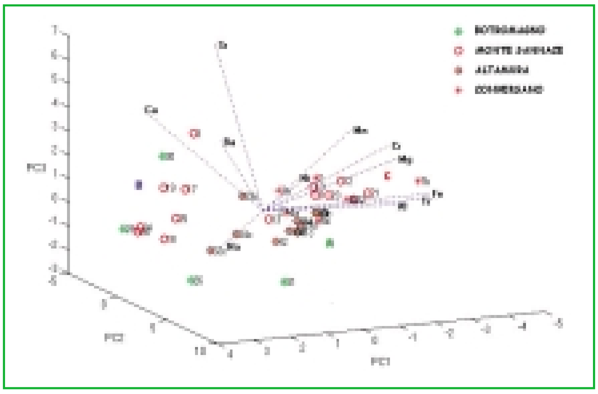
An Archaeometric Approach to Apulian Red-Figured Pottery in Southern Italy

by R. Albergo, P. Bruno, M. Caselli,
R. Laviano, A. Mangone, A. Traini



Plot of loadings and scores

During the late fifth and fourth centuries AD, an intense production of particular ceramic objects, known as "Apulian red-figured pottery", is attested in Apulia. The main feature of this pottery typology is related to the particular decorations: red-coloured figures, that stand out from a "black gloss" background, on which white and/or yellow-coloured decorative motifs are painted sometimes.

If the production technology seems to inherit the consolidated acknowledges of the Attic ceramists about red-coloured figures wares, the Apulian pottery presents peculiar stylistic and decorative features. The main intent of this research is the chemical and physical characterization of a large number of founds of "Apulian red-figured pottery", coming from different archaeological sites, by means the analytical determination of elements constituting the ceramic bulk, with subsequent statistic valuation of the results, and the surface analysis. The results, compared with those deriving from a stylistic textual and contextual classification, will allow to get a better definition of the following concepts: "local works", "imported works", "works in imitation of" and then to explain the chronology, the rate and the mechanism of the hellenization process of no Greek centres in southern Italy. The ceramic material has been dissolved by microwave acid mineralization. The analytical composition has been determined by Aas and Icp-Oes. The statistical multivariate treatment of the compositional data allows to evidence groups of similar objects according to the provenience and to the production technology (Figure). Moreover, the morpho-mineralogical examination of the bulk samples by optical microscopy with polarized light and scanning electron microscopy (Sem) has evidenced different granulometry of the objects forming different clusters. Sem analyses have also been carried out on cross-section in order to examine coverings and decorations. Sem images have shown how the black covering clearly differs from the ceramic body: with an average thickness of 10-20 µm, it is more compact, homogeneous and well-vitrified. Besides there is an evident structural and compositional continuity between the red-coloured surface and the bulk. As far as the white decorations are concerned, Sem images have displayed crystalline hexagon-structures not assignable to neo-formation crystals. Therefore, the white pigment could have been applied after the firing phase. The X-ray microanalysis has suggested the presence of Kaolinite in the white pigment.

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Degradation of Phenyl-Ureic Herbicides on Immobilized Titanium Dioxide

A study by Hplc-Esi-Ms

by A. Amorisco, I. Losito, F. Palmisano

The application of herbicides in modern agricultural practices is a cause of concern due to their relatively high solubility in water and their low degradation rates, which may result in contamination of surface and ground waters and become a risk for human health. The interest for technologies able to remove herbicides from water is then very high. Among them, the so-called Advanced Oxidation Processes (AOP) [1] are based on the generation (often assisted by UV radiation) of reactive species like the OH· radicals, which interact with organic pollutants, leading them to complete mineralization. Special AOP are photocatalitic processes [2], in which generation of OH· is mediated by inorganic semiconductors exposed to UV-visible radiation, like TiO$_2$ when exposed to radiation with $\lambda \leq 354$ nm.

In conventional TiO$_2$/photocatalysed processes aqueous suspensions of the catalyst are used; recently different techniques [3] have been developed to immobilize TiO$_2$ on solid substrates in order to reduce two main drawbacks of suspensions. Indeed the turbidity due to high suspended TiO$_2$ amounts can decrease the UV radiation penetration depth (shadowing effect) and then the rate of photocatalitic reaction. Moreover the catalyst needs complex filtration procedures after pollutants degradation.

A new method of TiO$_2$ immobilization, based on the use of a UV-transparent polymer (Pvdf) as entrapping membrane, has been recently developed in our laboratory and the catalytic substrates characterized by X-Ray Photoelectron Spectroscopy. In the present communication the Pvdf-TiO$_2$ catalysed degradation of phenyl-ureic herbicides (isoproturon and chlortoluron) in aqueous solutions will be presented. Electrospray-Ionization Mass Spectrometry (Esi-Mc) has been coupled to Hplc to analyse both unreacted herbicides and their degradation by-products. The latter have been identified by Sequential Mass Spectrometry (MS^n), *i.e.* exploiting consecutive fragmentation stages within the ion trap of the mass spectrometer, which provide characteristic fragmentation patterns for each by-product.

Hydroxylation reactions seem to occur on the aromatic ring of the herbicides, sometimes leading to substitution of linked groups with OH· Moreover, isomerization reactions are involved when UV radiation is used for photocatalysis.

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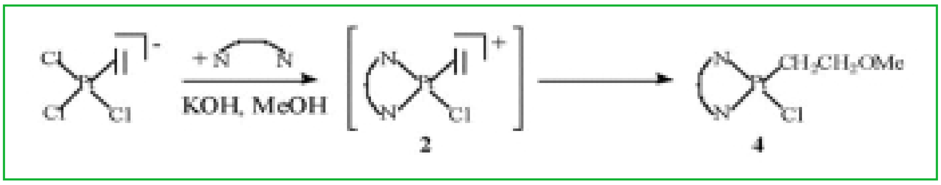
A Way to Trap Elusive Cationic Olefin Complexes of Platinum(II)

by M. Benedetti, F. Fanizzi, L. Maresca, G. Natile

Cationic metal complexes containing unsaturated molecules are interesting chemical species showing enhanced electrophilicity as compared to neutral analogues. They are therefore intermediates of several catalytic or useful stoichiometric processes.



Among other preparative strategies, cationic η^2-olefin complexes of platinum(II), [PtCl(η^2-olefin)(N-N)]$^+$, **2**, can be formed as a spontaneous evolution (*via* loss of an axial chloride) of the bipyramidal five coordinate species (L. Maresca, G. Natile, *Comments Inorg. Chem.,* 1993, **14,** 349), [PtCl$_2$(η^2-ethene)(N-N)] (**1**) (N-N=bidentate nitrogen donor). This reaction, however, had a limited synthetic relevance, allowing the preparation of cationic η^2-ethene complexes only when the N-N ligand was an aliphatic diamine bearing small substituents on the donor nitrogen atoms. Although kinetic studies had shown that, in polar solvents, species of type **2** were the reactive intermediates in the process of loss of ethylene from **1** (leading to square planar [PtCl$_2$(N-N)], **3**) in most cases the isolation of the cationic complex was not accomplished (further reaction with released chloride and formation of highly insoluble **3** were instead observed). Now we have found a general preparative procedure that allows the trapping of cationic complexes of type **2**.

When the classical reaction between Zeise's salt and the nitrogen ligand is carried on in basic methanol, the final isolated reaction product is a complex in which the MeO$^-$ anion has added to the η^2-ethene of **2**. Acid hydrolysis of **4** can reverse the last reaction step, allowing the isolation of **2**.

The success of the reaction is based on a careful control of temperature and base concentration: (i) the use of low temperature (ice-salt bath) is compulsory for the mixing of the reagents (Zeise's anion would otherwise decompose); (ii) the optimal base/complex ratio for the reaction is a function of the chelate nitrogen ligand and related to the stability of the corresponding complex of type **1**. Compound **4** has been obtained (yields ranging from 50 to >90%) with N-N=aromatic diamines (dipyridyl, unsubstituted and substituted 1,10-phenanthrolines), diimines (*N,N'*-bis(p-tolyl)acenafthenequinonediimine), sterically hindered alyphatic diamines (*N,N'*-diterbutylethylendiamine, *N,N,N',N'*-tetramethyl-1,2-diaminocyclohexane).

