. The reactions were carried out in DCM at room temperature to afford olefins in excellent yields and high regioselectivity. The Amberlist® was recovered and reused further without loss of activity.

Acknowledgments

Fundação para a Ciência e Tecnologia (FCT) and FEDER [Project PTDC/QUI/73061/2006 and grant SFRH/BPD/43853/2008 (L.M.T.F.)] for the financial support.

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Catalyst reuse by nanofiltration for asymmetric Rh(II) catalyzed intermolecular C-H insertion

Luís F. R. Gomes [1] | Frederico C. Ferreira [2] | Nuno R. Candeias [3] | Carlos A. M. Afonso [1]

[1] CQFM-Centro de Química-Física Molecular and IN - Institute of Nanosciences and Nanotechnology, Instituto Superior Técnico,1049-001 Lisboa
[2] IBB- Institute for Biotechnology and Bioengineering, DEQB- Instituto Superior Técnico,1049-001 Lisboa, Portugal
[3] iMed.UL, Faculdadade de Farmácia da Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa

luis.r.gomes@ist.utl.pt

The rhodium(II)-catalyzed C-H insertion is an attractive transformation since it can be used for saturated C-H bonds. The substrate diazo functionality reacts with the catalyst and the C-H insertion takes place, where the chiral ligands can induce a high asymmetric reaction with retention of configuration of the C-H target bond. The catalyst Rh_2(*s*-DOSP)$_4$ (**Fig.1**) can perform both intramolecular and intermolecular asymmetric C-H insertions, being the last one a characteristic of this catalyst [1]. Since rhodium is more expensive then platinum the catalyst reuse is crucial for potential industrial use. An efficient method for catalyst reuse was already described in which the catalyst was immobilised to a solid support and this heterogeneous catalysis achieved ten cycles without an appreciable yield and enantiomeric excess loss[2]. As an alternative approach we explored the catalyst reuse by nanofiltration technology since the Rh_2(*s*-DOSP)$_4$ catalyst has a high molecular weight (MW) compared to the common substrates and products, thereby a nanofiltration membrane with the appropriate MW cut off should be able to separate the catalyst from the reaction mixture (**Fig. 2**). The reaction mixture is subject to a pressure against the membrane and the catalyst should be retained. The results obtained indicate that the catalyst reuse is feasible although some erosion of both the yield and enantiomeric excess occurs in the course of the cycles due to the occurrence of some catalyst permeation across the nanofiltration membrane.

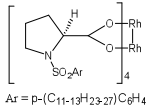

Fig. 1. The Rh_2(*s*-DOSP)$_4$ catalyst.

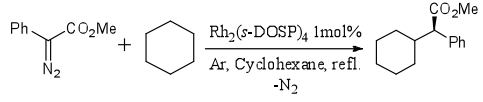

Fig. 2. The reaction model studied.

Acknowledgments
We thank to Fundação para a Ciência e Tecnologia and POCI (SFRH/BD/61220/2009, PTDC/QUI/66015/2006 and PTDC/QUI/66695/2006)) for the financial support.

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New tris(methylphosphonate)hydroxypropyl cyclen derivative for the complexation of copper(II) and lanthanide(III) ions as a potentially versatile bifunctional chelator

Luís M. P. Lima [1] | Rita Delgado [1,2]

[1] Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. República (EAN), 2780-157 Oeiras, Portugal
[2] Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

llima@itqb.unl.pt

Cyclen derivatives form transition metal and lanthanide complexes endowed with high thermodynamic stability and kinetic inertness. Such compounds have found great interest for medical applications, both as simple metal chelates or when coupled to targeting biomolecules in bifunctional chelators (BFC) [1,2]. A tris(methylphosphonate) cyclen derivative (H_6do3p, Fig. 1) has been previously described and found to form very stable copper(II) complexes with high affinity for calcified tissues, being a potential BFC for diagnosis or therapy using copper(II) radionuclides [3]. We have synthesized a new cyclen derivative (H_6do3p1ol, Fig. 1) with an additional 3-hydroxypropyl pendant arm. The thermodynamic stability of complexes of both H_6do3p and H_6do3p1ol with important transition metal and lanthanide ions was studied by potentiometric and spectroscopic techniques. Our results show that both ligands form complexes of similar stability, demonstrating that the additional pendant arm in H_6do3p1ol does not affect its binding ability and may be used for conjugation with a biomolecule. Moreover, the stability found for complexes of both ligands is very high for copper(II) and also high for lanthanides(III), proving that H_6do3p1ol has potential versatility to be used as BFC for radionuclides useful for diagnosis (*e.g.* ^{64}Cu) but also for therapy (*e.g.* ^{67}Cu, ^{153}Sm, ^{166}Ho, ^{177}Lu). Further structural studies to understand better the coordination properties of H_6do3p1ol are underway.

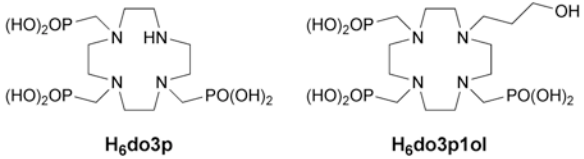

Fig. 1. Structure of the studied ligands.

Acknowledgments
The authors acknowledge the financial support from FCT (Fellowship SFRH/BD/18522/2004 and Project PTDC/QUI/67175/2006).

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Kinetic study of a Diels-Alder reaction in ionic liquid bmimBF_4

S. López-García | L. García-Rio | P. Rodríguez-Dafonte | M. Méndez-Pérez | J.R. Leis

Department of Physical-Chemistry, University of Santiago de Compostela, 15786, A Coruña, Spain.

susana.lopez4@rai.usc.es

The second-order rate constant for cycloaddiction reaction of cyclopentadiene with 3-phenyl-1-(2-pyridyl)-2-propen-1-one were determined spectrophotometrically in 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) at various concentrations of $Ni(NO_3)_2$ as Lewis acid catalyst. Rate constants of the reaction increase with concentration of catalyst to 0.01M and decrease for concentration higher than 0.01M. The inhibition of the reaction is caused for the increase of ionic strength. The endo-exo selectivity of the DA reaction has been studied by ^{1}H-NMR spectroscopy.

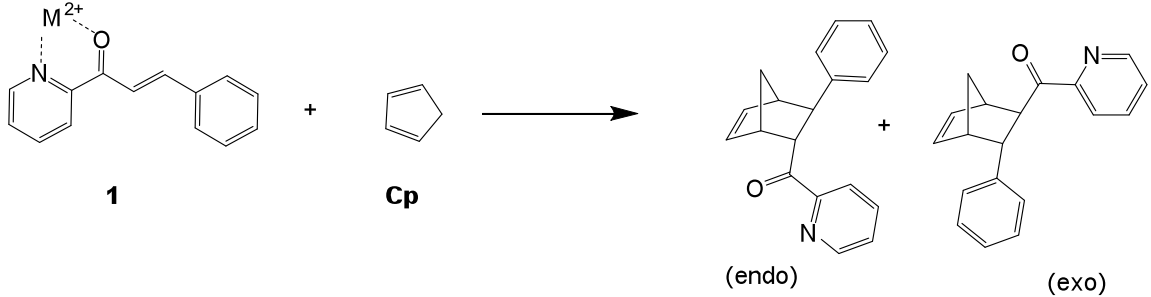

Fig. 1. Diels-Alder reaction between cyclopentadiene (**Cp**) and 3-phenyl-1-(2-pyridyl)-2-propen-1-one (**1**).

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Structural characterization of pectic polysaccharides by ESI-MS. Occurrence of hexoses directly linked to the galacturonic acid backbone

Lisete M. Silva | Cláudia Nunes | M. Rosário Domingues | Raquel P.F. Guiné | Manuel A. Coimbra

QOPNA, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro

li__ms@hotmail.com

Pectic polysaccharides include a large family of related polysaccharides based on a galacturonan-rich backbone. These polysaccharides are key components of the primary cell walls of fruits and vegetables, being important in determining tissues strength and flexibility. They can be viewed as multiblock components composed by four structural domains: homogalacturonan (HG), rhamnogalacturonan I (RG-I), which includes the arabinogalactan and arabinan side chains, the complex RG-II domain, and the xylogalacturonan (XGA). HG is a linear and partially 6-*O* methylated polymer constituted only by α-(1→4)-D-galacturonic acid residues [→4)-α-D-Gal*p*A-(1→]$_n$, which can be 2-*O* and 3-*O* acetylated. The repeating units of the disaccharide [→4)-α-D-Gal*p*A-(1→2)-α-L-Rha*p*-(1→] form the backbone of RG-I that comprises also branched at *O*-4 of Rha residues with Gal and/or Ara side chains. RG-II is described as a very complex heteropolysaccharide with a galacturonan backbone of around 30 residues substituted by side chains containing sugars such as 2-*O*-methyl-L-fucose and D-keto-3-deoxy-D-*manno*-2-octulosonic acid (KDO). In XGA, a HG chain is substituted on C-3 with D-Xyl.

The high sensitivity and capacity for the analysis of mixtures provided by mass spectrometry led to a re-emergence for oligosaccharides structural characterization in recent years.

In this study, we revisited the structures of pectic polysaccharides from commercial sources of citrus, as well as from plum and pear. The oligosaccharides from these pectic polysaccharide sources were generated by the selective hydrolysis of the GalA backbone with *endo*-polygalacturonase, followed by its partial separation on a Biogel size exclusion chromatography. The resultant fractions with lower molecular weight were analyzed by ESI-MS. Beyond uronic acid monomers (attributed to GalA) and the oligosaccharides characteristic of degraded HG such as $GalA_ndHex_q$ n=1,3; q= 1,3 (GalA-Rha series) and XGA, namely, $GalA_nPent_p$ n= 2,3; p=1, it was also observed oligosaccharides bearing hexose residues linked to uronic acids ($GalA_nHex_m$ n= 2,3 m= 1,2). The direct linkage of hexoses to the main galacturonan backbone is a structural feature of plant pectic polysaccharides that, until now, has been neglected but that should be included in the future structural models.

Acknowledgments
We thank the FCT for financial support through project PTDC/AGR-ALI/74587/2006.

Synthesis and calorimetry studies of metallic polialkoxides

L. M. C. Silva | T. A. Gasche | J. B. Branco | J. P. Leal

Unidade de Ciências Químicas e Radiofarmacêuticas, Instituto Tecnológico e Nuclear, 2686-953 Sacavém, Portugal

lmsilva@itn.pt

Alkoxides are among the most useful compounds in synthesis and catalysis. The properties of metal alkoxides make them remarkable useful as molecular precursors and an important part of advanced materials for high-tech applications that relay on high purity metal oxides. They are also the precursors in many of the sol-gel methods developed in the last years. Alkaline and alkaline-earth metal ones are of extreme importance in industrial and pharmaceutical products. However, in most cases; their energetics is not well known and in some cases not known at all. In our laboratory we had already studied reactions of alkaline and alkaline-earth metal and lanthanide metals with alcohols and phenols having in mind their energetic and applications as molecular precursors [1-8]. In this communication the synthesis, characterization and calorimetric measurements of some alkaline and alkaline-earth polialkoxides using ethyleneglycol are presented. The results will be also used, together with literature data, to expand a model developed for alkaline metal alkoxides and phenoxides and enlarged to include alkaline-earth metal alkoxides [1,4] that allows the estimation of lattice energies and enthalpies of formation for these families of compounds.

Acknowledgments
Authors acknowledge funding under FCT project PTDC/QUI/65507/2006.

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Novel biocomposite materials based on acetylated bacterial cellulose and poly(lactic acid)

Liliana C. Tomé | Eliane Trovatti | Carmen S.R. Freire | Armando J.D. Silvestre | Carlos P. Neto | Alessandro Gandini

Department of Chemistry and CICECO, Campus de Santiago, University of Aveiro, 3810-193 Aveiro, Portugal

liliana.tome@ua.pt

Biocomposites ("green composites") are a class of composite materials obtained by blending natural fibers with biodegradable polymers, which implies that they should be fully biodegradable. Biocomposites are gaining considerable and growing interest to the detriment of petroleum-derived counterparts [1], because of their renewable character, environmental friendly connotation and interesting performances. Cellulose, the most abundant polymer on earth, is biosynthesized not only by plants, but also by bacteria algae and fungi [2]. Bacterial cellulose (BC) is an extracellular polysaccharide produced in a highly pure form as a three-dimensional network of highly crystalline nano- and microfibrils, which possess unique physical and mechanical properties [3] and have been extensively explored for the development of new nanocomposite materials [4]. However, the extremely hydrophilic nature of cellulose causes a very low interfacial compatibility with less polar polymeric matrices like poly(lactic acid) (PLA).

In this study, the surface OH groups of vegetable cellulose (VC) and BC fibers were esterified with acetic anhydride under controlled heterogeneous conditions in order to promote/increase their compatibility with a PLA matrix. The occurrence of the surface modification was confirmed by elemental analysis, FTIR spectroscopy and contact angle measurements. The crystallinity and morphology of the modified VC and BC fibers were evaluated by X-ray diffraction and scanning electron microscopy, respectively. Novel composite materials were then prepared by compounding PLA with different contents of the unmodified or modified VC and BC cellulose fibers. The present communication will provide results on the preparation of these composite materials and on their characterization by different techniques, such as DMA, DSC, mechanical tests, and water uptake.

Acknowledgments

Liliana C. Tomé would like to thanks FCT for the awarding of a research grant (PTDC/QUI/68472/2006).

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The HO_2+O_3 reaction: *ab initio* and DFT studies

Luís P. Viegas | António J. C. Varandas

Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal

lpviegas@ci.uc.pt

We present new results [1] on the atmospherically important title reaction [2]. Experimental work suggests that this reaction may undergo via two distinct mechanisms, oxygen or hydrogen abstraction, the latter accounting for 88% or more of the reactive encounters. Theoretical studies are scarce in the literature, with only three papers being published so far [3-5]. This reaction is a great challenge to the state of the art *ab initio* methods due to the strong multi-reference character shown by some regions of the potential energy surface, and its mechanism remains unclear to both experimentalists and theoreticians. In this work [1] we have calculated the relative energies of the stationary points along the reaction coordinate of both mechanisms, while improving their description. This was accomplished by optimizing all structures at the CASSCF(11,11)/6-311++G(2df,2p) level, while the relative energies were obtained with single point energy calculations at the CCSD(T)/aug-cc-pVTZ and CASPT2(11,11)/aug-cc-pVTZ levels. More recent results employing the DFT methodology will also be presented, with the testing of different functionals belonging to different rungs of the so called Jacob's Ladder of density functional approximations to the exchange-correlation energy. Dispersion corrected functionals were also investigated, and all DFT results were compared to the *ab initio* calculations for the evaluation and benchmarking of this methodology.