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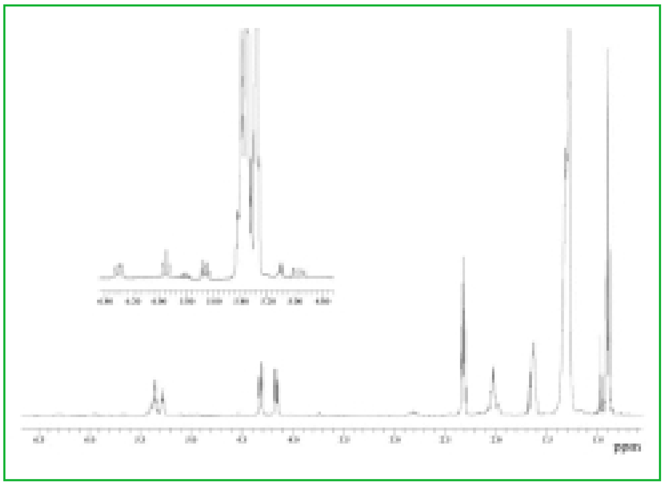
Application of Spectroscopic Methods to Milk Characterization

by M.A. Brescia, A. Sgaramella

European Community regulation No. 2081/92 gives important guidelines that discipline the “Protected designation of origin” (Pdo) of food products. In order to protect typical products it is necessary to find “authenticity markers” that could be employed to characterise them or that correlate the final product with the starting material. There is the need for techniques capable of analysing many classes of compounds in a relatively short time. In this context, the Nmr spectroscopy could be an interesting technique because it requires a very short time of analysis and furnishes information about different classes of compounds in a single spectrum [1]. An important source of information on the geographical origin of food products is the measure of isotopic ratios obtained by means of mass spectrometry (Irms). Indeed, the isotopic compositions are governed by the geo-climatic conditions under which plants grow [2]. The application of these two techniques will be described in order to show their potential in characterising authenticity and geographical origin of milk.

The ^1H-Nmr spectrum of the triglyceridic fraction of milk is shown in Figure. It is possible to distinguish principal and secondary compounds. Principal compounds are the fatty acids of triacylglycerols. The minor intensity signals could be due to CH=CH signals next to *trans,trans* peroxide groups. The amount of saturated and monounsaturated fatty acids together with linoleic, linolenic and butyric acid were obtained through the calculation of the areas of the Nmr signals due to triacylglycerols. These compositions were determined for thirty-six milk samples (14 from buffaloes and 22 from cows) in order to determine whether fatty acids composition can identify the milk species. All these parameters show significant differences between buffalo and cow milk samples and have been evaluated by Principal Component Analysis (Pca). A separation between milk samples according to their species was found. The natural abundance isotopic ratios of carbon and nitrogen ($^{15}N/^{14}N$ and $^{13}C/^{12}C$) were determined for cow milk samples coming from two different geographical production areas of the Apulia region in order to differentiate them according to their origin. The discrimination potential increased combining isotopic parameters and trace elements, determined using Inductively Coupled Plasma Emission Spectroscopy (Ba, Mn, Zn, Al, Fe and Cu). The collected data were processed using multivariate statistical methods. Samples were divided in two groups according to their origin. The most discriminating variables were isotopic ratios and Ba concentration. The investigation carried out has shown that Nmr and Irms could be useful in verifying different aspects of milk authenticity. The obtained results constitute a good starting point for the extension of this study to processed products, like mozzarella. In this case it could represent a more interesting application since the species and geographical origin differentiation could help the protection of Pdo products against adulterations (*e.g.* mislabelling of the origin, addition of cow’s milk in ewe’s or buffalo’s milk cheeses, etc.).



500 MHz ^1H-Nmr spectrum of the triacylglycerols of milk fat. The inset shows the signals due to secondary components

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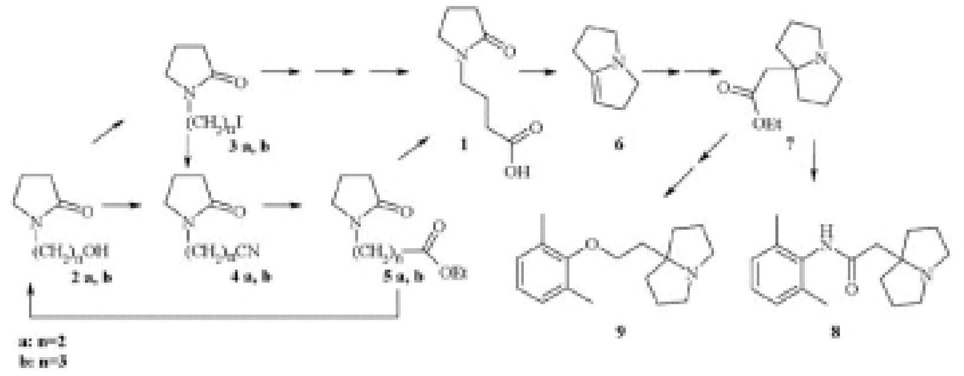
Synthesis of 7a-[2-(2,6-dimethylphenoxy)ethyl] hexahydro-1*H*-pyrrolizine, Bioisostere of Pilsicainide

by C. Bruno, A. Carocci, M.M. Cavalluzzi, C. Franchini, G. Lentini, V. Tortorella

The myotonias are congenital myopathies which share similar molecular defects at the sodium channel level with some forms of arrhythmias. Thus, I_B antiarrhythmic drugs, such as tocainide and mexiletine, have long been used for the treatment of these congenital pathologies of the skeletal muscle. However, I_B antiarrhythmic agents are far from being the ideal treatment, their use being tainted with several side effects. To look for new, more selective, and less toxic antimyotonic agents, we started a program choosing a rigid analogue of tocainide-pilsicainide (**8**) - as our lead compound. Differing from I_B antiarrhythmic drugs, pilsicainide acts preferentially on the open sodium channels (I_C antiarrhythmic drug) [1-3] and this peculiarity might suggest its use in the myotonic syndromes due to abnormal sodium channel openings. We decided to prepare the xylyloxyethyl perhydropyrrolizine (**9**) which can be considered as a bioisostere of **8**. In fact, several observations, in our and other laboratories, confirm that in the antiarrhythmic drug domain, the replacement of the carboxamide with an oxymethylene group generally causes an improvement in the pharmacological profile. The key intermediate for the preparation of both **8** and **9** is 2,3,5,6-tetrahydro-1*H*-pyrrolizine (**6**) but the only synthetic way available in the literature to this bicyclic tertiary amine starts from γ-butyrlactone [4], a regulated substance. Thus, starting from 1-(2-hydroxyethyl)-2-pyrrolidinone (**2a**), two alternative routes to its immediate precursor 4-(2-pyrrolidinon-1-yl)butanoic acid (**1**) - were explored. In the first approach, **2a** was converted into the corresponding iodo derivative **3a** which was easily transformed in ethyl 4-(2-pyrrolidinon-1-yl)propionate (**5a**) passing through the corresponding nitrile **4a**. **5a** was reduced to give the alcohol **2b** available to undergo a second three-step homologation.



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Even though this route can be shortened obtaining the nitriles **4a,b** directly from the alcohols **2a,b** under Mitsunobu conditions, our second approach is far more direct in that it introduces 2 carbon units at once giving **1** by means of a classical malonic synthesis run on **3a.** The intramolecular dehydratation and decarboxylation of **1** gave **6** and, in turn, the ethyl ester **7** from which our target compounds **8** and **9** were obtained.

In summary, a partially renewed synthesis of pilsicainide (**8**) has been developed: exploiting a novel efficient synthesis of the acid **1**, the same route afforded the pilsicainide bioisostere **9**. Both **8** and **9** are currently under investigation as new antimyotonic agents, possibly endowed with a more favorable pharmacological profile.

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Synthesis of Phthalocyanines

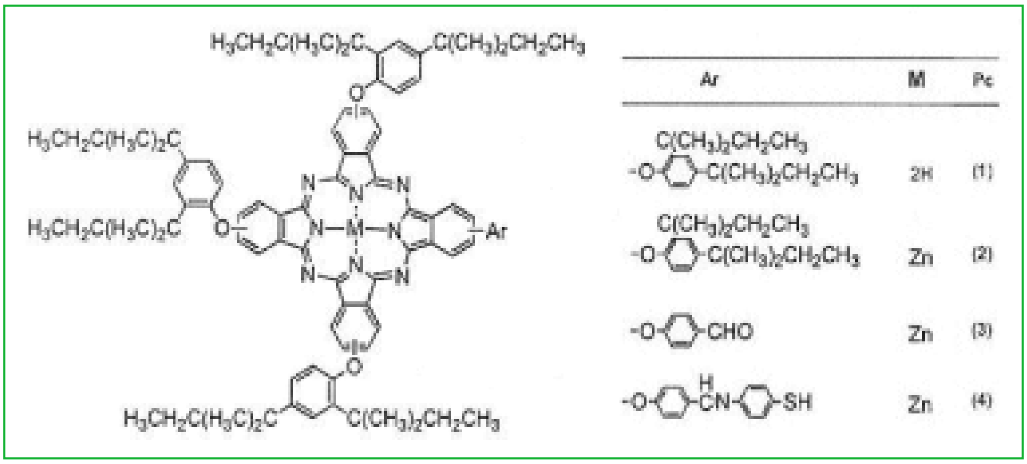
and Their Application in Volatile Organic Compounds Detection

by A. Buccolieri, G. Ciccarella, R. Rella, J. Spadavecchia, L. Valli, G. Vasapollo

Sensor technology is receiving a great interest in the last years because of the possibility to perform rapid and low cost screenings of various analytes in different applications (food analysis, workplace monitoring, environmental controls) [1]. Continuing our interest in the phthalocyanines synthesis we have focused our attention on the possibility to use the phthalocyanines (Pcs) molecules in the form of spin coated film for the detection of volatile organic compounds (amines, ketones, carboxylic acids) [2]. So that, we report here the synthesis of new phthalocyanines **1**-**4** (Figure) which have been used as active layers in thin film-based chemical sensors and the investigation of the variation in the UV-visible absorbance