Acknowledgments
Fundação para a Ciência e a Tecnologia, Portugal (contracts REEQ/128/QUI/2005 and SFRH/BPD/40807/2007).

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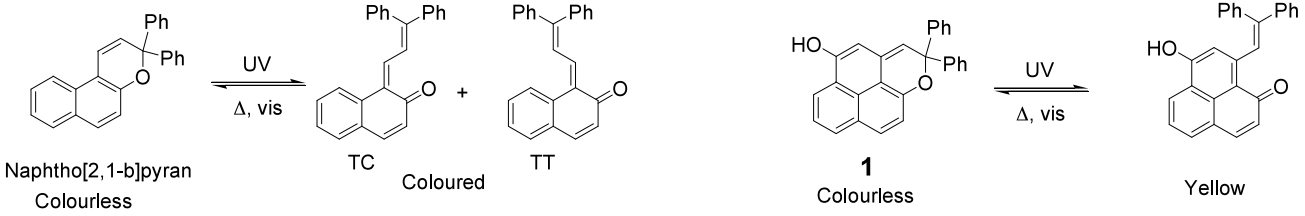
New Photochromic Naphthochromene

Céu M. Sousa | Luis M. Carvalho | Paulo J. Coelho

Centro de Química - Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-911 Vila Real, Portugal

ceumsousa@hotmail.com

Naphthopyrans are one of the most important classes of photochromic systems with excellent photochromic activity such as a remarkable fatigue resistance that have met considerable success in the production of variable-transmission optical materials, namely photochromic plastic ophthalmic lenses, which darken in the sunlight. Under near-UV light irradiation these uncoloured or faintly coloured molecules, either in solution or incorporated in polymeric matrices, undergo an electrocyclic pyran-ring opening with formation of mainly two photoisomers (TC and TT), with a strong absorption in the visible part of the spectrum (Scheme) but with very different thermal stabilities. While the TC isomer rapidly returns to the uncoloured closed form, the TT isomer is thermally more stable and is the responsible for the persistence of a residual colour for several minutes/hours after the removal of the light source. One way to prevent the formation of this unwanted photoisomer is to connect the pyran double bond to the naphthalene core. The opening of the pyran ring in such compound the can produce only one photoisomer. In this communication we describe the synthesis and the properties of the new photochromic naphtho[2,1,8-*def*]chromene **1**.



Acknowledgments
Thanks are due to the Fundação para a Ciência e Tecnologia (Portugal) and FEDER for financial support through Project PTDC/QUI/66012/2006.

The desprotonation of benzylmethileter by Butyllithium in tetrahydrofuran

Maria Luz Raposo Barreira [1] | Luis García Rio [1] | R. Paleo [2] | F.J. Sardina [2]

[1] Department of Physical-Chemistry
[2] Department of Organic Chemistry, School of Chemistry, University of Santiago de Compostela, 15782 Santiago de Compostela, Spain.

marialuz.raposo@usc.es

Reaction studies of the desprotonation of benzylmethileter with BuLi show the reaction to be first order in BuLi. The rate constant increase with concentration of the BuLi up to reaches plateau zone when the concentration of Buli is $2x10^{-1}$M, because decrease the dimeric aggregate that is the reactive specie, figure 1.
The adition of tetramethylethylenediamine TMEDA, increase the reaction of organolithium species, changes the concentration distribution of BuLi aggregates in favour of dimeric proportion, figure 2.

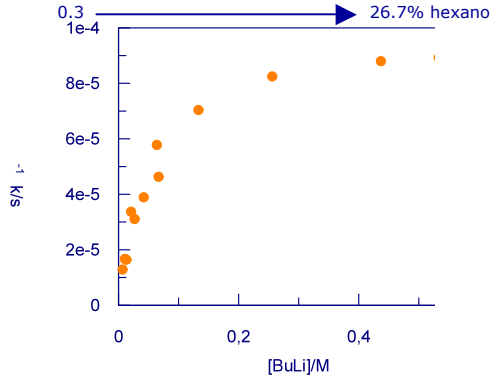


Fig. 1. Influence of the adition of BuLi in THF.

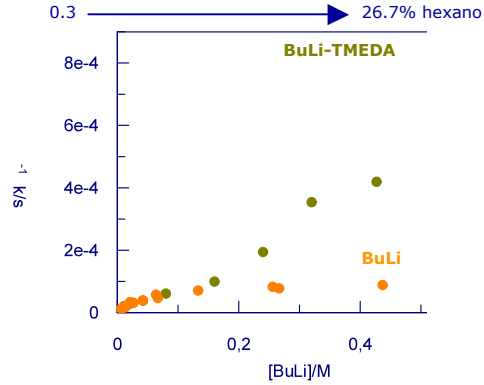


Fig. 2. Influence of the adition of TMEDA and BuLi solution in THF.

Phytochemical study and evaluation of the *in vitro* anticancer activity of *Artemisia gorgonum* extracts

Marina Bastos | Alice Martins | Zélia Tostão | Miguel Lopes | Margarida Meireles | Amélia P. Rauter

Grupo da Química dos Glúcidos, Centro de Quimica e Bioquímica/Departamento de Quimica e Bioquímica da Faculdade de Ciências da Universidade de Lisboa, Ed. C8, Piso 5, Campo Grande, 1749-016 Lisboa, Portugal

marinartb@hotmail.com

The genus *Artemisia* (*Compositae*, tribe *Arthemideae*) is one of the largest and most widely distributed genera of the *Asteraceae* family. With nearly 300 species, it has been the object of numerous chemical studies. *Artemisia* species have been used in folk medicine for its analgesic, anti-inflammatory, antimicrobial, antispasmodic, cytotoxic and antitumor activities. *Artemisia gorgonum* Webb is a plant endemic to the Cape Verde Islands (Africa) used as a herbal remedy in the Macaronesia (Santo Antão, Sal, Santiago and Fogo islands). The medicinal properties of the plant encouraged us to determine its chemical composition and for that purpose the chloroform extract of its aerial parts was fractionated by preparative column chromatography with increasing polarity solvents, affording fractions with a different chemical profile, which contained sesquiterpene lactones and highly methoxylated flavones. Four fractions with different polarity grades were tested over the human breast cancer (MCF-7) cell lines, using the *in vitro* MTT assay. A significant antiproliferative effect was observed by a less polar fraction, suggesting the potential of this plant as a source of new anticancer agents. Phytochemical studies are being carried out in order to establish the structure of the plant active principles.

Acknowledgments
Fundação para a Ciência e a Tecnologia (FCT) is gratefully acknowledged for the Post-Doc research grant of Alice Martins.

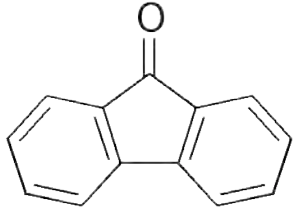
Vapour pressures and phase diagram of 9-fluorenone

Maria Miguel Calvinho | Manuel J. S. Monte

Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007, Porto, Portugal

c0870954@alunos.fc.up.pt

In this study, the vapour pressures of both solid and liquid 9-Fluorenone were measured in the temperature range from 319.87 K to 440.85 K, using a static apparatus equipped with MKS Baratron absolute gauges [1]. From the experimental results, the standard molar Gibbs energies, enthalpies and entropies of sublimation and of vaporization, at T = 298.15 K, as well as the triple point p,T coordinates, were derived. The molar enthalpy of fusion was derived from the vapour pressure results and was also determined directly using differential scanning calorimetry. The phase diagram of 9-fluorenone near the triple point will be presented.



9-Fluorenone

Acknowledgments
Thanks are due to Fundação para a Ciência e Tecnologia, FCT, Lisbon, Portugal, and to FEDER for financial support to the research project PTDC/QUI/102814/2008.

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Prins reaction between cyclopentadiene and formaldehyde

M. Carolina Carias | Alexandre F. Trindade | Carlos A. M. Afonso

CQFM - Centro de Química-Física Molecular and IN – Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, Complexo I, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

carolina.carias@ist.utl.pt

The Prins reaction between cyclopentadiene and formaldehyde, which is known since 1974 [1], due to its low selectivity gives rise to many products, from which 4-(hydroxymethyl)cyclopent-2-en-ol is the major (Fig. 1). This moiety is present in a large number of drugs, specifically carbocyclic nucleosides, such as abacavir (Fig. 2) [2,3]. In order to improve the reaction regio-selectivity, more than fifteen Lewis acids were tested as catalysts. From the screening, LaCl3 provided a very distinct selectivity furnishing a new type of Prins product (Fig. 3) [4], which may derive from two consecutive Prins addition reactions followed by elimination. It is of great interest to achieve innovative synthetic pathways to get this type of moieties with high enantiomeric purity due to its current pharmaceutical application.

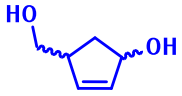

Fig. 1.

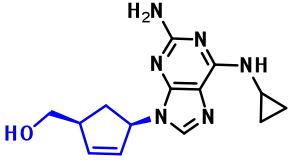

Fig. 2.

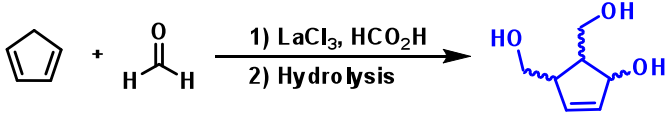

Fig. 3.

Acknowledgments
Fundação para a Ciência e a Tecnologia (SFRH/BD/30619/2006 and PTDC/QUI/66695/2006)

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Fighting Malaria: a computational approach

Marta Carrasco | Rui Moreira | Daniel J. V. A. dos Santos

Medicinal Chemistry Group, iMed.UL, Faculty of Pharmacy, University of Lisbon, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal

mcarrasco@ff.ul.pt

There are an estimated 500 million cases and 2 million deaths due to malaria per year, making this one of the most common infectious diseases worldwide [1]. Of the parasitic agents causing this disease in humans, *Plasmodium falciparum* and *P. vivax* are the most virulent [2]. The cytochrome bc_1 complex is a crucial element in the mitochondrial respiratory chain for it catalyzes electron transfer from ubiquinol to cytochrome *c* and, in parallel, transports protons to the intermembrane space in mitochondria. Being indispensable for the survival of several species of the *Plasmodium* genius that causes Malaria, cytochrome bc_1 complex is an attractive and already validated target for antimalarial drug development [3]. The recently published X-ray structures of the yeast bc_1 containing stigmatellin A as inhibitor, provided an important experimental support for the clarification of bc_1 complex inhibitors' binding modes. In this study, a set of known inhibitors with experimentally measured IC_{50} values for the bc_1 complex (3D7 strain) were docked into two independently obtained X-ray structures of *Saccharomyces cerevisiae* bc_1 (PDB codes: 3CX5 and 1KYO), using different molecular docking programs. A discussion of the molecules' activity based on the relevant docking output information will be made, namely using the poses and binding energies that will allow for the interpretation of the molecules' activity based on the information at a molecular level. Therefore, this study is also the first validation step towards a virtual screening procedure using commercially available compounds.

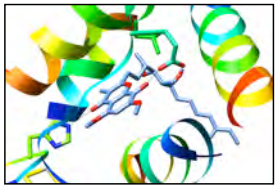

Fig. 1. Energy-minimized structure of stigmatellin A binding in the ubiquinol oxidation pocket of the yeast bc_1 complex.

Acknowledgments
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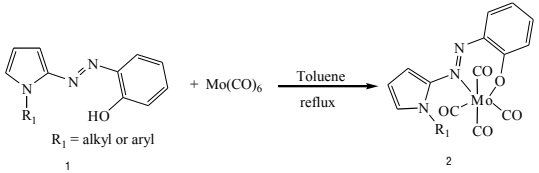
Synthesis and electrochemical and spectroscopic properties of molybdenum complexes bearing 1-alkyl(aryl)pyrrole ligands

M. Cidália R. Castro | C. Sofia G. S. Gomes | M. Manuela M. Raposo | A. Maurício C. Fonseca

CQ-UM, Center of Chemistry, University of Minho, Campus de Gualtar 4710-057 Braga, Portugal

cidaliacastro@quimica.uminho.pt

In the search for new materials for non-linear optical (NLO) applications many studies have focused on organic and organometallic molecules containing highly polarizable conjugated backbones [1]. More recently, much effort has been devoted to searching multifunctional materials in the area of transition metal coordination complexes because of their promising characteristics, including multiform structures, various oxidation states and the unique roles they play in optical and magnetic applications [2]. In these compounds the low energy charge transfer (metal to ligand or ligand to metal) which typically occurs in organometallic complexes is combined with the high mobility of π electrons in a conjugated organic ligand to obtain high hyperpolarizabilities. In this way the organometallic moiety forms an alternative type of donor or acceptor group for the traditional push-pull system. It is well known that introduction of the heterocyclic nucleus enhances the NLO properties on organic and organometallic materials [3-4].



The present communication reports the synthesis and characterization of pyrrolic azo dyes 1 as ligands and the corresponding molybdenum carbonyl complexes 2 (Scheme). The electrochemical studies of these complexes were performed by means of cyclic voltammetry in order to get an insight on the electronic properties of the complexes and the results, together with the spectroscopic data, are discussed under the scope of the structural features that can be related to the NLO properties.

Acknowledgments

Thanks are due to the Fundação para a Ciência e Tecnologia (Portugal) and FEDER for financial support through Centro de Química - Universidade do Minho, through Project PTDC/QUI/66251/2006.