Table - Absorbance variation related to Pc (2)-(4)

Analyte vapours	*Pc (2)*		*Pc (3)*		*Pc (4)*	
	$\Delta A/A$ % (Q_{II})	*$\Delta A/A$ % (Q_I)*	*$\Delta A/A$ % (Q_{II})*	*$\Delta A/A$ % (Q_I)*	*$\Delta A/A$ % (Q_{II})*	*$\Delta A/A$ (Q_I)*
Diethylamine	45.2	68.2	7.1	5.8	10.2	53.2
Dibutylamine	40.6	23.9	53.6	8.1	9.7	30.6
Tertbutylamine	50.5	62.1	5.4	4.1	13.6	23.9
2-butanone	16.6	30.1	3.5	2.3	4.3	17.9
Acetic acid	4.2	3.7	6.5	5.3	4.0	8.8



in the presence of five volatile organic compounds (butylamine, diethylamine, dibutylamine, 2-butanone, acetic acid). The vapours effect on the absorption properties of the active layer was measured in a dynamic pressure system where dry air was used as the carrier and reference gas.
The sensing elements are placed into a stainless steel chamber connected to the gas line collecting the headspace from a vial containing the liquid sample at room temperature. In the Table is reported the value ΔA/A related to two absorption band (Q_I and Q_{II}) of the phthalocyanines **2**-**4** in the presence of five volatile compounds. The response, calculated as $\Delta A/A=(A_{gas}-A_{air})/A_{air}$, where A_{gas} is the absorbance value corresponding to the absorption peak in the presence of analyte vapours and A_{air} is the absorbance at the same wavelength in presence of dry air. The metal-free phthalocyanine **1** ,tested in order to determine the role of the central metal in the interactions with the analytes, has shown no sensing activity whereas the behaviour of Zn (II)-phthalocyanines **2-4** led us to suppose that the transient interaction between the analyte vapours and the metal is fundamental. The comparison of the responses shows a different sensing behaviour for each analyte and repeated cycles of analyte exposure do not result in any loss of response. The different responses obtained in the presence of different analytes put in evidence a certain selectivity of the macromolecules films on the basis of its structure. In conclusion, spin coated thin films of metallo-phthalocyanines **2**-**4** can be considered suitable molecules for the construction of reversible optical sensor devices in the UV-Vis spectral range.

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Determination Of Polycyclic Aromatic Hydrocarbons in Atmospheric Particulate

Set Up of a New Analytical Methodology

by P. Bruno, M. Caputi, M. Caselli, D. Cassano, G. de Gennaro, M. de Rienzo

Although many different PAHs have been identified as components of the airborne particulate, there are limited published toxicological data on them. The Us Epa has identified 16 priority PAHs, based on concerns that they do or might cause cancer in animals and humans. PAHs in the ambient air predominate in the particulate-bound phase and especially in particles smaller than 10 µm diameter (PM10).
The environmental Italian law provides, as the quality target, that the concentration of BaP has to be kept below 1 ng m^{-3}. For other PAHs it is not provided any indication. In Italian Ministry Decree, 25 August 2000, the steps for the determination of particle bounds PAHs with 4-6 rings, classified by Iarc as probably carcinogenic, are described. Sampling is performed using a high volume sampler with a flow of 70 m^3 h^{-1}, on glass fibre filters for a sampling time of 24 hours. Particle bound PAHs are ultrasonically extracted with cyclohexane. A new methodology which reduces the sample manipulation and the cost of the analysis have been developed in our laboratory [1]. This method has been validated using a certified standard material and has been tested on real samples collected in the urban area of Bari.
Now we are carrying out some experiments in order to try to use a thermal desorption technique for PAH analysis. In this way it should be possible to eliminate the extraction with solvents and therefore the use of organic solvents, decreasing

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the time of analysis and the probability of analyte losses. At our knowledge only a paper [2] exploring this possibility has been published. The our thermal desorption device, connected with a GC-MS, involves a two-stage thermal desorption. The samples are heated in a flow of inert gas to extract target compounds into the vapour stream via a process of dynamic gas extraction. The desorbed analytes are transferred to a system of refocusing for concentrating them; in a second step they are released in the analytical system using as small a volume of vapour as possible. The refocusing system is a small electrically-cooled sorbent trap, which is heated rapidly to desorb 99% of analytes in the first few seconds.

The aim is to desorb PAHs directly from the filter introducing a piece of a glass fiber filter, used for sampling PM10, in the desorbing tube. During the first tests we have carried out PHA analysis on simulated samples to find the best desorption conditions. There are four parameters that can be manipulated to optimise a thermal desorption method. They are the same four parameters used in conventional gas-chromatography, i.e. temperature, time, gas flow, sorbent (stationary phase in conventional GC). The tests which have been performed show that in PAHs, with MW lower than 276, thermal desorption directly from the filter is possible. This new methodology allows reproducible results but many efforts have to be spent in order to lower limit of quantification. In fact for carrying out analysis on real samples a lower quantification limit is needed. Alternatively a different sampling strategy should be tested.

Moreover many efforts have to be spent in order to try to desorb quantitatively also the PAHs with MW higher than BaP modifying the adsorbent of the trap.

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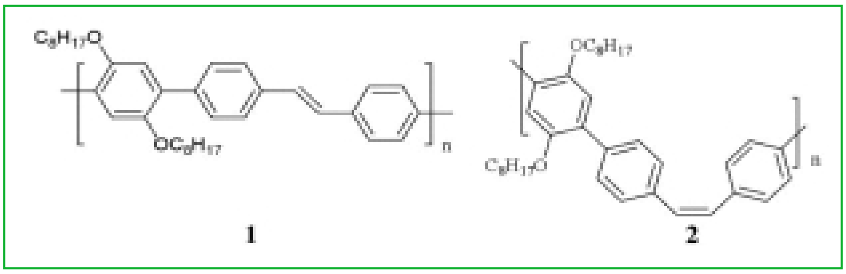
Synthesis and Optical Properties of Poly(Arylenevinylene)s Containing *Cis* Double Bonds

by F. Babudri, A. Cardone, T. Cassano, G.M. Farinola, F. Naso, R. Tommasi

Organic molecular and polymeric compounds possessing long conjugated π-systems have been extensively investigated, in the last years, as novel materials for photonics and electronics [1]. Indeed, the combination of the electrical and optical properties of semiconductors with the mechanical features and the processing advantages typical of organic polymers makes them attractive candidates as active materials for the fabrication of a number of devices, such as chemical sensors, optically pumped plastic lasers, light emitting diodes and photovoltaic cells. Furthermore, optical nonlinearities of conjugated polymers offer potential applications in electro-optical and all-optical devices. Our work have demonstrated that organometallic methodologies provide convenient opportunities for the stereoselective synthesis of conjugated oligomers and polymers[2] and represent a powerful tool for the control of the properties through proper structural modifications [3]. We have recently focused our interest on the synthesis of poly(arylenevinylene)s containing *cis* double bonds, in order to evaluate the effects of the stereochemistry of double bonds on the properties of the materials. Using the Suzuki-Miyaura cross-coupling reaction we synthesized three soluble poly(terphenylenevinylene)s having all *trans* **1**, all *cis* **2** or mixed (8:2 *trans:cis*) configuration of the double bonds. We found that the introduction of *cis* double bonds blue-shifts the absorption due to reduction of the effective conjugation length. Third-order nonlinear optical properties were also demonstrated to be strongly dependent on the *cis/trans* ratio.



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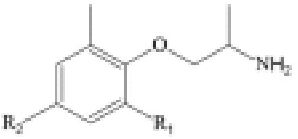
Stereospecific Synthesis of p-Hydroxymexiletine and Hydroxymethylmexiletine: the two Main Metabolites of Mexiletine

Sodium Channel Blocker Activity Evaluation in the

by A. Carocci, A. Catalano, M.M. Cavalluzzi, G. Lentini, V. Tortorella, D. Conte Camerino, A. De Luca

Mexiletine (Mex) is a class IB antiarrhythmic agent and it is administered as a racemate. However, Mex enantiomers are endowed with different pharmacodynamic and pharmacokinetic properties. In particular, the (-)-(R) form should be the eutomer [1], but the question whether Mex enantioselective disposition may partially compensate the clinical action of its more active enantiomer remains unanswered. Several studies have demonstrated that Mex is extensively metabolized in humans [2], unchanged Mex in urine corresponding to only 10% of the administered dose [3]. Aliphatic and aromatic hydroxylation are the two major metabolic routes, leading to the formation of the so called hydroxymethylmexiletine (HMM) and *p*-hydroxymexiletine (PHM) respectively. The metabolic hydroxylation of Mex has been reported to be enantioselective. In vitro studies, performed with human liver microsomes, demonstrated that aliphatic hydroxylation is predominant for (-)-(*R*)-Mex, whereas aromatic hydroxylation is favoured for the (+)-(S) enantiomer [4]. Data also suggest that the metabolic conversion of the hydroxylated metabolites into the corresponding glucuronides is enantioselective [5] determining the preferential elimination of (-)-(R)-Mex. In order to give an ultimate answer to the above question, the activity of the major Mex metabolites, in their optically active form, should be checked. According to a personal communication of Donneberg and Haselbarth, the metabolites of Mex are lacking in antiarrhythmic activity [6], while Kamey has recently claimed the lack of antinociceptive activity in both HMM enantiomers [7]. Thus, a clear evidence of the inactivity of PHM enantiomers is not available. In this communication we present several synthetic routes to PHM and HMM in their racemic and enantiomeric forms. The activity of PHM enantiomers was tested on skeletal muscle Na$^+$ channels. Both PHM enantiomers are less active than the parent compound, presenting the same pattern of stereoselectivity [(R)>(S)]. According to the preliminary results of this study, the clinical use of (-)-(R)-Mex, in lieu of the currently adopted racemic form, should be advisable.