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Eu^{3+} - doped gelatin biopolymers

Miguel Conde | Luísa C. Rodrigues | M. Manuela Silva*

Centro de Química, Universidade do Minho, Gualtar, 4710-057 Braga, Portugal

*nini@quimica.uminho.pt

In the domain of solid state electrochemistry, polymer electrolytes have attracted significant interest in the last two decades, in particular for the fabrication of advanced batteries, sensors, electrochromic and photoelectrochemical devices [1-3].
In this presentation gelatin (biopolymer) doped with europium triflate, $Eu(CF_3SO_3)_3$, have been prepared and characterized. Electrolytes compositions were represented as $Gelatin_nEu(CF_3SO_3)_3$ (where n indicates the europium triflate salt proportion in the electrolyte samples). Samples were studied and characterized by complex impedance measurements, thermal analysis (DSC and TGA) and cyclic voltammetry at a gold microelectrode. Electrolyte films produced were obtained as transparent films with encouraging optical characteristics that may allow future applications.

Acknowledgments
The Authors are pleased to acknowledge University of Minho and FCT for financial support SFRH/BD/38616/2007.

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Polyesters from renewable resources based on 2,5-furandicarboxylic acid

Mónica Gomes | Alessandro Gandini | Armando J. D. Silvestre

CICECO and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

monicadgomes@ua.pt

The growing interest in materials based on renewable resources [1] has led to the development of an attractive family of polymers, namely macromolecules bearing furan moieties. Furan monomers can be obtained from two first-generation precursors available from (poly)saccharidic sources, *i.e.* furfural (F) and hydroxymethylfurfural (HMF), which are converted into a whole host of monomers simulating those presently prepared from fossil resources [2]. The realm of furan polyesters has already been actively investigated, but, surprisingly, the synthesis and characterization of the furan homologue of poly(ethylene terephthalate) (PET), *viz.* poly(ethylene 2,5-furandicarboxylate) (PEF), had never been reported before our recent study on the polytransesterification reaction [3]. The purpose of this communication is to describe the preparation and detailed characterization of PEF and of a series of polyesters based on 2,5-furandicarboxílic acid and several diols and to compare their most salient features with those of their aromatic counterparts prepared with terephthalic moieties.

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Antioxidant capacity and phenolic content of agro-industrial by-products

Manuela M. Moreira | Inês M. Valente | Luís F. Guido | Aquiles A. Barros

REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, no 687, 4169-007 Porto, Portugal

manela_smoreira@hotmail.com

By-products from the processing of fruits and vegetables, traditionally considered as an environmental problem, are being increasingly recognized as sources for obtaining valuable products. To this regard, the recovery of phenolic compounds from industrial wastes is gaining considerable attention, especially ascribable to the antioxidant properties that these compounds exert [1]. Food, pharmaceutical and cosmetic industries are nowadays claiming for natural solutions to some of the customers' needs such as the use of natural colorants, texturizers, functional ingredients or shelf life extenders. Phenols have also physiological functions which can additionally result in benefit for human health. Therefore, it is very important to know the contribution and composition of by-products from food industry. The principal aim of this work was to study the phenolic and antioxidant capacity of inexpensive residual sources (consisting of skins, seeds and stems from different fruits such as apple, citrus, mango, pineapple, kiwi, papaya) from food industry. The by-products were extracted with three different solvents (70% acetone, 70% methanol and pure water) and two different extraction methods (Soxhlet and classical solvent extraction). After filtration, extracts were analyzed in terms of total phenolic content (Folin-Ciocalteau and Analytica EBC methods), flavan-3-ols and proanthocyanidins content by vanillin assay. Their antioxidant capacity was also evaluated using DPPH and ABTS radical scavenging capacity assay, ferric reducing antioxidant potential (FRAP) assay and ferricyanide reducing power assay [2]. The obtained extracts with considerable antioxidant and antiradical activities were further characterized by LC/DAD and LC/MS/MS (work is in progress).

Acknowledgments
Manuela M. Moreira is recipient of a PhD studentship from Fundação para a Ciência e Tecnologia (FCT) - SFRH/BD/60577/2009.

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A novel encapsulation method for naringinase in lens-shaped particles of alginate, polyvinyl alcohol and polyvinyl alcohol-alginate hydrogels

Mário A.P. Nunes [1] | Ana I. Afonso [1] | Pedro Fernandes [2] | Maria H.L. Ribeiro [1]

[1] Research Institute for Medicines and Pharmaceutical Sciences (i-Med-UL), Faculdade de Farmácia, University of Lisbon, Av. Prof. Gama Pinto, Lisbon, Portugal
[2] IBB-Institute for Biotechnology and Bioengineering, Centre for Biological and Chemical Engineering, Instituto Superior Técnico, Lisboa, Portugal

mario.nunes@netcabo.pt

An innovative encapsulation method in lens-shaped particles of Ca-alginate, polyvinyl alcohol (PVA) and polyvinyl alcohol-alginate hydrogels was developed for naringinase immobilization. Naringinase is an enzyme complex expressing α-L-rhamnosidase and β-D-glucosidase activities [1]. Naringin was the substrate used in this bioconversion, and the product, its aglycone, naringenin, are healthy compounds with biological and pharmacological activities, such as anti-oxidant, anti-inflammatory and anti-cancer, showing a high potential in the pharmaceutical industry.

A simple and economical technique of enzyme immobilization with PVA is PVA–boric acid method. However there are problems associated with this method, such as PVA gel beads agglomeration and toxicity of saturated boric acid. Nevertheless, these problems can be overcome using different conditions and particles with different shapes. In this work the gelation was carried out by controlled partial drying at room temperature, resulting in lens-shaped particles.

The main focus of this study was to investigate the feasibility of the PVA, alginate and PVA-alginate methods to form lens-shaped particles with different sizes, in terms of enzyme activity within the lens, immobilization yield, and enzyme stability. Different sodium alginate and PVA concentrations were used. The effects of matrix concentration, enzyme load, temperature, and pH on immobilization efficiency will be presented.

Acknowledgments
Mario Nunes is grateful to FCT for the financial support of his PhD. Grant (SFRH/BD/65002/2009).

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Micellization of cationic surfactants in presence of cucurbit[7]uril

M. Pessêgo [1,2] | N. Basílio [1] | L. García-Río [1] | J. A. Moreira [2]

[1] Departamento de Química Física, Facultad de Química, Universidad de Santiago de Compostela, 15782 Santiago de Compostela (Spain).
[2] CIQA, Departamento de Química e Farmácia, Faculdade de Ciências e Tecnologia, Univ. do Algarve, Campus de Gambelas, 8005-139 Faro

marciapessego@hotmail.com

Cucurbiturils are pumpkin-shaped cavities composed of *n* glycoril units linked by a pair of methylene groups. Their two identical carbonyl-fringed portals have a considerable negative charge density, which facilitates the binding of metal ions and cationic organic compounds, while the inner cavities are relatively hydrophobic and can host neutral molecules that fit within. We present a systematic study of mixed systems of cationic surfactants and CB7. To study these systems, we use as chemical probe the hydrolysis of 4-methoxybenzenesulfonyl chloride (MBSC). Fig. 1 shows the solvolysis of MBSC in Surfactant/CB7 mixed system.

The presence of CB7 inhibits the hydrolysis of MBSC, however the addiction of surfactant to the medium increases the observed rate constant. The competitive formation of the inclusion complex, CB7- Surfactant displaces the MBSC toward the aqueous medium, where the rate constant is higher. The formation of this complex occurs until the concentration of surfactant monomers reaches the value at which the micellization process begin. When the micelles have been formed, its observed an inhibiting effect on the hydrolysis of MBSC.

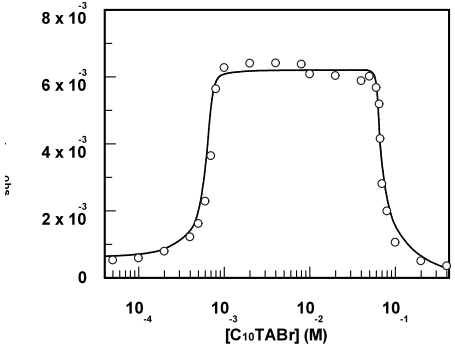

Fig. 1. Influence of CB7 on the observed rate constant for the hydrolysis of MBSC in the presence of C10TABr surfactant.

Acknowledgments
M. P. and N. B. acknowledge FCT for PhD Grant SFRH/BD/60911/2009 and SFRH/BD/29218/2006 respectively.

Alkali and microwave extraction of arabinoxylans from brewers' spent grain

M. Angélica M. Rocha | Jorge Saraiva | Manuel A. Coimbra

QOPNA, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.

angelicamartins@ua.pt

The brewers' spent grain (BSG) is a by-product resultant of the filtration of the liquid extracted from the mashing process during the brewing of beer. The BSG is composed exclusively of material from barley husks. The chemical composition of dry BSG consists mainly of polysaccharides and protein [1]. The majority polysaccharides are arabinoxylans (AX, 28%), cellulose (17%) [2], and β-glucans. BSG arabinoxylans is composed by a backbone of β-(1→4)-linked xylose residues containing single arabinose units as side chains [3]. These polymers have been shown to be a source of polysaccharides with prebiotic activity [4].

To consider the BSG a source of AX economically feasible, the extraction of these polysaccharides need to be improved and diversified. This is possible by combining conventional and newer technologies. As microwave extraction has been recently proposed for extraction of AX from the flour industry barley residue [5], in this study, the extraction of BSG AX was performed with KOH solutions with increasing concentration (0.1 M, 0.5 M, 1 M, and 4 M) at room temperature during 2 h each and with microwave irradiation of aqueous suspensions. Temperatures of microwave extraction was from 140 to 210ºC during 2 min. The amount of AX isolated alkali extraction totalized 69% of the total in BSG and those extracted by microwaves accounted for 43%. The AX extracted with KOH are longer are the ratio of arabinose/xylose is lower than those extracted by microwaves. These two technologies proved to be relevant for the extraction of a large range of AX and AX oligosaccharides that are available as food ingredients with possible prebiotic activity.

Acknowledgments

The authors thank Unicer, Bebidas S.A. for providing the brewers' spent grain. Thanks are also to Prof. Diana Pinto for microwave facilities.

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Accurate vapour pressures of $[C_1mim][NTf_2]$, $[C_2C_2im][NTf_2]$, $[C_1C_2mim][NTf_2]$

Marisa A. A. Rocha [1] | Bernd Schröder [3] | Lígia R. Gomes [2] | Isabel M. Marrucho [3,4] | João A. P. Coutinho [3] | Luís P. N. Rebelo [4] | Luís M. N. B. F. Santos [1]

[1] CIQUP, Departamento de Química e Bioquímica, FCUP, Porto
[2] CIAGEB-Faculdade de Ciências da Saúde, UFP, Porto
[3] CICECO, Departamento de Química, UA, Aveiro
[4] ITQB, Universidade Nova de Lisboa, Oeiras

marisa.alexandra.rocha@gmail.com

One of most peculiar properties of ILs is their extremely low vapour pressure at room temperature, which makes them distinct from molecular liquids. The knowledge of vapour pressures of ILs is fundamental for the development of theoretical models and for the interpretation of many other physical properties. A high-accurate volatility study of this IL family, ($[C_nmim][NTf_2]$ with n =2 – 8, 10, 12) has already been performed in our laboratory, in order to clarify the discrepancy between the enthalpies of vaporization present in the literature[1] and to support the development, parameterization and test of computational models.

In this work, the vapour pressures of three imidazolium based ionic liquids, 1,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_1mim][NTf_2]$), 1,3-diethylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2C_2im][NTf_2]$) and 1-ethyl-2,3-dimethylimidazolium bis (trifluoromethylsulfonyl)imide ($[C_1C_2mim][NTf_2]$), were measured using a Knudsen effusion apparatus combined with a quartz crystal microbalance.

Based on the measured vapour pressures, the standard molar enthalpies, entropies and Gibbs energies of vaporization were derived. The relationship between the cohesive energies, volatility and structure will be evaluated and rationalized based on the enthalpic and entropic contribution.

Acknowledgments

This work was supported by Fundação para a Ciência e a Tecnologia. B. Schröder and M. A. A. Rocha acknowledge the financial support from Fundação para a Ciência e a Tecnologia for the award of a research grant with reference SFRH/BPD/38637/2007 and SFRH/BD/60513/2009, respectively. Thanks are also due to FCT for the financial support to the project PTDC/EQU-FTT/65252/2006.

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The effect in catalysis of Mo(II) complexes in MCM-41

Marta S. Saraiva [1] | Carla D. Nunes [1] | Teresa G. Nunes [2] | Maria José Calhorda [1]

[1] Departamento de Química e Bioquímica, CQB, Faculdade de Ciências da Universidade de Lisboa, 1749-016 Lisboa, Portugal
[2] Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

mssaraiva@fc.ul.pt

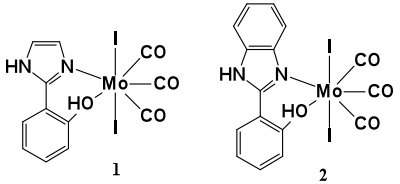

Fig. 1 - $[MoI_2(CO)_3(lig1)]$ (**1**) and $[MoI_2(CO)_3(lig2)]$ (**2**)

$[MoI_2(CO)_3(N\text{-}O)]$ (N-O=L1, L2) complexes (Figure 1) were prepared by reaction between the precursor $[MoI_2(CO)_3(MeCN)_2]$ and the ligands 2(2-hydroxyphenyl)imidazole (L1) and 2(2-hydroxyphenyl)benzimidazole (L2). MCM-41 was synthesized and functionalized with $Cl(CH_2)_3Si(OEt)_3$ (MCM-Cl), and the two complexes were immobilized by reaction of the N-H groups with MCM-Cl, as shown in Figure 2. The complexes were characterized by FTIR, ^1H and ^{13}C NMR, and elemental analysis and all the materials were characterized by powder X-ray diffraction, N_2 adsorption analysis, FTIR, and ^{29}Si and ^{13}C CPMAS solid state NMR spectroscopy. Both the complexes and the final materials were tested as catalyst precursors for the epoxidation of cyclooctene and styrene with TBHP.

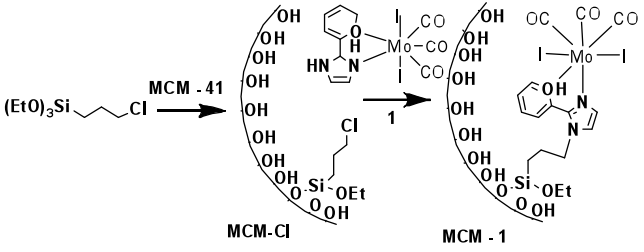

Fig. 2 - Synthetic pathway for the immobilization of complexes **1** and **2** in MCM-41

Acknowledgments
We thank FCT (Project PTDC/QUI/71576/2006) for financial support. MSS (SFRH/BD/48640/2008) thanks FCT for research grant.

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Biological activities of Spent Sulphite Liquor (SSL) polyphenols and fingerprint analysis by CZE-DAD

Manuel B. Silva | Luísa B. Roseiro | Alice I. Martins | Catarina Sepúlveda | Joana Almeida | Margarida Meireles | Amélia P. Rauter

Centro de Química e Bioquímica/Departamento de Química e Bioquímica da Faculdade de Ciências da Universidade de Lisboa Ed C8, Piso 5, Campo Grande, 1749-016 Lisboa, Portugal

manelsbbs@gmail.com

The thin spent sulphite liquor (SSL), obtained in pulp and paper mills by acidic magnesium-based sulphite pulping of *Eucalyptus globulus*, is a biomass resource. Studies on its chemical composition are scarce [1,2], but give a good indication of the potential for high added-value products. SSL consists of a dark liquid of pH 3-4, with ca.13% dry solids. The major constituents are, in average, 3% inorganic compounds, 3% hemicellulose-derived sugars, mainly xylose and glucose, and 6% lignosulphonates (LS) which constitute ca. 50% of the dry solids [1]. The ethyl acetate extracted compounds from SSL revealed tannins and some phenolic acids, mainly gallic acid, probably due to degradation of hydrolysable tannins during the acidic sulphite pulping. In the present study, methanolic fractions of the SSL were obtained and the fingerprint was determined by Capillary Zone Electrophoresis (CZE-DAD). Total phenolics content, antioxidant activity and anticancer activity on two different human tumour cell lines (N1E-115 – neuroblastoma cells and MCF-7 – breast cancer cells) were also investigated for the relevant extracts. Results suggest that methanolic extracts have significant biological activities. Isolation and structure elucidation of SSL phenolic components is currently in progress.

Acknowledgments
The authors thank FCT for the Post-Doc research grants of Luísa B. Roseiro and Alice I. Martins.

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Dielectric relaxation spectroscopy applied to study the mobility of a liquid crystalline mixture in cellulose acetate membranes

Miriam Sousa [1] | Ana Rita Brás [1] | Isabel M. Veiga [2] | Frederico Castelo Ferreira [3] | Maria Norberta Pinho [4] | Natália Correia [1] | Madalena Dionísio [1]

[1] REQUIMTE, DQ, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[2] Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. República, Apart. 127, 2780-901 Oeiras, Portugal
[3] IBB-Institute for Biotechnology and Bioengineering, CBCE, DEQB, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[4] Technical University of Lisbon, Instituto Superior Técnico, DEQB, Av. Rovisco Pais, 1, 1049-001 Lisbon, Portugal

smiriam@gmail.com

In this work, three different cellulose acetate membranes, with different thicknesses of the active layer and pore radius ranging from ~7.7 to ~3.0 nm, were prepared by phase inversion. The membranes were characterized for their hydraulic permeability performance, structure (SEM), composition and physical properties. After a careful drying process, moderately water uptake readily occurs in membranes (<3% w/w) as quantified by TGA. DSC revealed that all samples are semi-crystalline however with a low crystalline degree. The nano-porous structure was advantageously used to entrap a nematic mixture, E7. Different impregnation methods of the liquid crystalline mixture in CA membranes were developed and tested.
Dielectric relaxation spectroscopy (DRS) was used to evaluate both host and guest mobility from 0.1 Hz to 10 MHz. It was observed that water plays an important role in the matrix mobility. For confined E7, it was confirmed the efficiency of impregnation and a correlation between pore size and guest molecular mobility was established. The results showed, by comparison with bulk material, that the mobility of the liquid crystal inside pores is accelerated, with greater enhanced mobility for the lower pore size. This is a promissory outcome that can be further explored in e.g. pharmaceutical/medical applications as controlled drug delivery.

Acknowledgments
Financial support to Fundação para a Ciência e Tecnologia (FCT, Portugal) through the project PTDC/CTM/64288/2006 is acknowledged. A. R. Brás acknowledges FCT for a PhD grant SFRH/BD/23829/2005.

Enzymatic resolution-separation of *sec*-alcohols based on ionic-acylating- agents

Nuno M. T. Lourenço | Carlos M. Monteiro | Carlos A. M. Afonso

IBB-Institute for Biotechnology and Bioengineering,Centre for Biological and Chemical Engineering, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

nmtl@ist.utl.pt

Enantiomerically pure alcohols are important intermediates in pharmaceutical industry on the production of active drugs. At large scale apart of chiral natural resources, they can be obtained by classical chemical asymmetric or biotechnological processes. Enzymatic kinetic resolution of racemic alcohols is a well-established method and often the unique and/or most practical route for the preparation of enantiomerically alcohols, especially when both enantiomers are need [1]. In the context of the development of new methodologies on enzymatic resolution of alcohols, recently it was developed by us a new ester ionic acylating agent and a preparative methodology for the one-pot resolution-separation of sec-alcohols in good yields and ee's [2]. This methodology appears quite simple, robust and reliable allowing the reuse of the enzyme, ionic acylating agent and the ionic liquid medium. The great advantage of this approach is the possibility to circumvent the use of chromatography separations, since both enantiomers are removed just by organic solvent extraction. Herein is present the progresses achieved in these laboratories on the enzymatic one-pot resolution-separation of several *sec*-alcohols.

Acknowledgments
FCT (POCI 2010) and FEDER (POCI/QUI/60175/2004), SFRH/BPD/41175/ 2007 and SFRH/BD/48395/2008 for their financial support, Novozymes and Amano enzyme for their generous enzyme supply.

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Bacterial cellulose: production and preliminary assessment of its potential as drug delivery membranes

Nuno Hélder Silva | Eliane Trovatti | Iola Duarte | Carmen Freire | Armando Silvestre | Carlos Pascoal Neto

Department of Chemistry and CICECO Associated Laboratory – University of Aveiro

nhsilva@ua.pt

Bacterial cellulose (BC) is a natural polymer produced by some aerobic non-patogenic bacteria like *Gluconacetobacter* genus. This cellulosic material forms a 3D network of highly crystalline nano- and microfibrils which confers unique properties and potential applications such as in pharmaceutical area. In this work, we followed *the Gluconacetobacter sp*. growth and BC production, and then BC membrane application as matrix for drug delivery in transdermic systems, using lidocaine as a model drug. This study involved absorption tests in wet and lyophilized membranes and release tests in wet, dry and lyophilized ones. The solutions of both absorption and release tests were analysed in drug concentration, in order to predict the kinetics of drug absorption and drug release. Lyophilized membrane showed the best results of absorption capacity (mass of drug absorbed by mass of BC) while the wet membrane had the slowest kinetics of drug release (mass of drug release by mass of drug absorbed). The results of this work show how BC is an excellent and promising material for drug delivery.

Acknowledgments
CICECO, 'Fundação para a Ciência e Tecnologia' (BII_contract) and University of Aveiro.

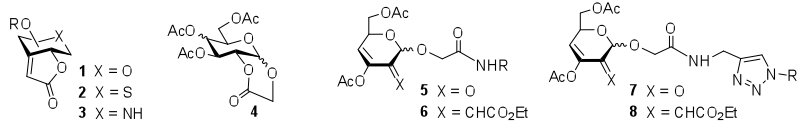
Carbohydrate-fused lactones as templates towards new potentially bioactive compounds

Nuno M. Xavier [1,2] | Yves Queneau [2] | Amélia P. Rauter [1]

[1] Grupo da Química dos Glúcidos, Centro de Química e Bioquímica/Departamento de Química e Bioquímica da, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal
[2] Laboratoire de Chimie Organique, INSA Lyon, Bât J. Verne, 20 Avenue A. Einstein, Villeurbanne, France

nmxavier@fc.ul.pt

Carbohydrate-based lactones have found broad application as chiral synthons for important bioactive compounds, natural products and new carbohydrate derivatives [1]. Among them, bicyclic systems may offer the possibility of maintaining the main carbohydrate cyclic structure after manipulation at the lactone unit, which makes them useful intermediates for a variety of molecular targets [1]. A significant biological profile may also be enhanced by the lactone moiety [2]. With these motivations in mind, we focused our research on two types of bicyclic compounds, which synthesis involved few steps and easily available starting materials. We have studied the access to compounds type **1**, comprising a bioactive butenolide motif, including their thiosugar (**2**) [3] and iminosugar analogues **3**, for further bioactivity screening. Moreover, the use of triacetylated carboxymethyl glycoside-derived lactones (compounds type **4**) [4] as precursors for 1,2- bisfunctionalized systems, such as 3-enopyranosid-2-uloses (**5**) and unsaturated 2-*C*-branched-chain diene pyranosides (**6**), was explored. (*N*- Propargylcarbamoyl)methyl glycosides arising from the opening of the lactone of **4** with *N*-propargylamine, were used for the insertion of an additional triazole ring, leading to compounds **7**-**8**. The biological evaluation of these new series of compounds is currently in progress.



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Probing platinum diimine acetylide complexes as solar cells dyes

Octávio Fontes [1] | Carlos Serpa [1] | Julia A. Weinstein [2] | Alexander H. Shelton [2] | Luis G. Arnaut [1] | Hugh D. Burrows [1]

[1] Chemistry Department, University of Coimbra, 3004-535 Coimbra, Portugal
[2] Department of Chemistry, University of Sheffield, S3 7HF Sheffield, United Kingdom

octavio_fontes@hotmail.com

In recent years Pt(II) coordination complexes have been studied for their potential use in the area of dye-sensitised solar cells (DSSCs) and in solar to chemical energy conversion [1]. In a DSSC, a dye molecule is adsorbed on to the surface of a semiconductor (SC). Upon illumination, the photo-excited dye injects an electron into the conduction band of the SC. The efficiency and energy of this electron injection are quite important for the overall efficiency of these DSSCs. Photophysical, photochemical and electrochemical characteristics of the dyes adsorbed on the SC surface affects directly the electron transfer thermodynamics and kinetics having direct influence on cell efficiency. Platinum diimine acetylide complexes [2] have metal-to-ligand charge transfer excited states that can feature a combination of desirable characteristics, including visible light absorption, photoluminescence, long excited state lifetimes, and tuneable HOMO and LUMO energies making these molecules good candidates as potential dyes in DSSC.

In this work a series of Pt diimine acetylide complexes are probed as dyes for DSSCs. The dyes photophysical and electrochemical characteristics in solution were obtained and compared to the DSSC efficiency, accessed by measuring the IPCE profiles and I-V curves, yielding their IPCE, V_{OC}, J_{SC} and η values. The energy for the electron injection is usually estimated from the redox potential of the dye in the electronically excited state and the SC conduction band energy. We also used time-resolved photoacoustic calorimetry to measure electron injection efficiencies and energies from exited dyes into TiO_2 films [3].

Acknowledgments
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Can the veterinary drugs ivermectin, enrofloxacin, penicillin and ceftiofur be analyzed by gas chromatography?

Pedro N. Carvalho | C. Marisa R. Almeida | M. Clara P. Basto | M. Teresa S. D. Vasconcelos

CIMAR/CIIMAR – Centro Interdisciplinar de Investigação Marinha e Ambiental and Faculdade de Ciências, Universidade do Porto

pedro.carvalho@fc.up.pt

The use of veterinary drugs has become integral to the growing animal food industry. These drugs are used worldwide to protect animal health, prevent economic loss and help ensure a safe food supply.
Veterinary drugs release rates and effects into the environment are poorly known. The large variety and the matrices were they are found pose difficult challenges to the detection and analysis of these compounds.
A wide variety of techniques have been used for the analysis of broad therapeutic classes of drugs, worldwide consumed, in environmental samples. However, to our knowledge, solid phase microextraction (SPME) coupled to gas chromatography (GC) with mass spectrometry detection (MS) methodology has not been applied to veterinary drugs. Therefore, the positive outcomes of SPME-GC application to organic pollutants in environmental sample matrices prompted us to survey the possibility of using it for analysis in water of some veterinary drugs largely used in livestock industry.
Here we describe the studies carried out in order to be able of optimizing a GC method for the analysis of five veterinary drugs (ivermectin, enrofloxacin, penicillin V, penicillin G and ceftiofur). GC-MS preceded of *in situ* derivatization and SPME, using different derivatizing agents and different types of fibers, applied both in headspace and direct immersion of the SPME fiber, were tested. Additional determinations by direct injection of the samples for analysis by GC-FID were also performed. The tested drugs could not be determined in any case. The study led to admit that GC will not be a suitable technique for the analysis of the tested veterinary drugs.

Acknowledgments
The authors acknowledge the Portuguese Foundation for Science and Technology for the financial support of equipment (REEQ/304/QUI/2005) and the Pedro Carvalho's PhD fellowship (SFRH/BD/44934/2008).