$R_1 = CH_3$, $R_2 = H$ **Mex**
$R_1 = CH_3$, $R_2 = OH$ **PHM**
$R_1 = CH_2OH$, $R_2 = H$ **HMM**

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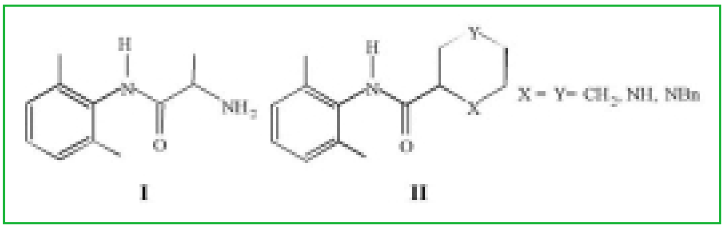
N-(2,6-Xylyl)Piperazine and Piperidine Carboxamides as New Antimyotonic Agents

by A. Catalano, F. Corbo, C. Franchini, M. Muraglia, A. Scilimati, R. Todaro, V. Tortorella

Myotonic syndromes are skeletal muscle diseases caused by either genetic or acquired forms of channelopathies [1]. Various channel disfunctions lead to both spasmodic and involuntary muscle contractions which appear after a voluntary contraction. These syndromes could be relieved by antiarrhythmic drugs such as mexiletine and tocainide (**I**), that are known skeletal muscle sodium channel blockers. The major structural component of voltage gated Na$^+$ channels is a 260 KDa α subunit, in turn formed by four homologous domains (D1-D4), each containing six transmembrane α-helices (S1-S6). The S5 and



S6 segments of each domain are arranged in a C4 symmetry array, delimiting the pore of the channel. The interaction of protonable antiarrhythmic drugs with the binding site is assumed to involve the protonated species. Recently, Catteral and coworkers [2] have presented a comprehensive model of the sodium channel which shows that the cavity of the binding site is mostly formed by lipophilic aminoacidic residues and that is not completely occupied by the so far used 1B antiarrhythmic agents. This observation prompted us to synthesize new more complex **I** analogues. In our previous studies [3], we reported that the introduction of the basic nitrogen of tocainide in a pyrrolidine cycle and its benzylation leads to a remarkable increase in the sodium channel blocking activity. These findings were used to design new six-membered heterocycle analogues **II** bearing the basic nitrogen and the stereogenic centre into a piperidine or piperazine ring, such as 2,6-xylydides of pipecolic acid (X=NH, NBn; Y=CH$_2$), nipecotic acid (X=CH$_2$; Y=NH, NBn) and 2-piperazinecarboxylic acid (X=Y=NH; NBn). **II** were efficiently synthesized as racemic mixtures from not expensive and easily available starting materials. The activity of **II** on skeletal muscle sodium channels is currently under evaluation. The preparations as well as pharmacological results will be presented and discussed in details.

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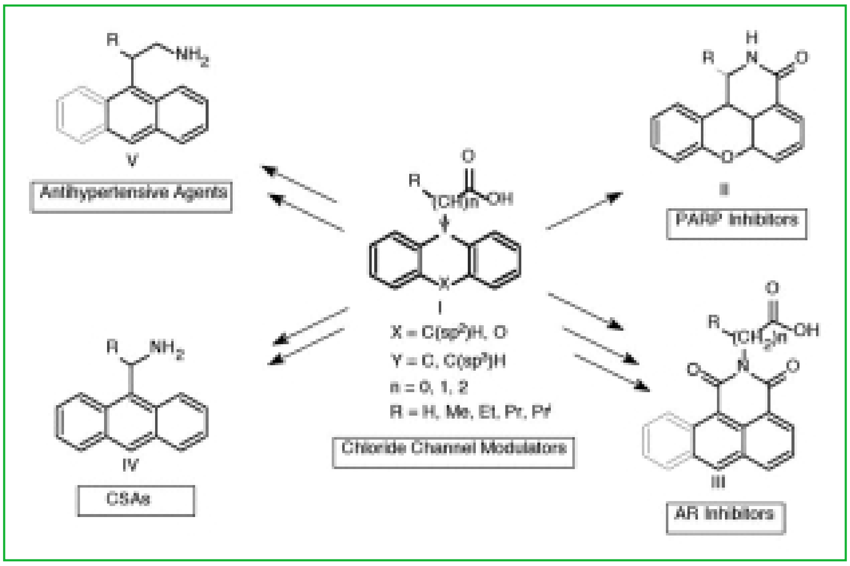
Preparation Of Chiral 2-(9-Anthryl)Alcanoic Acids, 9-Xanthenyl Isosteres, and Derivatives

Pharmacologically Relevant Compounds

by M.M. Cavalluzzi, C. Bruno, A. Carocci, N. Tangari, V. Tortorella, A. DeLuca, D. Conte Camerino

2-Arylalcanoic acids constitute a pharmacologically relevant class of compounds, mainly investigated as antiinflammatory agents [1]. Our interest in α-arylalcanoic acids, however, originates from the early observations of the potent chloride channel blocking properties of 9-anthracenecarboxylic acid (9-ACA) which make 9-ACA both a potent myotonia inducer and a useful pharmacological tool in the field of myopathic disease studies [2]. Later on, it has been shown that some chloride channel blockers act as peroxisome proliferator activator receptor (PPAR) agonists and might be clinically relevant in the treatment of dyslipidemic diseases [3]. Thus a program has been started with the aim of preparing α-(9-anthryl)alcanoic acids **I** [X=C(sp^2)H, Y=C] as pharmacological relevant myotonic inducers and, possibly, hypolipidemic agents.

Stating that a series of PPAR agonists bear an electron rich benzene ring, some α-xanthen-9-yl analogues **I** [X=O, Y=C(sp^3)H] were also designed. Furthermore, both α-(9-xanthenyl)- and α-(9-anthryl)alcanoic acids may be easily lactamized to obtain potential poly (ADP-ribose) polymerase (PARP) and, respectively, aldose reductase (AR) inhibitors (**II** [4] and **III** [5], respectively). Finally, α-(9-anthryl)alcanoic acids may be referred to as useful synthetic intermediates for the preparation of α-alkyl-9-anthracenemethaneamines **IV** which are useful chiral solvating agents (CSAs) [6], and β-alkyl-9-anthrace-



neethaneamines **V** which are analogues of antiarrhythmic [7] and antihyperthensive [8] agents (the structures of known reference compounds were drawn using heavy lines). Here we present a facile synthesis of several 2-(9-anthryl)alcanoic acids and relative synthetic intermediates: to the best of our knowledge, most of the final products and relative intermediates have never been reported before.

The preparation of some xanthenyl isosteres will also be described. 9-Xantheneacetic acid has been converted into the corresponding lactam. The extension of the process to the α-alkyl homologues will provide chiral compounds hopefully useful as pharmacological tools to explore the catalytic site structural features of PARP. Some of the 2-(9-anthryl)alcanoic and 2-(9-xanthenyl) alcanoic acids herein presented were proved to modulate the skeletal muscle chloride channel currents.