Amino acids profile of fresh and dried pears

Pedro R. Cunha | Raquel P. F. Guiné | Manuel A. Coimbra

QOPNA, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro

pedror@ua.pt

Amino acids (AA), both in free form or associated in proteins, affect the aroma, colour and taste of fruits due to their participation in Maillard reactions and browning processes, among others. Different AA patterns can be observed for different fruits, varieties, stages of maturity, and types of processing. The S. Bartolomeu pear is an open air sun-dried small reddish-brown pear with unique sensorial properties. To develop a drying methodology able to keep its organoleptic properties and yet comply with the food safety standards, these pears were experimentally dried in two greenhouses (GH1, GH2) and in a hot air tunnel (HAT) to compare with the traditional ones (T). The protein content of fresh fruits was 280±11 mg/100g dry weight, which is in accordance to literature (231 mg/100g dry weight) for *Pyrus communis* L. Glx (20%), Leu (18%) and Asx (13%) were the predominant AA in fresh pears, contrasting with the high Asx (35%) and low Glx (8%) and Leu (5%) found in literature [1]. Also present were the essential AA Ile (10%), Val (7%), Lys (6%), Thr (4%) and Phe (3%), revealing that the S. Bartolomeu pear is a source of AA with nutritional value. The amount of proteins and the AA profiles in processed fruits was comparable with the fresh. Free AA accounted for 52±11 mg/100g dry weight in fresh pears, representing 16% of total AA. Glx (45%), Asx (21%) and Ala (13%) were the predominant free AA in fresh pears. Also present was the essential AA Val (8%). The amount of free AA was lower than in fresh in T (32±3 mg/100 g dry weight) and GH1 (29±1 mg/100 g), and comparable in HAT and GH2. All drying processes promoted the increase in the amount of Pro (3.6 mg/100g in fresh to 6.2-29.6 mg/100 dry weight in processed samples). On the contrary, all drying processes induced a reduction in the amount of Glx (from 23.5 mg/100g in fresh to 7.2-10.4 mg/100 dry weight in processed samples) and Ala (from 6.6 mg/100g in fresh to 2.4-3.9 mg/100 dry weight in dried samples). Therefore, S. Bartolomeu pear is a source of the essential AA Leu, Ile, Val, Lys, Thr and Phe. The drying processes affect the free AA profile, increasing the amount of Pro and decreasing the amount of Glx and Ala, characteristic of the drying processes.

Acknowledgments
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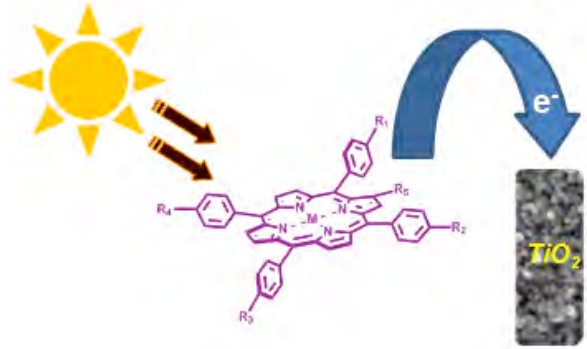
Carboxylic porphyrins and metalloporphyrins as potential dyes for solar cells

Patricia Jesus | Diana Ferreira | Carlos J. P. Monteiro | Mónica Barroso | Carlos Serpa | Mariette M. Pereira | Luis G. Arnaut

Chemistry Department, University of Coimbra, 3004-535 Coimbra (Portugal)

patricia_m.jesus@hotmail.com



TiO_2 nanocristalline ruthenium polypyridyl Dye-Sensitized Solar Cells (DSSCs) are alternative and very promising devices for solar energy conversion [1]. However, these devices still present low efficiencies (11%) and high cost. Therefore, research efforts are now focussed toward finding organic-based dyes that avoid the use of noble metals. Porphyrins and metalloporphyrins are particularly attractive dyes attending to their primary role in photosynthesis. Furthermore, porphyrins can be easily derivatized with different substituents and metals in order to enhance their affinity to TiO_2 as well as their redox and spectroscopic properties, making them extremely versatile organic dyes for application in DSSCs. In this work DSSCs devices were prepared with porphyrins and metalloporphyrins containing COOH anchor groups, in order to connect to the TiO_2 semiconductor. The DSSC performance was accessed by measuring the IPCE profiles and I-V curves, yielding their IPCE, V_{OC}, J_{SC} and η values. Solar cell performances are rationalized in terms of the photophysical and electrochemical properties of the porphyrin dyes and compared with the performance of DSSC prepared with ruthenium polypyridyl dyes.

Acknowledgments
We thank FCT and FEDER for financial support and a grant to P. Jesus through project PTDC/QUI/70637/2006. CJPM thanks FCT for PhD grant BD/37652/2007.

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A new copper(II) polyaza macrobicyclic complex as a receptor for the recognition of carboxylates

Pedro Mateus | Rita Delgado

Instituto de Tecnologia Química e Biológica, UNL, Av. da República, Estação Agronómica Nacional, 2780-157, Oeiras, Portugal

pmateus@itqb.unl.pt

The carboxylate functionality is part of a wide range of biologically active entities, and in many cases accounts for their biochemical properties. Not surprisingly, much work has been done on the supramolecular chemistry field in the design of new synthetic receptors for the recognition of carboxylates and carboxylate containing substrates, as for instance amino acids [1,2].
Aiming to contribute to this subject, we synthesized a new polyamine macrobicyclic compound, through a [1+1] "tripod-tripod coupling" strategy and using the Schiff-base condensation reaction, followed by sodium borohydride reduction. The resulting compound is a heteroditopic cage in which one of the head units is appropriate for the coordination of copper(II) while the other head is available for additional hydrogen bonding and electrostatic interactions with the substrates. The protonation constants of the new compound, the stability constants of its complex with Cu^{2+} and the association constants of the copper(II) complex with carboxylate substrates were determined by potentiometry at 298.2 K in H_2O and at ionic strength 0.10 mol dm^{-3} in KNO_3. The selectivity pattern of the studied receptor towards the carboxylate substrates will be discussed.

Acknowledgments
The authors acknowledge FCT, with coparticipation of the European Community funds FEDER, for financial support under projects PTDC/QUI/68582/2006. Pedro Mateus thanks FCT for the grant (SFRH/BD/36159/2007).

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Unexpected gas-phase behaviour of *H_2-TDMImP* in ESI negative and positive ion mode

Patrícia M. R. Pereira | Catarina I. V. Ramos | M. G. O. Santana-Marques | Rodrigo de Paula | M. Graça P. M. S. Neves | J. A. S. Cavaleiro

QOPNA, Chemistry Department, University of Aveiro, Campus de Santiago 3810-193 Aveiro

patriciamanuela@ua.pt

Nowadays, the interaction of cationic porphyrins with DNA is the focus of many research projects. In the specific case of 5,10,15,20-*tetrakis*-(1,3-dimethylimidazolium-2-yl)porphyrin, *H_2TDMImP,* previous studies reported an interaction by outside binding in the "*minor groove*" [1]. However, DNA adducts of this porphyrin were not detected when we used electrospray mass spectrometry (ESI) in the negative ion mode. This unexpected behaviour prompted us to investigate further the gas-phase chemistry of *H_2TDMImP*.
Mass spectrometry studies in the negative ion mode confirmed the dominant formation of *H_2TDMImP* adducts with acetate ions (from the buffer), that is facilitated by the delocalization of the charges in the imidazolium rings and in the π moieties of the acetate ions. The elimination of acid acetic molecules when with an inert gas is an indication of their high binding strength. In the positive ion mode *H_2TDMImP* is reduced during the ionization process with formation of hypervalent radical cations. Although the reductions in the ESI positive ion mode are unlikely processes, has already been shown that these processes occur for other cationic porphyrins such as *H_2TMPyP* [2]. Nevertheless the different behaviour of these two porphyrins is remarkable. *H_2TDMImP* is exclusively reduced through electron capture (formation of M^{3+} and M^{2+}) but *H_2TMPyP* is reduced through protonation and electronic capture (formation of $[M+2H]^+$). Moreover, the fragmentations of the reduced species of *H_2TDMImP* are different from those reported for the corresponding species of the other porphyrins because only in the case of *H_2TDMImP* we observed ions formed through internal bond breaking of the *meso* substituent rings. Presently, we are using electrospray mass spectrometry in positive and negative ion mode to study the interactions of other similar cationic porphyrins with DNA.

Acknowledgments
Patrícia MR Pereira thanks FCT for a BII-UA/QOPNA scholarship; Catarina IV Ramos and Rodrigo De Paula thank FCT for the PhD scholarships SFRH/BD/30755/2006 and SFRH/BD/25666/2005 respectively.

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Chemical composition of rainwater in Aveiro, Portugal

Patrícia S. M. Santos | Marta Otero | Eduarda B. H. Santos | Armando C. Duarte

CESAM and Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

patricia.santos@ua.pt

Aveiro, as many other European coastal regions, experienced a remarkable population growth, an increment of concentrated animal feeding operations and an extensive deforestation, during the last twenty years. As a consequence, atmospheric emissions increased dramatically. To stop this sort of situations, the European Community established limit values for emissions of the main pollutants responsible for the environment deterioration. Limit values of SO_2 and NO_x emissions, established by Directive 1999/30/CE of 22 of April, improvements on the control of volatile organic compounds emissions, and the increase of ammonia emissions, all are supposed to contribute to the decrease of H^+ concentration in precipitation. This acidity decrease is important because solution pH plays a key role not only in atmospheric reactions but also in terrestrial and aquatic ecosystems.

Rainwater samples were collected at the campus of the University of Aveiro between September 2008 and September 2009. Samples were analysed for pH, conductivity, Cl^-, NO_3^-, SO_4^{2-}, and NH_4^+ concentrations, besides other analysis. In order to evaluate temporal changes in rainwater composition along the last twenty years, our results were compared with those obtained by Pio *et al.* (1991) between 1986-1989.

Acknowledgments

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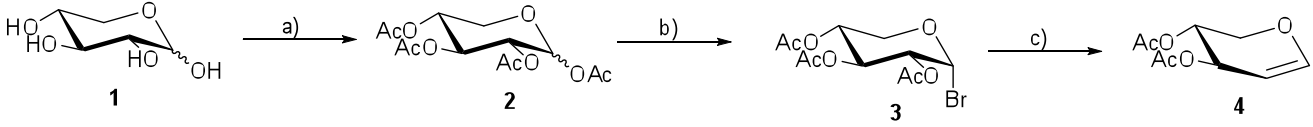
3,4-Di-*O*-acetyl-D-xylal: Synthesis of antibiotics key precursors

Patrícia Serra | João Sardinha | Alice Martins | Amélia P. Rauter

Grupo da Química dos Glúcidos, Centro de Química e Bioquímica, Departamento de Química e Bioquímica da Faculdade de Ciências da Universidade de Lisboa
Edifício C8, 5o piso, Campo Grande, 1749-016 Lisboa, Portugal

patriciafaserra@gmail.com

Synthesis of 3,4-di-*O*-acetyl-D-xylal [IUPAC name: 1,5-anhydro-3,4-di-*O*-acetyl-2-deoxy-D-*threo*-pent-1-enitol (**4**)] was envisaged in order to achieve a suitable precursor for the preparation of antimicrobial products [1,2]. The synthetic strategy involves acetylation of D-xylopyranose **1** with acetic anhydride and pyridine to afford a full protected derivative **2** which then undergoes selective bromination at the anomeric position to yield 2,3,4-tri-*O*-acetyl-xylopyranosyl bromide **3**. The formation of 3,4-di-*O*-acetyl-D-xylal **4** was accomplished by reductive elimination of the bromide derivative, employing either the system activated zinc/1-methylimidazole/ethyl acetate at 90 ºC or zinc/phosphate buffer/acetone [3] at room temperature. Compounds type **4** have been used in our group as starting materials for the preparation of potent inhibitors of *Bacillus cereus* and *Bacillus subtilis* [1,2].
The structure of the isolated products was elucidated by means of physical and spectroscopic techniques, namely nuclear molecular resonance which was used as prime tool.



a) Ac_2O, pyridine; b) HBr, CH_3COOH or DCM; c) Zinc, ethyl acetate, 1-methylimidazole or zinc/NaH_2PO_4/acetone

Acknowledgments
Fundação para a Ciência e a Tecnologia is gratefully acknowledged for the Post-Doc research grant of Alice Martins.

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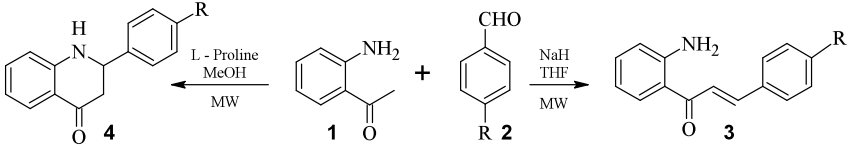
Synthesis of 2-aryl-2,3-dihydroquinolin-4(1*H*)-one and 2'-aminochalcone derivatives under microwave irradiation

Patrícia A. A. M. Vaz | Diana C. G. A. Pinto | Artur M. S. Silva | José A. S. Cavaleiro

Department of Chemistry & QOPNA, University of Aveiro, 3810-193 Aveiro, Portugal

patriciavaz@ua.pt

Quinolones have proven importance due to their microbial properties and increasing applicability on various infectious diseases. A great number of synthetic 4-quinolone derivatives possess a broad spectrum of antibacterial activity. 2-Aryl-2,3-dihydroquinoline-4(1*H*)-ones (**4**) substituted in both aromatic rings demonstrate to be important precursors in the synthesis of important medicinal compounds [1]. On the other hand, 2'-aminocalcones (**3**) are also of great importance due to their significant cytotoxicity against tumor cells lines [2] and as precursors for the synthesis of 2-aryl-2,3-dihydroquinoline-4-(1*H*)-ones (**4**). In this work we developed effective methods for the synthesis of 2'-aminochalcones (**3**) and 2-aryl-2,3-dihydroquinoline-4-(1*H*)-ones (**4**), from 2'-aminoacetophenone (**1**) and benzaldehyde derivatives (**2**), under microwave irradiation (Scheme). The obtained results and the characterization of all compounds will be shown and discussed in this communication.



Scheme

Acknowledgments

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Synthesis of a substituted triazachrysene by an acid catalyzed cascade reaction

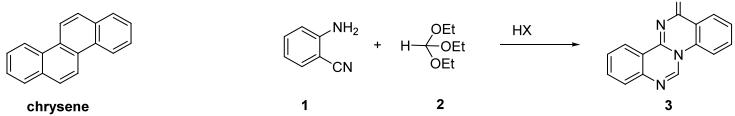
Rui Araújo | Elina Marinho | Carlos Silva | Fernanda Proença

University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

rui.araujo@quimica.uminho.pt

Azachrysenes are tetracyclic compounds containing nitrogen in one of the ring positions. They have been important for the drug industries, especially as anticancer, antimicrobial and anti-inflamatory agents, muscle relaxants and cardiotonic agents. Their unique structure makes them valuable intermediates in the synthesis of azasteroids [1]. Substituted diaza- and triazachrysenes are less known and their synthesis and biological properties are mainly reported in patented work. These compounds proved to be potent topoisomerase- targeting agents with exceptional cytotoxic activity and have been studied as anticancer agents [2].