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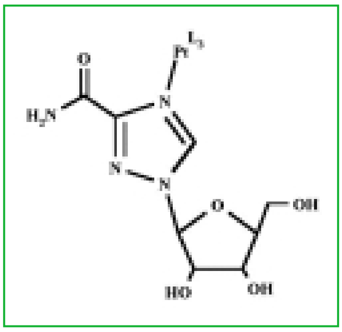

Platinum(II) Complexes with the Antiviral Agent Ribavirin

by L. Cerasino, J. Kobe, G. Natile

The search for new platinum based drugs that would display therapeutic properties better than those of *cisplatin* is still actively pursued [1]. Complexes of the type *cis*-$[PtCl_x(NH_3)_{3-x}(L)]$ (x=1 or 2), in which L represents one antiviral agent having purine structure (Acyclovir and Penciclovir) have been already explored for their antitumor and antiviral activity. Among these, the compound *cis*-$[PtCl(NH_3)_2(Acyclovir)]^+$ proved to be very effective both as antitumor and antiviral agent [2]. On the basis of the above results, the preparation of analogous complexes with Ribavirin was undertaken. Ribavirin was discovered as antiviral drug in early Seventies and is currently used in therapy [3]. Some metal complexes with this ligand have already been reported in literature [4]. In this communication we report the synthesis and characterisation of the following complexes: *cis*-$[PtCl(NH_3)_2$ (Ribavirin)](NO_3), *cis*-$[PtCl_2(NH_3)$(Ribavirin)], *cis*-$[Pt(NH_3)_2$ (Ribavirin)$_2](NO_3)_2$, [Pt(ethylenediamine)(Ribavirin)$_2](NO_3)_2$, and [Pt(pmdien)(Ribavirin)]$(NO_3)_2$. These compounds differ for the number of antiviral ligands per platinum atom and for the sterically demand of the ancillary ligands. These differences influence the overall charge and consequently the solubility properties of the complexes. All these features could play a different role in determining the activity or the inactivity of the compounds as antitumor/antiviral agents.

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Fluoropolymers Modified by Metal Nanoparticles

Vapour-sensing Properties, Analytical Characterization and Sensing Mechanism

by N. Cioffi, L. Torsi, D. Altamura, I. Farella, A. Valentini, T. Bleve-Zacheo, L. Sabbatini, P.G. Zambonin

Ion beam co-sputtering technique can be successfully applied to the deposition of fluoropolymers (CF_x) modified with metal nanoparticles. By suitably choosing ion beam parameters, such as energy and current, it is possible to synthesise metal-CF$_x$ composites with a controlled thickness and structure, this last parameter being expressed as the polymer cross linking extent and the metal volume fraction φ. In this study, the vapour-sensing properties and the spectroscopic/morphological characterization of fluoropolymers modified with gold or palladium nanoparticles are presented and the results are used for the interpretation of the sensing process. Upon exposure to organic vapours, the composites undergo swelling phenomena that modify their fundamental properties and that can be employed to perform vapour-sensing measurements by means of ellipsometric, mass- or conductivity-variation measurements [1-6]. The sensitivity of the composites increases as the metal loading (φ) and the analyte polarity increase. Moreover, the sensing properties also depend on the metal embedded in the fluoropolymer.

Afm (Atomic force microscopy), Tem (Transmission electron microscopy) and Cross-Sectional Tem microscopies have been used to study the composite morphology. Xps (X-ray photoelectron spectroscopy) has been employed to study the structure of the organic matrix and the polymer/cluster interface. At increasing φ values, the average length of the linear polymeric segments shortens and the amount of unsaturated fluorinated carbons, as well as the polymer cross-linking extent, increases. Fluoride and oxide species are also detected on the metal cluster surface. The concentration of these polar and reactive species increases as φ increases.

The influence of the different driving forces on the vapour-sensing mechanism is discussed on the basis of thermodynamic models and of the materials analytical characterization. Finally, *ad hoc* FT-IR experiments on swollen metal-CF$_x$ composites interacting with acetone, chosen as target odour, demonstrate the occurrence of the analyte complexation with electron poor metal oxidized species.

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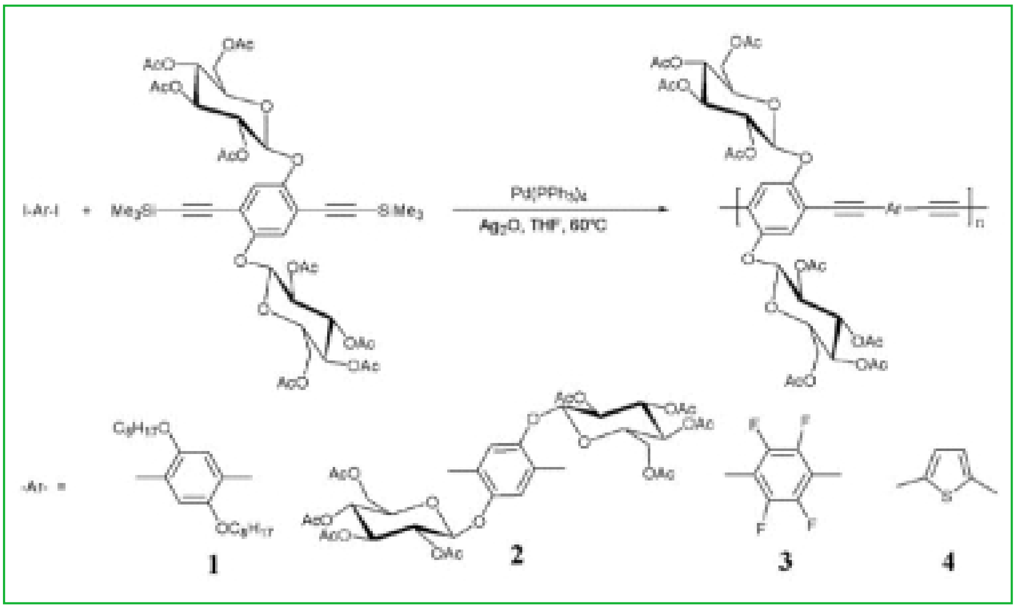
Synthesis of Poly(Aryleneethynylene)s Bearing Glucose Units as Side Chains

Their Application in Chiral Discrimination

by F. Babudri, N. Cioffi, D. Colangiuli, P.A. Di Lorenzo, G.M. Farinola,
O. Hassan Omar, F. Naso, M.C. Tanese, L. Torsi



The development of new polyconjugated polymers represents an active research field in synthetic organic chemistry, in view of their applications as active materials in a number of electronic and photonic devices [1]. Conjugated polymers are available in a number of molecular structures: poly(arylenevinylene)s, polyphenylenes, polythiophenes and poly(aryleneethynylene)s are some of the most interesting classes of such new organic materials. A further level of structural modification is represented by the introduction on the conjugated main chain of side groups, with the aim of achieving solubility and processability of the resulting materials, and also of tuning optical and electronic properties of the compounds. A very interesting structural modification, not frequently described in the literature, is represented by the introduction of biomolecules as side groups, aimed to confer properties such as biocompatibility and supramolecular organization. In the frame of our studies dealing with the development of organometallic methodologies for the preparation of polyconjugated polymers, we have recently synthesized a series of poly(aryleneethynylene)s bearing glucose units as side chains by a Pd-catalyzed cross-coupling reaction between trimethylsilylethynyl derivatives and aromatic halides in the presence of silver oxide [2]. We have assembled a gravimetric vapour sensor with polymer **1** as the active layer, based on a quartz crystal microbalance resonator, which is able to perform chiral discrimination due to the presence of the glucose side chains. The performance of the device has been tested for enantioselective sensing of the natural and non-natural menthol.

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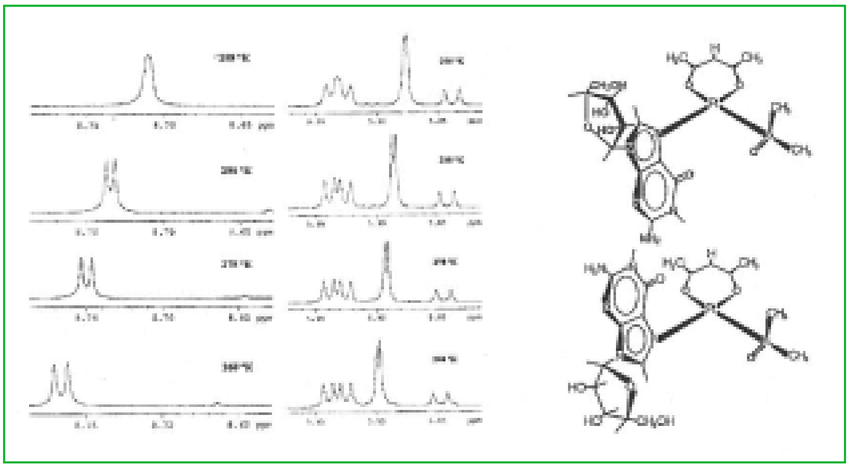
Slowing Down Dynamic Motion of Nucleobases

Effects of Diketonate Carrier Ligand in Cisplatinum Analogues

by S.A. De Pascali, R. Caforio,
A. Ciccarese, F.P. Fanizzi



Most of Pt anticancer compounds have NH-bearing carrier ligand, generally considered responsible for conformational changes produced on Dna. On the other hand, it has been recently reported that the kind and distribution of conformers in unlinked or phosphate linked guanine derivatives *cis*-PtA$_2$G$_2$ (A$_2$=Me$_2$ppz, N,N'-dimethylpiperazine, lacking NH groups) appear to depend on steric hindrance of the carrier diamine ligand rather than hydrogen bonding [1]. Furthermore, the empirical rule which required carrier amine ligands with at least one hydrogen to obtain active anticancer platinum drugs in not longer observed in nowadays *Cisplatinum* analogues [2]. To assess carrier ligand effects, we have investigated dynamic motions of nucleobases in platinum complex with a chelate acetylacetonate (acac) as carrier ligand. In this system: i) the steric hindrance of the carrier ligand towards the *cis* nucleobase is due to a coordinated sp_2 oxygen of the six member chelate ring; ii) on the contrary with respect to NH's bearing amine ligands, the platinum bond oxygen should eventually act as nucleophylic counterpart in hydrogen bonding.