A recent area that attracts the attention and efforts of researchers is the preparation of functionalized carbon-based nanomaterials through non-covalent interactions. This approach uses substituted polyaromatic compounds, in particular pyrene derivatives [3], and azachrysenes can also be envisaged as promising candidates for this type of application. The present work reports the reaction of 2-aminobenzonitrile **1** with triethylorthoformate **2** in acidic media. A cascade condensation- cyclization reaction occurs, ultimately leading to the triazachrysene structure **3**. The pure product was isolated as a salt, in 86% yield, after 19 h at room temperature. A detailed study of the experimental conditions enabled a controlled preparation and isolation of all the intermediate species involved in the synthetic pathway. Compound **3** was acylated upon reaction with anhydrides and isocyanates, under mild experimental conditions. All the compounds were fully characterized by elemental analysis and spectroscopic techniques.



chrysene **1** **2** **3**

Acknowledgments

We gratefully acknowledge the financial support from FCT and a Ph.D. grant awarded to Rui Araújo (SFRH/BD/38318/2007)

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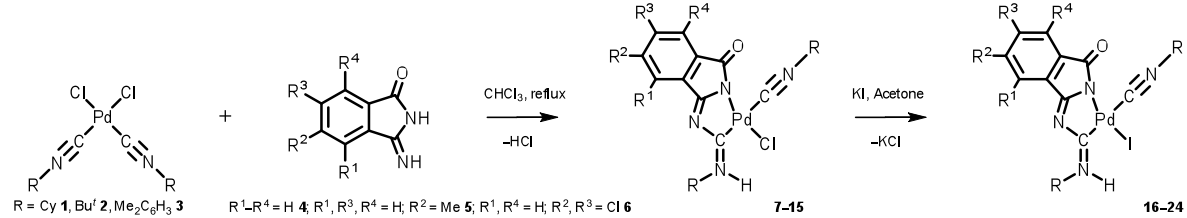
Novel type of the catalytically active palladium aminocarbene complexes

Rogério S. Chay [1] | Konstantin V. Luzyanin [1] | Armando J.L. Pombeiro [1] | Vadim Yu. Kukushkin [2]

[1] Centro de Química Estrutural, Instituto Superior Técnico, TU Lisbon, 1049–001 Lisbon, Portugal Department of Chemistry,
[2] St. Petersburg State University, 198504 Stary Petergof, Russian Federation

rogeriochay@gmail.com

Coupling of the isonitrile in *cis*-[$PdCl_2(C{\equiv}NR)_2$] [R = Cy **1**, Bu^t **2**, C_6H_3(2,6-Me2) **3**] with various 3-iminoisoindolin-1-ones $HN{=}CC_6R^1R^2R^3R^4CONH$ (**4**–**6**] provides complexes [PdCl{C(N=C($C_6R^1R^2R^3R^4$CON))=N(H)R}(C≡NR)] (**7**–**15**, 80–85% isolated yields) bearing a novel type of carbene ligands, *viz*. iminoaminocarbene [1].



Complexes **7**–**24** were characterized by elemental analyses (C, H, N), ESI-MS, IR, ^{1}D (^{1}H, ^{13}C{^{1}H}) and ^{2}D (^{1}H,^{1}H-COSY, ^{1}H,^{13}C- HMQC/ ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC) NMR spectroscopies, and complex **7** by single crystal X-ray diffraction analysis. The study of catalytic properties of **7**–**24** in the Suzuki–Miyaura cross-coupling of aryl bromides $BrC_6H_4R^2$-4 with phenylboronic acid (in EtOH) accomplishing biaryl species, demonstrate that **7**–**24** exhibit high catalytic activity (yields up to 98%, TONs up to $1.4{\times}10^6$).

Acknowledgments
Authors are grateful to the Fundação para a Ciência e a Tecnologia (FCT), Portugal – Project PTDC/QUI-QUI/098760/2008. Authors thank Prof. Matti Haukka (University of Joensuu, Finland) and Dr. M. Fatima C. Guedes da Silva (IST, Portugal) for X-ray diffraction studies.

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Isomorphous substitution of Ti by Fe in ETS-4

R. Craveiro | Z. Lin* | F. Paz

CICECO, Department of Chemistry. University of Aveiro, Campus of Santiago, 3810-193 Aveiro, Portugal

*zlin@ua.pt

ETS-4 is a well known small pore microporous titanosilicate, with the ideal composition $(Na,K)_2TiSi_2.5O_{13}.xH_2O$. Its structure consists of interconnected octahedral-tetrahedral framework, which can be contracted through dehydration at high temperatures. This contraction makes possible the fine tuning of the relative pore size [1]. It also contains geometrically well-defined –OTiOTiO- chains, which can exhibit quantum confinement effects and behave as "quantum wires". In ETS-4, titanium atoms exist in both tetrahedral and octahedral coordination [2]. This material is used for gas separations, pervaporation, and storage of radioactive elements.
In order to explore new properties of this material, we made the attempt of replacing some of the titanium in the ETS-4 structure by iron, in different percentages (5, 10, 15 and 20 % of the initial Ti content in ETS-4). The presence of iron, may give rise to new magnetic properties of ETS-4. The samples were prepared by direct hydrothermal synthesis and ion exchange method. Several different techniques were used to prove the formation of the phase and to compare the different results, such as XRD, SEM, UV-Vis, etc.

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Polyelectrolyte compaction by pH-responsive agents

Andreia F. Jorge | Jorge M.G. Sarraguça | **Rita S. Dias** | Alberto A.C.C. Pais

Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal

rsdias@qui.uc.pt

Compaction of negatively charged polyanions by polycations with different characteristics is investigated using Monte Carlo simulation in a coarse-grain model. Two different routes are tested and the results compared. In one, the polycation/polyanion charge ratio is varied by increasing the amount of polycations, keeping all the chain characteristics constant. The set of systems in which the linear density changes, is used as a model for a system comprising chains with different degrees of ionization under different pH conditions. In both cases, polycation/polyanion charge ratios ranging from 0.25 to 1.25 are addressed. The system with unitary is common to both routes.
It is observed that, although the overall trends followed by the two sets of systems are similar, marked differences can be discerned both for low charge ratios and for the higher ones, where the systems are overcharged. Coexistence of more compact and extended chains arises, in both sets, close to unitary charge ratios. Such coexistence situations seem to be related with intrachain segregation, involving a discrete number of polycation chains. Additionally, such systems show a large dispersion in sizes and conformations and, concomitantly, a lower degree of compaction.
The results obtained computationally are in good agreement with some experimental observations and can be used to guide practical applications. For example, polyelectrolyte complexes prepared above charge neutralization and at higher pH values are generally more compact and the excess positive charge is accommodated in the form of tails protruding from the complex. We speculate that such polyplexes are the most appropriate for gene delivery since the “positive tails” would act to electrostatically stabilise the complex, avoiding aggregation and precipitation, and facilitating the approach to the cell membranes. The size would still be sufficiently small to overcome the cell membrane and yet sufficiently expanded to allow the access of the DNA to the cell machinery.

Acknowledgments
R.S. Dias is grateful to Fundação para a Ciência e Tecnologia (FCT), Portugal (Programa Ciência 2007).

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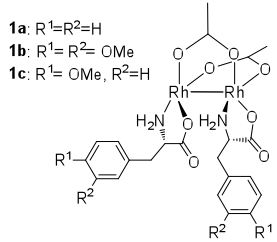
A dirhodium complex with anti-proliferative activity towards cancer cells

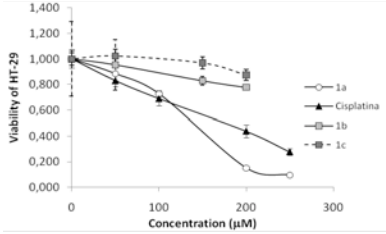
Raquel Frutuoso M. Frade [1] | Nuno R. Candeias [2] | Catarina M. M. Duarte [3] | Carlos A. Afonso [1]

[1] CQFM - Centro de Química-Física Molecular and IN - Institute of Nanosciences and Nanotechnology, Instituto Superior Técnico,1049-001 Lisboa
[2] iMed.UL, Faculdade de Farmácia da Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa
[3] IBET –Instituto de Biologia Experimental e Tecnológica, Av. da República, Quinta-do-Marquês, 2784-505, Oeiras

raquel.frade@ist.utl.pt

A search for new metal pharmaceuticals has risen since the discovery of the anti-cancer drug - cisplatin, also associated with serious side-effects. Other complexes with palladium, ruthenium and rhodium have been studied, and their interaction with DNA to form adducts seem to be their predominant mode of action [1]. Dirhodium complexes were newly synthesized by this laboratory and were tested *in vitro* with two human colonic cell lines (CaCo-2 and HT-29). CaCo-2 monolayer, a good model to study toxicity, was treated with the complexes (**1a –** R^1=R^2=H, **1b –** R^1=R^2= MeO and **1c –** R^1=MeO, R^2=H) and cisplatin. None of compounds were seen to change considerably CaCo-2 monolayer viability after a 4 hours treatment.





However, complex **1a** was the only seen to reduce significantly HT-29 cells viability in a 24 hours growing assay, as cisplatin, in a concentration dependent manner. It is interesting to note that this complex is the one containing no methoxy groups within the studied group. Complex **1a** and cisplatin seemed to trigger different cellular responses. Study of complex **1a** should be encouraged due to the narrow range of compounds able to treat cancer patients and the serious side-effects caused by current drugs.

Acknowledgments
The authors are grateful to Fundação de Ciência e Tecnologia, (POCI 2010) and FEDER for financial support (Ref. PTDC/QUI-QUI/099389/2008).

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How do trivalent metal ions can affect the enthalpy-entropy compensation of dodecyl sulfate micellization?

Rui F.P. Pereira | Artur J.M. Valente | Hugh D. Burrows

Department of Chemistry, University of Coimbra, 3004-535 Coimbra

rpereira@qui.uc.pt

The effect of unsymmetrical 3:1 electrolytes on ionic surfactants has been studied because of its importance for fundamental and practical applications in areas such as, detergency, catalysis, wastewater treatment, analytical chemistry and materials. Such applications are strictly related with the effect that trivalent ions can induce on surfactant in either micellar or monomer forms [1]. In this work, we report the effect of the trivalent cations of lanthanum, gadolinium, aluminum and chromium on the formation of aggregates with sodium dodecyl sulfate (SDS), at surfactant pre-micellar concentrations, and how the micellization properties of the surfactant are affected by the presence of these trivalent cations. A relationship between hydrated radius of metallic ions and the decreased capacity of ions to induce aggregation was found, where an increase of the effective charge density leads to a decrease in the critical aggregation concentration. However, the formation of SDS/Cr(III) aggregates is not only driven by a charge density criterion due to the very important role of water molecules of the hydration shell on the interaction between these metal ions and SDS.

The presence of metallic ions affects directly the SDS micellization process [2]. An analysis on the entropy and enthalpy sheds light on the balance of forces involved in micelle formation. The SDS micellization is entropically-driven in the presence of the lowest metal ion concentration. However, upon increasing the ionic strength, the enthalpic factor becomes more significant and, in the case of solutions with 1.0 mM Cr(III) or Al(III), the micellization is enthalpy driven. In the case of Gd(III), the increase of its concentration leads to a micellization process which is more exothermic but in which both enthalpic and entropic factors balanced in terms of absolute value. The exception occurs with La(III) where, in the concentration range considered, the micellization process is always clearly entropy-driven, since only a slight decrease of enthalpy is observed upon increase of La(III) concentration.

Acknowledgments

Rui F. P. Pereira thanks FCT for a Ph. D. grant (SFRH/38696/2007)

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GCxGC-ToFMS combined with HS-SPME as a powerful methodology for quantification of ethyl carbamate in fortified wines

R. Perestrelo [1,2] | Sílvia Petronilho [1] | José S. Câmara [2] | Sílvia M. Rocha [1]

[1] QOPNA, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro
[2] Centro de Química da Madeira, Departamento de Química da Universidade da Madeira, Campus Universitário da Penteada, 9000-390 Funchal

rosaperestrelo@gmail.com

The study of toxic and carcinogenic substances in foods represents one of the most demanding area in the food safety, due to their repercussions for public health. Ethyl carbamate (EC), also known as urethane, is potentially toxic and was classified, in 2007 by the International Agency for Research on Cancer (IARC), as possible human carcinogen compound (Group 2B) [1].
The determination of EC in alcoholic beverages has been studied since 1985. EC is generally present in trace amounts (μg/L) in wines, consequently the presence of matrix interferents requires specific sensitive methodologies and a previous isolation and/or concentration step. The aim of this study was to develop an analytical methodology for EC quantification in fortified wines based on headspace solid-phase microextraction (HS-SPME) combined with comprehensive two dimensional gas chromatography - time-of-flight mass spectrometry (GCxGC-ToFMS). The methodology performance was assessed, and a good linearity was obtained ($r^2 > 0.981$). A good precision was attained (RSD < 20 %) and low detection limits (LOD) were achieved for dry (4.31 μg/L) and sweet (2.75 μg/L) model wine solutions. The quantification limits (LOQ) and recovery for dry wines were 14.38 μg/L and 88.62 %, respectively, whereas for sweet wines were 9.16 μg/L and 99.36 %, respectively. Finally, the analytical methodology was successfully applied to determine EC in Madeira fortified wines. The results obtained by the developed showed that approximately 50 % of fortified wines analysed exceeded the international limit (100 μg/L). The lower EC values, on average, were obtained in medium dry wine (84.56 μg/L), followed by sweet (109.71 μg/L), medium sweet (110.85 μg/L) and dry (113.26 μg/L) fortified wines.

Acknowledgments
R. Perestrelo was supported by a Ph.D. grant from Fundação para a Ciência e Tecnologia (SFRH/BD/38855/2007). The authors thank the financial support of Research Unit 62/94, QOPNA and Madeira wine company for providing the samples used in this study.