Reaction of [PtCl(acac)(Me$_2$SO)] [3] with excess guanosine (Guo), followed by Nmr spectroscopy, shows formation of [Pt(acac)(Me$_2$SO)(Guo)]$^+$ which consists of two rotamers, due to slow rotation of Guo around the Pt-N(7) bond, in the Nmr time scale. By lowering the temperature, two sets of proton signals (H8, H1',γ-CH of acac) are clearly seen offering the most convincing evidence for the existence of the rotamers pair. In the variable temperature Nmr experiment it is also worth noting the deshielding for the H8 signals due to the different anisotropy of the platinum felt when the guanosine, at low temperature, approaches an orientation perpendicular to the coordination plane. Slow dynamic motion of metal bonded nucleobase in [Pt(acac)(Me$_2$SO)(Guo)]$^+$ can be due to steric and/or electronic effects of O-chelated acac ligand but also to the steric bulk of the *cis* Me$_2$SO ligand. Interestingly in the analogous [Pt(en)(Me$_2$SO)(Guo)]$^{2+}$ (en=ethylenediamine) there is no ^{1}H Nmr evidence of two rotamers down to 274 K [4] indicating that acac may show special features as carrier ligand in these systems.

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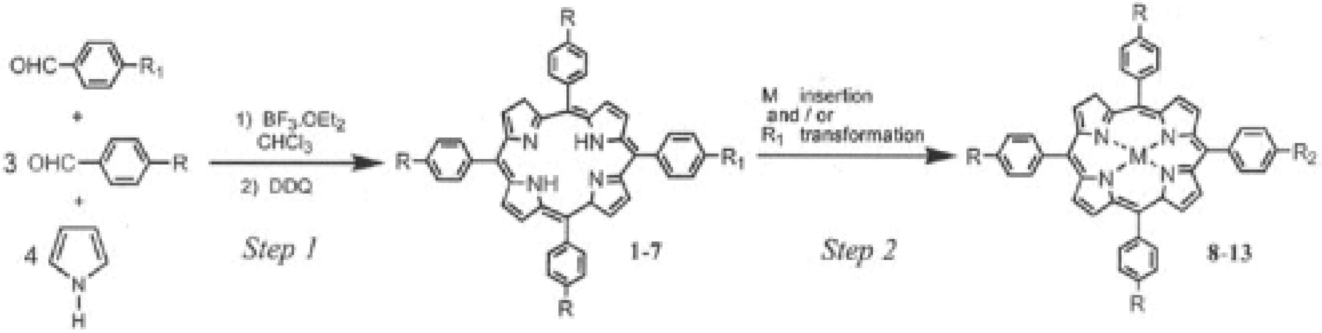
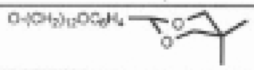
Synthesis and Characterization of new *Meso*-Substituted Porphyrin Derivatives

by R. Del Sole, G. Mele, G. Vasapollo

The chemistry of macrocyclic molecules such as porphyrins and phthalocyanines has been intensely developed in the recent years in view of their possible applications as active layers for gas sensors [1], heterogeneous catalysts [2, 3], promoters for photoinduced electron transfer processes [4]. The peripheral substitution in such molecules seems important to control their molecular organization especially for the realization of hybrid organic, metallo organic and inorganic molecular devices. Continuing our research in this area, we have synthesized new *meso*-substituted porphyrins containing long alkyl chains having at their head reactive groups with molecular parameters suitable for thin films formation. The porphyrins and metal porphyrins were synthesized according to methods reported in the literature [5].



Compound	R_1	R_2	R	M
1	OH		t-Bu	
2			t-Bu	
3	 $O-(CH_2)_{12}OC_6H_4$		t-Bu	
4	$O\ (CH_2)_2Br$		H	
5	$O\ (CH_2)_{12}Br$		t-Bu	
6	$O\ (CH_2)_2SCOMe$		t-Bu	
7	$O\ (CH_2)_{12}SCOMe$		t-Bu	
8		OH	t-Bu	Cu
9		CHO	t-Bu	2H
10		$O\ (CH_2)_{12}\ C_6H_4CHO$	t-Bu	2H
11		$O\ (CH_2)_{12}O\ C_6H_4C=N\text{-}PhSH$	t-Bu	2H
12		$O\ (CH_2)_{12}O\ C_6H_4C=N\text{-}PhSH$	t-Bu	Cu
13		$O\ (CH_2)_2Br$	H	Cu

Thus, a mixture of two different aldehydes and pyrrole were reacted in chloroform at room temperature for 1 hour in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to produce different substituted porphyrin derivatives **1-7** (Scheme, *step 1*). In particular, porphyrins **1-4**, prepared according to *step 1*, were successively reacted in different conditions in order to introduce metals or other functional linking groups; and, in a second step, were synthesized the porphyrins **8-13** (Scheme, *step 2*). In the Table we have reported the metal and metal-free mono substituted porphyrin derivatives synthesized as shown in the Scheme. All the compounds where purified by chromatography and successively characterized by Uv-Vis, Ft-Ir, Nmr, Lc-Ms spectroscopy. The new meso-substituted porphyrins containing a long aliphatic chain have been synthesized with the aim to obtain two main objectives:

1) prepare new porphyrins having in their structure one or more linking groups capable to bond these molecules onto the surface of various inorganic substrates (glass, gold etc.);
2) to introduce a spacer between such molecules and others (such as for example fullerene, phthalocyanine) in a possible acceptor-donor electronic transfer process.

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Catalytic Activity of a Polymer Supported Palladium Complex
in Carbon-Carbon Bond Forming Reaction

by M.M. Dell'Anna, V. Gallo, P. Mastrorilli, C.F. Nobile, G. Romanazzi

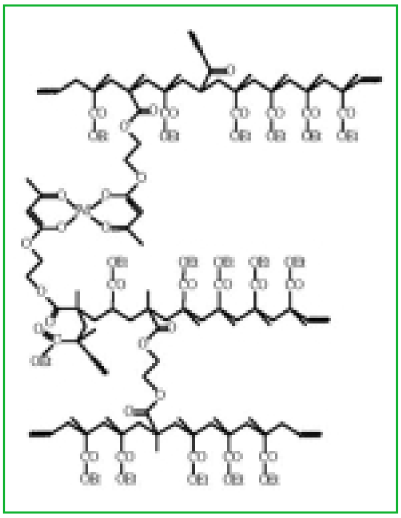
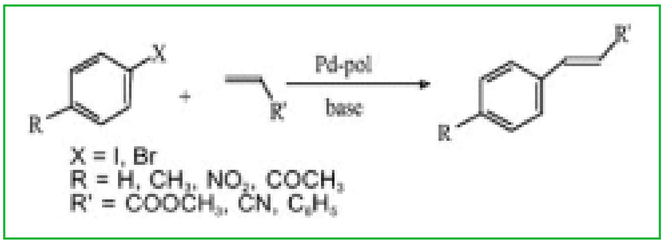


Figure - Pd(II) supported polymer

We have recently synthesised a new Pd(II) supported polymer (Figure), by reaction between $Pd(AAEMA)_2$ [$AAEMA^-$= deprotonated form of 2-acetoacetoxy(ethylmetacrylate)], ethyl methacrylate (comonomer) and ethylene glycol dimethacrylate (cross-linker) [1]. This presentation describes the catalytic activity and recyclability of the $Pd(AAEMA)_2$ supported complex (Pd-pol) towards carbon-carbon bond forming reactions, such as the Heck reaction between aryl iodides or bromides and several alkenes [2] (Scheme) and the influence of solvent, base, temperature and additives, on the performance and the recyclability of the catalyst. Under suitable conditions (which are DMF solvent, 2 equivalent base, absence of phosphane additives, molar ratio ArI/ Pd=1000 and ArBr/Pd=500, T=90 °C for aryl iodides and T=160 °C for aryl bromides) the catalyst is air stable, active, selective and recyclable several times with negligible metal leaching.