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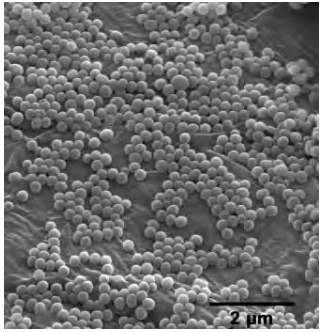
Electrostatic assembly and growth of gold nanoparticles in cellulose fibres

R. Pinto | T. Trindade | P. Marques | M. Martins | C. Pascoal Neto

CICECO, University of Aveiro, Campus de Santiago P 3810-193 Aveiro

r.pinto@ua.pt

The development of new hybrid materials based on natural substrates, with both high availability and low toxicity, is an enormous challenge. In particular, there has been an increasing interest in the preparation of new materials derived from the combination of inorganic and organic components for specific applications [1]. Following our previous studies on SiO_2 [2] based materials, we describe here the preparation and characterization of nanocomposites obtained from the incorporation of finely divided metals, specifically gold, into substrates of polysaccharide origin, including vegetal and bacterial cellulose. The nanocomposites were obtained by the synthesis *in situ* of gold nanoparticles, in the presence of the fibres, or by polyelectrolyte-assisted deposition [3]. This work describes some approaches to create a set of cellulose based nanocomposites with specific optical characteristics and showing an excellent long term chemical and optical stability, whose interest range from special paper applications (security) and to functional pigments for paints and natural fibres.



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Dehydroindigo, the forgotten indigo and its contribution to the color of Maya Blue

Raquel Rondão [1] | J. Sérgio Seixas de Melo [1] | Vasco D. B. Bonifácio [2] | Maria J. Melo [2,3]

[1] Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal
[2] REQUIMTE-CQFB and Faculty of Sciences and Technology of the New University Lisbon, Campus da Caparica, Portugal
[3] Department of Conservation and Restoration, New University Lisbon, Campus da Caparica

rrondao@qui.uc.pt

Indigo, a molecule which has influenced mankind's history for several millennia, considered a chemical icon, still harbours mysteries. Dehydroindigo (DHI), the oxidized (and third) form of the blue indigo, has been the forgotten form of indigo. A comprehensive investigation of the electronic spectral and photophysical properties of the oxidized form of indigo, dehydroindigo (DHI), has been carried out in solution [1]. It was found that both the oxidized and the keto indigo forms are present in solution. In marked contrast to what has been found for keto-indigo [2,3], where the internal conversion channel dominates >99% of the excited state deactivation, or with the fully reduced leuco-indigo, where fluorescence, internal conversion, and singlet-to-triplet intersystem crossing coexist, in the case of DHI in toluene and benzene, the dominant excited state deactivation channel involves the triplet state. The contribution of DHI to the color of the pigment Maya Blue was further investigated by optical and fluorescence spectroscopy in the solid state. The comparison between the spectra of DHI, indigo and synthetic Maya Blue in the solid state was obtained and it suggests that DHI is present, together with indigo, in the spectra of Maya Blue. The results provided for DHI constitute additional elements aiming understanding the rich palette of colours displayed by the ancient blue of the Maya civilization, in view of the demonstrated presence of this form of indigo in the formation and constitution of Maya Blue.

Acknowledgments
We are grateful to POCI (through projects PTDC/EAT/65445/2006 and PTDC/QUI-QUI/099388/2008), FCT and FEDER for further funding. Raquel Rondão acknowledges FCT for a PhD grant (SFRH/BD/38882/2007)

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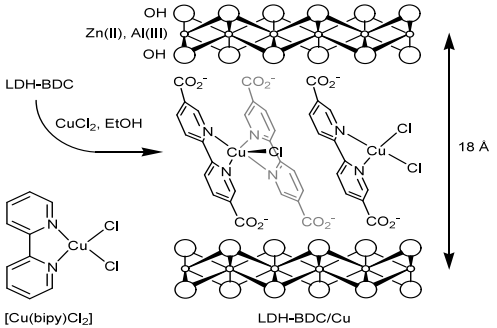
Liquid-phase oxidation catalysed by copper(II) immobilised in a pillared LDH

Salete S. Balula [1] | Bernardo Monteiro [2] | Sandra Gago [2] | Anabela A. Valente [2] | Isabel S. Gonçalves [2] | Martyn Pillinger [2]

[1] REQUIMTE, Department of Chemistry and Biochemistry, Science Faculty, Rua Campo Alegre s/n, 4169-007Porto, Portugal
[2] Department of Chemistry, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal



In recent years, considerable progress has been made in the use of copper catalysts for the oxidation of alkanes, alkenes, alcohols, arenes, benzylic substrates, ketones and sulfides [1]. Of particular importance is the oxidation of cyclohexane due to the large demand for its oxidised products such as cyclohexanone and cyclohexanol, which are important raw materials for the production of adipic acid and caprolactam, both of which are intermediates used in the production of nylon [2]. Styrene is a major industrial chemical used extensively in the production of plastics, resins and synthetic rubbers. In the present work the catalytic performances of $[Cu(bipy)Cl_2]$ and a supported copper(II) catalyst were investigated in the oxidation of styrene, ethylbenzene, cyclohexane and cyclooctane at room temperature, using acetonitrile/water as solvent, and hydrogen peroxide (30%) or *tert*-butyl hydroperoxide (70%) as terminal oxidant. A layered double hydroxide (LDH) pillared by 2,2'-bipyridine-5,5'-dicarboxylate (BDC) was applied as a solid support to immobilize $CuCl_2$ (LDH-BDC/Cu). The catalytic experiments were performed using 1,2-dichloroethane, ethanol or methanol as alternative solvents to acetonitrile. The main products were benzaldehyde from styrene, acetophenone from ethylbenzene and a mixture of cyclohexanol and cyclohexanone from cyclohexane. Titration experiments showed that LDH-BDC/Cu was significantly more efficient than $[Cu(bipy)Cl_2]$ in terms of the "productive" consumption of the oxidant.

Acknowledgments
This work was supported by the FCT, OE and FEDER (POCI/CTM/58507/2004). We also wish to thank the FCT for post- doctoral (S.G. and S.S.B.) and PhD (B.M.) grants.

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1,4-cyclohexanediol isomers: molecular conformation and polymorphism

Suse S. Bebiano [1] | Teresa M. R. Maria [1] | Mário T. S. Rosado [1] | Ricardo A. E. Castro [2] | João Canotilho [2] | M. Ermelinda S. Eusébio

[1] Department of Chemistry,
[2] Faculty of Pharmacy, University of Coimbra, 3004-535 Coimbra, Portugal

susebebiano@gmail.com

In this communication an investigation on the structural modifications of *trans* and *cis* isomers of 1,4-cyclohexanediol is undertaken. Dihydroxyl cyclohexane derivatives are simple molecules which bear structural features that make them interesting candidates to perform research on the correlations between molecular conformation and crystal structure. In *trans*-1,4-cyclohexanediol two chair conformations are possible, the biequatorial and the biaxial one, while in the *cis* isomer one of the OH groups has to be in the axial position. From the complex hydrogen bonding systems possible in polyols, the existence of polymorphic forms could be expected for both compounds. The solids were characterized by differential scanning calorimetry (DSC) and polarized light thermal microscopy (PLMT). For *trans*-1,4- cyclohexanediol isomer three polymorphic forms have been identified, and in the two known crystalline structures the biaxial and the biequatorial conformers coexist in the crystal lattice [1]. C*is*-1,4-cyclohexanediol presents, before fusion, a solid-solid transition giving rise to an isotropic solid. High level theoretical conformational analysis (MP2/aug-cc-pVDZ) of the monomers are also carried out in order to provide insight in some selected features.

Acknowledgments
We are grateful to FEDER/POCI 2010 for financial support.

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Cyclodextrins as molecular building blocks

Ana I. Ramos | José A. Fernandes | Paulo Ribeiro-Claro | Filipe A. Almeida Paz | **Susana S. Braga**

CICECO and Dep. of Chemistry of University of Aveiro, 3810-193 Aveiro, Portugal

sbraga@ua.pt

Cyclodextrins (CDs) are naturally-occurring alpha-D-glucose rings with six to eight units, forming a bottomless-cup-shaped set of molecules of variable width. Their ability to include small molecules, to pile up in stacks or brickwall modes, to dock onto specific molecular targets and to thread along polymeric chains has promoted their use as building blocks to form supramolecular architectures. The threading is used to form rotaxanes and polyrotaxanes, commonly with organic polymeric guests [1]. The present work briefly describes the most relevant CD-based architectures with support of relevant application examples such as a rotaxane-based molecular abacus, and a self-assembled microtubule from an alpha-CD rotaxane.

Preparation of CD-based inorganic coordination polymers remains largely unexplored, even though CDs were shown to coordinate directly with some metals [2], and some examples are known of CD threading onto inorganic or organometallic oligomers [3]. Some insight on the progress of our work on using CDs as building blocks for inorganic polymers will be presented.

Acknowledgments

This work was funded by the FCT, project PTDC/QUI/69302/2006.

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Monitoring prenatal disorders through the characterization of urine by Nuclear Magnetic Resonance (NMR) spectroscopy

S. Diaz | G. Graça | A. Barros | I. F. Duarte | B. J. Goodfellow | I. M. Carreira | E. Galhano | C. Pita | A. M. Gil

CICECO, Departmento de Química, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

silvia.oliveira@ua.pt

NMR-based metabonomic of human biofluids has recently begun to be explored for pregnancy monitoring, namely through the study of amniotic fluid [1,2], serum and plasma [3]. This work describes an NMR metabonomics study of the mother's urine to probe the metabolic effects of gestational diabetes (GD), foetal malformations and pre-term delivery. Urine was collected from pregnant women, at the time of amniocentesis (15-22 weeks of gestation). Pregnancies were followed so that, at the end of gestation, four subgroups emerged: GD (n=13), foetal malformations (n=18), pre-term delivery (n=11) and control group (n=48). The ^{1}H NMR spectra of all samples were acquired and Principal Component Analysis (PCA), Partial Least Squares Discriminant Analysis (PLS-DA) and Orthogonal PLS-DA (O-PLS-DA) were applied to probe consistent metabolite variations between pathological and healthy pregnancies.
It was found that women developing GD show early evidence of metabolic changes (several weeks before GD clinical diagnosis), namely: a) increased ketone bodies, citrate, succinate, trimethylamine, N-methylnicotinamide, creatinine, choline and b) decreased lactate, alanine, γ-amino-butyrate, creatine, phenylacetylglycine, tyrosine and hippurate. The biochemical relevance of these changes is presently under investigation. Preliminary analysis of pregnancies affected by malformed fetuses or by pre-term delivery also shows significant correlations with urine composition, at 15-22 g.weeks. The potential of urine metabonomics for the understanding and early diagnostic of disorders of the mother and foetus during pregnancy is discussed.

Acknowledgments
Authors thank Fundação para a Ciência e Tecnologia - FCT (PTDC/QUI/66523/2006, SFRH/BD/41869/2007 and SFRH/BD/64159/2009) for funding.

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Antioxidant activities and phenolic composition of crude extracts from flowers of *Andryala glandulosa*

Sandra Gouveia | João Gonçalves | Paula Castilho

Centro de Química da Madeira, Departamento de Química, Universidade da Madeira, campus da Penteada, 9000-390 Funchal

sgouveia@uma.pt

Total equivalent antioxidant capacity (TEAC) and phenolic contents of flowers extracts of *Andryala glandulosa* spp. *varia* (Asteraceae), collected in Madeira Island, were investigated. Three different methods were performed in order to measure the antioxidant activity of extracts: $ABTS^{+}$ (2,2'azinobis-(3-ethylbenzthiazoline-6-sulfonic acid)) [1], DPPH. (2,2-Diphenyl-1-picrylhydrazyl radical) [2] and ferric reducing antioxidant power (FRAP) [3].

The methanolic extract showed a strong antioxidant activity by the DPPH and ABTS assays, 0.53 ± 0.03, 2.06 ± 0.3 mM Trolox equivalent/ mg extract, respectively. However, the dichloromethane extract showed a higher antioxidant activity (7.7 ± 0.8 mM Trolox equivalent/ mg extract) in the FRAP assay. Total phenolic content was measured using the Folin-Ciocalteu assay [4] and once more the methanolic extract showed a higher total phenolic content (24.6 ± 0.2 mg GA/ g extract). The phenolic profile in the methanolic extract was investigated by LC-DAD-MS in negative electrospray ionization (ESI-) mode. A total of 11 compounds were identified or tentatively characterized based on their HPLC retention time, UV, mass spectra. Most of these compounds were identified as quinic acid derivatives.

Acknowledgments

Sandra Gouveia is gratefull to Fundação para a Ciência e Tecnologia (Portugal) for a Ph.D. grant SFRH/BD/24227/2005. This work made use of equipments from MS National Network REDE/1508/REM/2005.

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On the dynamics of peptide folding: a time resolved study of Trichogin GA IV analogues

Sónia P. Lopes | Emanuela Gatto | Carlos Serpa | Luis G. Arnaut | Mariano Venanzi

Chemistry Department, University of Coimbra, 3004-535 Coimbra, Portugal
Department of Sciences and Chemical Technologies, University of Rome Tor Vergata, Rome, Italy

splopes@portugalmail.pt

Trichogin GA IV is a member of the lipopeptaibols family, peptides with anti-microbial properties by permeabilization of the lipid membrane. In the Trichogin aminoacid composition we can denote the presence of Gly (glycine) giving conformational flexibility, while the Aib (a-aminoisobutyric acid) inhibits the conformational flexibility of the peptide, causing steric restrictions to the peptide folding dynamics [1,2]. The objectives of this work is to understand the influence of a single Aib vs. Gly substitution on the conformational dynamics of fluorescent Trichogin analogues. In the Trichogin analogues investigated (F0T8 and F0A6T8) a fluorene group (Fmoc) and a quencher (TOAC), were inserted in the peptide chain for FRET studies. In F0T8 Gly6 was replaced by an Aib residue (F0A6T8).