Scheme - Heck reaction between aryl iodides or bromides and several alkenes

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Development of new Supramolecular Sensitizers for Photodynamic Therapy

by A. Agostiano, L. Catucci, P. Cosma, P.L. Dentuto, P. Fini

Photodynamic therapy (Pdt) is an attractive modality to treat cancer and hyperproliferative diseases based on the use of a photosensitizer in presence of oxygen and light [1]. The effectiveness of Pdt treatment depends on physico-chemical and photophysical properties of the sensitizer and on biochemical composition and characteristics of the target tissue [2]. In general an ideal photosensitizer have to meet the following requirements: high chemical purity, a high molar extinction coefficient at the absorption maximum in the red spectral region, a low tendency to aggregate in aqueous media, a good photostability, a long triplet lifetime and a high yield of $^1O_2$. None of the photosensitizers studied in vitro/in vivo fulfils satisfactory these requirements and hence the Pdt is limited to treat tumor located just under the skin or on the lining of internal organs. These limitations have driven the research for other photosensitizers that may increase the effectiveness of Pdt against tumour located below skin or inside an organ. Among the various classes of compounds explored as potential photosentizers in PDT, porphyrins and their analogs [3, 4] are considered the most promising since their spectra is usually characterised by intense absorption bands in the 600-850 nm wavelength region, where the maximal light depth penetration into mammalian tissues is obtained [5]. Recently we have undertaken a systematic study on the use of natural porphyrins as photosensitizers for Pdt combined with cyclodextrins (CDs) as delivery systems. Cyclodextrins are cyclic oligosaccharides consisting of glucopyranoside units linked together by α-1,4 bonds to form macrocyclics. They are used for pharmacological applications to increase the solubility of poorly water soluble drugs and to increase their bioavailability and stability [6]. We have studied the behaviour in aqueous solutions of the chlorophyll *a* (Chl *a*), the main photosynthetic amphiphilic pigment of green plants, and cyclodextrins (α-cyclodextrin, hydroxypropyl-β-cyclodextrin, heptakis (2,6-di-O-methyl)-β-cyclodextrin and hydroxypropyl-γ-cyclodextrin). The

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study was carried out by using different spectroscopic (UV-Vis, fluorescence, circular dichroism, time resolved absorption and luminescence) and calorimetric (Itc) techniques. The obtained results indicate that the nature and concentration of cyclodextrins play a relevant role in modulating aggregation properties of Chl *a* in aqueous solutions. In particular HP-β-CD and Dimeb resulted suitable carriers of Chl *a* as monomer in water. Moreover the $^1O_2$ production in pigment-CD solutions makes these systems suitable for possible application in Pdt.

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Individual Rotamers Of (R,S,S,R)-(N,N'- Me_2-2,3-Diaminobutane)PTG_2 Complexes

Their Ground-State Stability and Rotational Activation Parameters

by N.G. Di Masi, G. Colonna, L.G. Marzilli, G. Natile

Anticancer compounds such as *cis*-$[Pt(NH_3)_2Cl_2]$ (cisplatin) and its derivatives are known to produce a critical lesion on Dna, forming two Pt-N7 bonds [1] with adiacent purine bases on the same strand. These lesions are referred to as “intrastrand cross-links”. The platinum can also cross-link guanine bases of opposite strands to form “interstrand cross-links”, however the latter constitutes only a minor lesion. In the first type of lesion adjacent purines generally assume a head-to-head (HH) conformation in which the H8 atoms of the purines are on the same side of the coordination plane [2]. In contrast, in the interstrand cross-link, the two purine residues have the two H8 on opposite sides of the coordination plane; the latter orientation is termed head-to-tail (HT). The simplest models for the bifunctional adducts described above are complexes of the type *cis*-PtA_2G_2 in which A_2 stands for two unidentate or one bidentate amine ligand and G for a guanine derivative (G=9-Etg, 3'-Gmp and 5'-Gmp) [3]. These models can form different rotamers having either an HH or an HT conformation. In the present work, the rate constants for guanine rotation about Pt-N7 bond for the title compounds were evaluated from line-shape analysis of the H8 resonances. Three diastereomers, two in HT (ΔHT and ΛHT) and one in HH conformation exist in equilibrium in solution. The two H8 protons are equivalent in ΔHT and ΛHT conformers and non equivalent in the HH form, therefore four rate constants were evaluated. Activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) were calculated from rate constant dependence upon temperature. In this investigation also the equilibrium constants between HT and HH rotamers were evaluated together with the corresponding thermodynamic parameters ΔH and ΔS.

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Michael Addition of Chloroalkyloxazolines to Electron-Poor Alkenes

Synthesis of Heterosubstituted Cyclopropanes

by M.T. Rocchetti, V. Fino,
V. Capriati, S. Florio, R. Luisi

Recent contributions from our [1] and other research labs [2] have disclosed that certain metalated haloalkyl heterocycles, which proved to be good Darzens reagents, are good nucleophiles towards several electrophilic species such as carbonyl compounds [3], imines [4] and nitrones [5] to give substituted oxiranes, aziridines and alkenyl heterocycles, re-

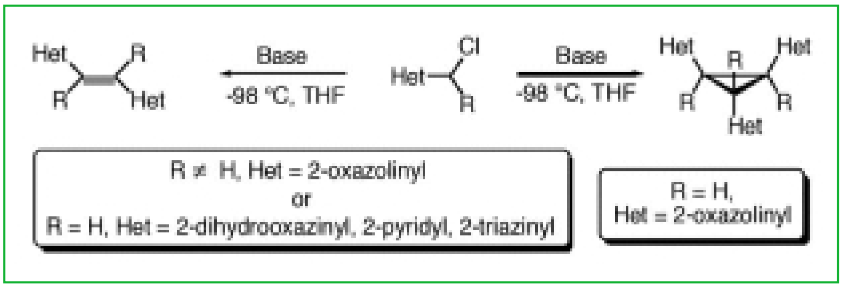

Figure 1

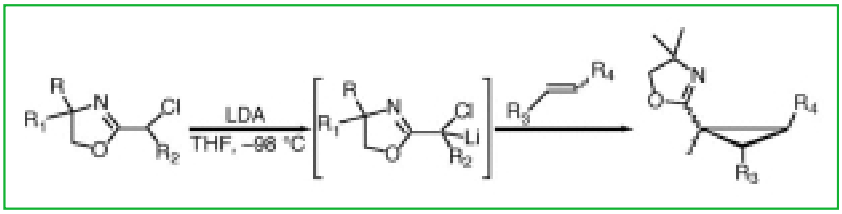

Figure 2

spectively. In the absence of an external electrophile these metalated compounds tend to undergo a sort of "trimerization" giving cyclopropane derivatives. Such a remarkable propensity turned out to be very much dependent upon the nature of the heterocyclic system; in some cases, a "dimerization" reaction to give diheterosubstituted alkenes was observed. In this communication the preparation of substituted cyclopropanes via a Michael-type addition of lithiated 2-(1-chloroalkyl)oxazolines to symmetrical and unsymmetrical electron-poor alkenes will be discussed. The synthesis of chiral non racemic tris(oxazolinyl)cyclopropanes together with mechanistic aspects will be highlighted as well.

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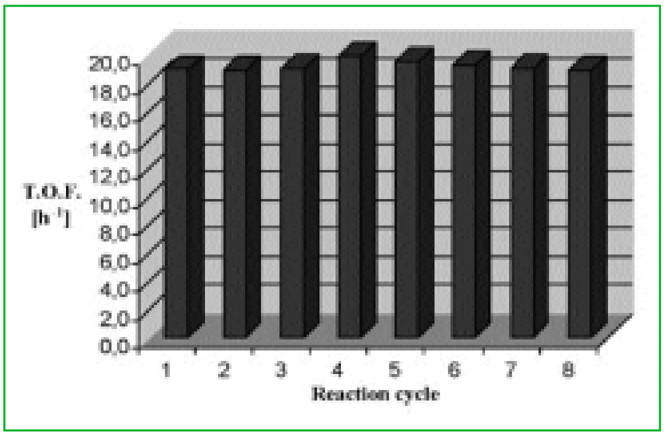
Michael Addition of Acetylacetone to Methylvinylketone in Ionic Liquids

by M.M. Dell'Anna, V. Gallo, P. Mastrorilli, C.F. Nobile, G. Romanazzi, G.P. Suranna

Ionic liquids (IL) or molten salts have been demonstrated to be innovative solvents which offer an attractive alternative to conventional organic solvents. Their intriguing properties have been primarily explored for applications in electrochemistry technologies and in liquid-liquid extraction processes. Furthermore, their physical properties, in particular air and moisture stability, wide liquid range, low melting point and negligible vapour pressure prompted to use ionic liquids as reaction media as an alternative to volatile organic compounds (Voc). Following our interest (P. Mastrorilli *et al., J. Mol. Catal. A,* 2002, **184,** 73) on the topic, [bmim]BF_4 (1-*n*-butyl-3-methylimidazolium tetrafluoroborate) has been used as solvent for transition metal catalysed Michael addition. $Ni(acac)_2 \cdot 2H_2O$, $Yb(TfO)_3$ and $FeCl_3 \cdot 6H_2O$ have been tested as catalysts focusing on the addition of acetylacetone to methylvinylketone as a model reaction. Comparing the obtained results with literature data, $Ni(acac)_2 \cdot 2H_2O$ in IL appears to be outstanding in terms of activity and selectivity in 3-acetyl-2,6-heptanedione. Being the Ni(II) based system more active than both Fe(III) and Yb(III), its recyclability has been studied by removing the product by distillation under reduced pressure after each cycle and by adding fresh reagents. The results are reported in the figure and reveal that the catalytic system is recyclable at least 7 times without loss of activity.