F0: **Fmoc**-Aib-Gly-Leu-Aib-Gly-Gly-Leu-Aib-Gly-Ile-Leu-OMe
F0T8: **Fmoc**-Aib-Gly-Leu-Aib-Gly-Gly-Leu-**TOAC**-Gly-Ile-Leu-OMe
F0A6T8: **Fmoc**-Aib-Gly-Leu-Aib-Gly-**Aib**-Leu-**TOAC**-Gly-Ile-Leu-OMe

Circular dichroism and static fluorescence at various temperatures probe the Aib conformational influence. Fluorescence quenching (nanosecond range) was used to probe peptide structure, while triplet quenching (microsecond range) was used to probe peptide dynamics. Metal ion binding properties of Trichogin analogues ware also studied. Time-resolved fluorescence with changing temperatures was quite informative about both the conformational distribution of two conformers and about the inter-conformational barrier between those conformers. When terbium is added to the peptide a complex is formed, slowing the peptide motion.

Acknowledgments
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First approach to *Sharpless* dihydroxylation of carbohydrate olefins in ionic liquids

S. D. Lucas [1] | L. C. Branco [2] | A. P. Rauter [1]

[1] Carbohydrate Chemistry Group/Centro de Química e Bioquímica/Departamento de Química e Bioquimica da Faculdade de Ciências da Universidade de Lisboa, Campo Grande, Ed. C8, 5o Piso, 1749-016 Lisboa, Portugal.
[2] REQUIMTE, CQFB, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

sdlucas@fc.ul.pt

Sharpless dihydroxylation is a well known and efficient methodology for the synthesis of vicinal diols but the toxicity of the osmium catalyst can be considered an important issue for its application [1]. Our research group has been using this reaction to obtain dihydroxylated lactones fused to a carbohydrate motif (compounds type *iii*), which are valuable intermediates for the synthesis of miharamycins sugar moiety. These antibiotics display a potent activity against *Pyricularia oryzae*, a fungus which causes the rice blast disease and is also considered a bioterrorism agent [2]. In our efforts to achieve green methodologies, the dihydroxylation of carbohydrate olefins type *i* using $K_2OsO_2(OH)_4$ as catalyst and NMO as co-oxidant has been investigated using ionic liquids as reaction medium (described in step *i*). Room temperature ionic liquids (RTILs) proved to be an efficient reaction media for dihydroxylation of other olefins and a promising eco-friendly approach with the possibility of selective recovery of the products and re-use of the catalyst which is retained on the RTIL phase [3]. Here we present a screening of RTILs for the dihydroxylation of carbohydrate olefins type *i* to afford diols type *ii* in moderate to very good yields. Catalytic system recycling as well as the evaluation of supercritical CO_2 extraction of the products is also discussed.

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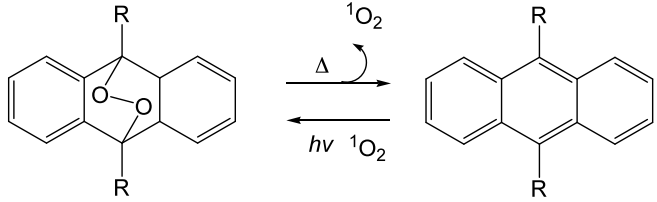
Kinetics of formation and thermolysis of anthracene and naphthalene endoperoxides

Sofia Martins | Carlos Baleizão | Mário N. Berberan-Santos

CQFM-Centro de Química Física Molecular and IN-Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, 1049-001 Lisboa

sofia.a.martins@ist.utl.pt

The endoperoxides of polycyclic aromatic hydrocarbons are known to release singlet oxygen upon thermolysis, e.g.:



Anthracene and naphthalene endoperoxides are relatively stable at room temperature [1]. They can therefore be used as a source of singlet oxygen. Some work has been published reporting the synthesis and thermal decomposition of several aromatic endoperoxides with potential applications in biological studies [2, 3]. However, the kinetics of these reactions is not completely understood. In the present study, the kinetics of formation and thermolysis of anthracene and naphthalene endoperoxides is presented and discussed.

Acknowledgments
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An experimental thermochemical study of fluorene

Sónia Pinto | Ana I. M. C. Lobo Ferreira | Maria D. M. C. Ribeiro da Silva

Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007, Porto, Portugal

c0870968@alunos.fc.up.pt

Polycyclic aromatic compounds (PAHs), both hydrocarbons and heterocycles, have attracted great attention because they constitute a complex group of important environmental pollutants, with relevant negative impact for health. On the other hand, PAHs are having an increasing interest on the field of organic electronics due to their good performance as active components in a new generation of electronic devices, as organic light-emitting diodes. There is little knowledge of the physical and chemical properties, which has resulted in a growing interest in the study of this class of compounds. The thermochemical characterization of these species is essential for the understanding of the relations between energetic and structural properties, and hence of the reactivity of this class compounds.

The lack of reliable energetic data for polycyclic aromatic hydrocarbons (PAHs) and their derivatives justifies our attention to this theme. In which concerns the fluorene the situation is not clear, since several experimental results are not in good agreement among them [1] and also with the computational calculations [2]. These aspects justify this presentation, reporting new experimental thermodynamics studies for fluorene. The standard (p^o = 0.1 MPa) molar enthalpy of formation, at T = 298.15 K, of the fluorene, in the solid phase, was derived from the respective massic energy of combustion, determined by static-bomb combustion calorimetry. The standard molar enthalpy of sublimation, at T = 298.15 K, was determined by high temperature Calvet microcalorimetry. We intend to continue this study measuring the vapour pressures of the fluorene, as a function of the temperature, using the static method, from which the standard molar enthalpy of sublimation, at T = 298.15 K, will be derived using the Clarke-Glew equation. The combination of the values of the standard molar enthalpy of formation, in crystalline phase, and of the standard molar enthalpy of sublimation, allowed the calculation of the standard molar enthalpy of formation in the gaseous phase, at T = 298.15 K.

Acknowledgments

Thanks are due to Fundação para a Ciência e Tecnologia, FCT, Lisbon, Portugal, and to FEDER for financial support to the research project PTDC/QUI/102814/2008.

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The thermochemical and structural properties of di- and triaminopyrimidines

Tiago L.P. Galvão | Ana Filipa L.O.M. Santos | Manuel A.V. Ribeiro da Silva

Centro de Investigação em Química, Department of Chemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, 687, P-4169-007, Portugal

tlpgalvao@gmail.com

Pyrimidine and aminopyrimidine derivatives can be found in nature as part of nucleic acids (cytosine, thymine and uracil). In this work, a joint experimental and theoretical study is carried out in order to evaluate the effect of the changing in position of the amino groups in di- and triaminopyrimidine isomers on the enthalpic stability and on the aromaticity of the pyrimidine ring. The standard ($p°$ = 0.1 MPa) molar enthalpies of formation of 2,4-diaminopyrimidine and 2,4,6-triaminopyrimidine, in the gaseous phase, at T = 298.15 K, were calculated combining the respective standard molar enthalpies of formation, in the crystalline phase, and the standard molar enthalpies of sublimation, derived, respectively, from the standard massic energies of combustion, in oxygen, at the same temperature, measured by static bomb combustion calorimetry, and the vapour pressures, at several temperatures, measured by the Knudsen effusion technique. The standard molar enthalpies of formation, in the gaseous phase, of 2,4-diaminopyrimidine and 2,4,6-triaminopyrimidine, were also calculated by computational chemistry. The results are compared with the experimental values. In order to further evaluate the computational approach, the enthalpies of formation of 2-, 3- and 4-aminopyridines were also calculated by computational Thermochemistry and compared with their experimental literature values [1]. The computational study was extended to other diamino- and triaminopyrimidine isomers. The nucleus-independent chemical shift (NICS) was used as a criterion for evaluating the aromaticity of the different isomers.

Acknowledgments
T.L.P.G. and A.F.L.O.M.S. thank FCT and the European Social Fund (ESF) under the Community Support Framework (CSF) for the award, respectively, of the Ph.D. (SFRH/BD/62231/2009) and the post-doctoral (SFRH/BPD/41601/2007) research grants.

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(1*H*-pyridin-4-ylidene)amines: a new scaffold for antimalarial drug candidates

Tiago Rodrigues | Rita C. Guedes | Daniel J. V. A. dos Santos | Marta Carrasco | Jiri Gut | Philip J. Rosenthal | Rui Moreira | Francisca Lopes

iMed.UL, Faculty of Pharmacy, University of Lisbon, Av. Prof. Gama Pinto, 1649-003 Lisbon, Portugal

trodrigues@ff.ul.pt

Malaria is one major disease in the world, killing 1 to 3 million people a year [1]. The emergence of resistant strains of malaria parasites suggests the need to discover both new drug targets and active molecules [2]. Cytochrome bc_1, is one validated drug target [3]. Clopidol, is a known bc1 complex inhibitor and has been taken as a lead for structural optimization [4]. Our quantum mechanical studies with compounds containing the (1*H*-pyridin-4-ylidene)amine scaffold, 1, showed that they might be considered as clopidol bioisosters [5]. Compounds 1 are easily accessible from appropriate 4- chloropyridines. In this work, a series of compounds 1 was synthesised and the antimalarial activity on the *P. falciparum* W2 and FCR3 strains assessed. Compounds 1 were obtained with good yields and their antimalarial activity found to be in the μM range. A docking study was designed to predict the major ligand-protein interactions [6]. SAR for this series of compounds and future perspectives will be discussed.

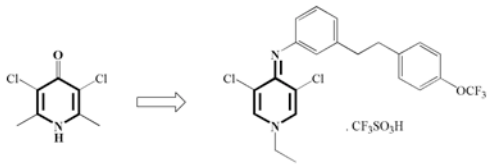

Fig. 1. Structure of clopidol and one of the most active compounds presented in this study

Acknowledgments
T.R. acknowledges FCT for the Ph.D. grant SFRH/BD/30689/2006.

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Effects of organic matter on the photodegradation of the psychiatric drug diazepam

Vânia Calisto | Valdemar I. Esteves

Department of Chemistry and CESAM, University of Aveiro, Campus de Santiago 3810-193, Aveiro, Portugal

vania.calisto@ua.pt

The benzodiazepine diazepam, a psychiatric drug with anxiolytic and sedative effects, is one of the most traded pharmaceuticals, being consumed across all the regions of the world. The generalized occurrence of diazepam in surface and ground waters and in Waste Water Treatment Plants influents and effluents, suggests limited degradation of this contaminant in environmental conditions. Moreover, literature data indicate that this pharmaceutical is being potentially accumulated in the environment [1].

In this investigation, the photochemical degradation of diazepam, expected to be an important process of remediation of contaminated surface waters, was studied. The effect of dissolved organic matter on the photodegradation rates were evaluated using humic acids, fulvic acids and XAD-4 fraction extracted from freshwater, collected in Canal de Mira, Ria de Aveiro (Poço da Cruz), Portugal. The experiments were carried out using a solar light simulator equipped with a Xenon lamp. Samples containing diazepam and 1ppm of dissolved organic matter (humic acids or fulvic acids or XAD-4 fraction), dissolved in ultra-pure water, were irradiated for 48 hours and monitored using a micellar electrokinetic chromatography (MECK) based method.

The results showed that, for the concentration used, the different fractions of organic matter have different influence on the photodegradation rate of diazepam. Humic acids inhibited the photodegradation and fulvic acids and XAD-4 fraction increased the photodegradation rates by a factor of 2. These results are a helpful tool to understand the persistence of this contaminant on an environmentally relevant scenario.

Acknowledgments
Vânia Calisto thanks Fundação para a Ciência e Tecnologia (FCT, Portugal) for her PhD grant (SFRH/BD/38075/2007).

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Formation of unilamellar vesicles by self-assembly of host:guest complexes

Vítor Francisco [1] | Nuno Basílio [1] | Luis Garcia Rio [1] | J. Ramón Leis [1] | Eduardo F. Marques [2] | Carlos Vásquez-Vásquez [1]

[1] Departamento de Química Física. Facultad de Química. Universidad de Santiago. 15782 Santiago. Spain
[2] Centro de Investigação em Química, Department of Chemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, no. 687, 4169-007 Porto, Portugal

francisco.vms@gmail.com

Vesicle is a colloidal structure, commonly spherical, which consist of a self-folded amphiphilic bilayer enclosing a volume of solvent secluded from the bulk. In this work we study an mixed system formed by the most common p-sulfonatocalix[4]arene (SC4) with tetradecyltrimethylammonium bromide (TTABr), which after sonication give unilamellar vesicles. A solution containing 2mM of SC4 and 5mM of TTABr was been studied by direct visualization through light microscopy and transmission electron microscopy (TEM), in combination with data from more quantitative techniques such as NMR and dynamic light scattering (DLS). As show in figure 1 we observe the presence of unilamellar vesicles in aqueous solution, with an average hydrodynamic radius of ca. 57.2±0.7 nm, supported by DLS. The data from ^{1}H NMR suggest that the surfactant polar head is included in the aromatic cavity of the calixarene. In order to study the stability of the vesicles, the time evolution of the relaxation time spectra was studied by DLS. No change is observed in the relaxation time spectra up to 4-5 days, however to avoid evolution of size distribution with time to larger structures, the sample was dehydrate by the freeze-drying method. Then the white powder obtained is rehydrated yielding spontaneous vesicles, with no significantly change in size or shape, as confirmed by DLS and TEM. Furthermore the used of lyoprotectant for lyophilization or sonication after rehydration wasn't needed.

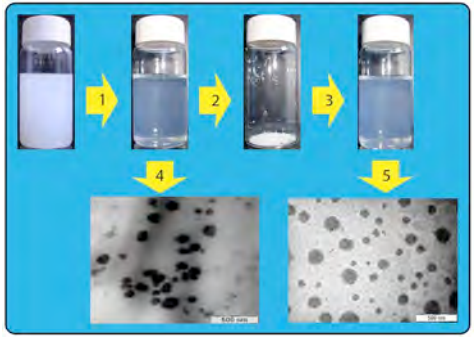

Fig. 1. Schematic representation for vesicle storage method and rehydration. Step 1,2 and 3 corresponds to sonication, lyophilization and rehydration, respectively. The TEM images (negatively stained 2% phosphotungstic acid, pH=7) are before (step 4) and after the lyophilization (step 5).

Acknowledgments
V. F. and N. B. acknowledge to FCT (Portugal) for PhD Grants SFRH/BD/43836/2008 and SFRH/BD/29218/2006

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