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Anti-Beer Evaluation Of Hydrochlorothiazide And Losartan By Uv Derivative Spectrophotometry

by A. Giannandrea, C. Vetuschi

An UV derivative method, for the simultaneous determination of hydrochlorothiazide (HCT) and Losartan (LST) in the commercial forms, was developed. The fourth derivative spectrum, from the alcoholic solution, was used. HCT can be determined by a specific signal at 330-340 nm (Pc), while LST uses the signal Ps, common to both products.
By examining the relationships on Ps as function of the drug concentrations in wide range (HCT 4-500 10^{-3}, LST 16-2000 10^{-3} mg mL^{-1} and their 1:4 ± 0.5 mixtures), two zones could be observed. A first, at low concentrations, in which the absorbance of the mixtures increases and a second, for high concentrations, in which the absorbance decreases.
The second behaviour is due to intramolecular reactions of the drugs. For both intervals linear regressions were obtained by correlating the above mentioned signals with the drug concentrations. Several procedures for the drug quantitation were proposed. In order to reduce or, at least, to keep reproducible the degradation reactions, all the solutions were prepared adding exactly weighted drug amounts to the stirred final volume of the solvent, without any dilution. This produces a higher statistical variability with a greater imprecision, but it makes the method more rigorous.

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Figure 1

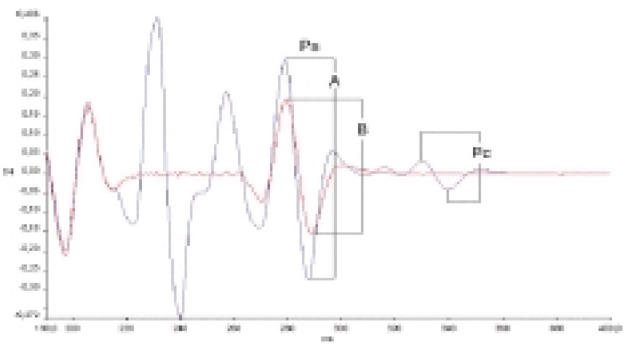
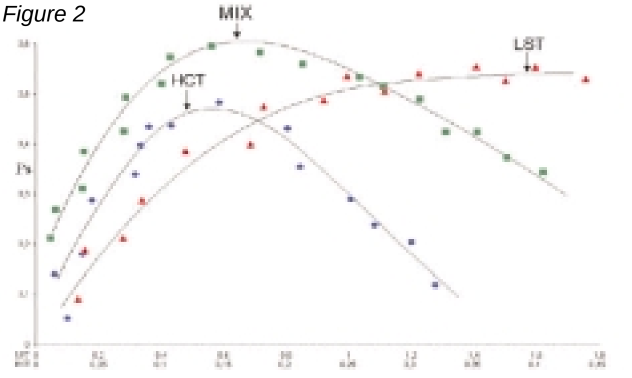


Figure 2



Quinone Exchange in Photosynthetic Reaction Centers

by L. Giotta, M. Trotta, F. Milano, A. Agostiano

Long chain ubiquinones play a central role in energy trasduction. In bacterial photosynthesis the conversion from electromagnetic to chemical energy takes place into the reaction centre (RC), an integral membrane protein. The primary event is a charge separation process which takes place between an electron donor (Bacteriochlorophyll Dimer D) and an acceptor (a quinone Q). In this work we present a kinetic study based on the numerical solution of the differential equation set proposed by Shinkarev and Wraight [1]. In isolated RCs, following a flash light excitation, a charge recombination takes place. When the Q_B pocket is empty, a monoexponen-

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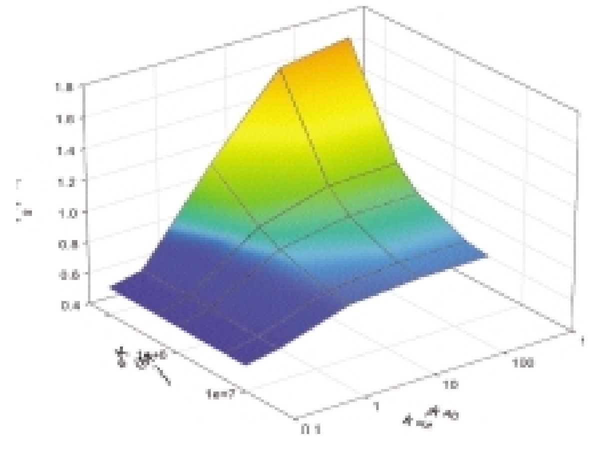

Three-dimensional representation of the slow rate constant k_S as function of the binding constant and the ratio k_{out}/k_{AD}. The graph was obtained for a quinone/RC = 0.73 tial charge recombination occurs with a rate constant k_{AD} of about 8 s^{-1}. In RCs having the Q_B pocket occupied, the electron rapidly equilibrates between the two quinones with a constant $L_{AB}=k_{AB}/k_{BA}$. When the Q_B pocket is fully occupied the charge recombination is again monoexponential with a rate constant $(k_{AD}+k_{BD}L_{AB})/(1+L_{AB})$ [2]. For RCs with partially occupied Q_B-site the D^+ dark relaxation can be described by the sum of two exponential decays, the fast k_F and slow k_S ones, where the latter depends on the ratio between the quinone exchange rate and k_{AD}. We focused the attention on the influence played by the ratio quinone/RC on the slow decay, by preparing liposomes containing a fixed amount of Q_B-depleted RC and a variable quinone amount. The experimental signals were fitted with the sum of two exponential decays keeping $k_F=k_{AD}=8.3$ s^{-1}. Increasing the quinone concentration increases the slow decay amplitude and k_S decreases. By solving numerically the complete set of kinetic differential equations, the signal decay due to charge recombination kinetic has been simulated. For $k_{out}/k_{AD}<<1$ the experimental behaviour observed in the case of slow quinone exchange can be obtained for any values of K_B. The fitting constant k_S remains almost equal to $(k_{AD} + k_{BD}L_{AB})/(1+L_{AB})$ for all the binding constant values. For larger values of k_{out}/k_{AD}, only a pair of k_{out} and K_B (25 s^{-1} and 10^{-6} M^{-1} respectively) can be used to reproduce the experimental quinone concentration dependence of k_s and of the normalized amplitude. The main finding of our work is that the release constant of quinone from RC found in artificial vesicles is comparable to the charge recombination rate k_{AD}. This implies that after each charge separation, the electron has a finite chance to reach the secondary electron acceptor even in those RCs lacking the secondary quinone improving the efficiency of energy conversion.

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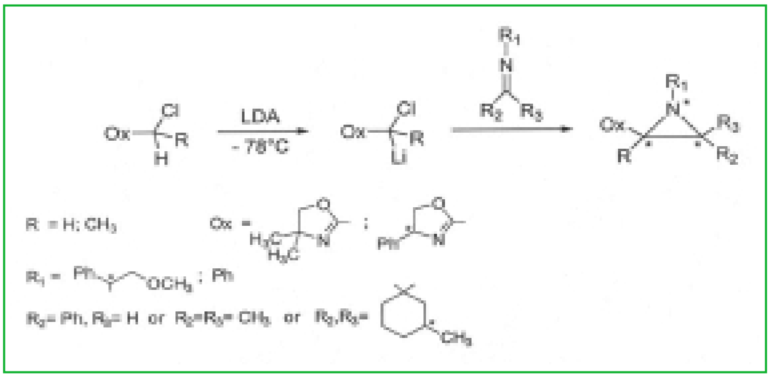
Diastereo and Enantioselective Synthesis of (oxazolinyl)alkyl Aziridines

by C. Granito, L. Troisi, S. Florio, G. Ingrosso, L. De Vitis



Many procedures have been reported for aziridinic heterocycle synthesis, many from alkenes [1], or by addition of α-halosulfonyl carbanions [2] to imines. Recently, we have reported the “one pot” coupling reaction of α-oxazolinylalkyllithiums with carbonyl compounds and imines leading to oxiranes and aziridines, respectively [3]. The aziridinic heterocycle is of great synthetic interest because of his ability to undergo ring-opening reactions and to act as intermediate for the preparation of a variety of organic compounds [4]. In this communication we describe the diastereo- and enantioselective synthesis of chiral (oxazolinyl)alkyl aziridines having different chiral centres. The coupling reaction of α-oxazolinylalkyllithiums with imines having an asymmetric centre on R_1 (R_1=Ph-C*HCH_2-OCH_3) afforded, in good yield and hight enantiomeric enrichments (*ee* ≈ 99%), aziridines containing different chiral centres. A different asymmetric induction, with diastereoselectivity, was noticed using α-oxazolinylalkyllithiums in the coupling with chiral imines having the stereocentre in the ketonic moiety. An inseparable mixture (6:4) of *E* configuration structures was obtained. Using, instead, a chiral α-oxazolinylalkyllithium in the coupling with non chiral imine (R_1=R_2=Ph; R_3=H) two aziridines of *E* and *Z* configuration (ratio 1:1) were isolated, by chromatography, in enantiomerically pure form. Similar results were obtained with different α-chloroheteroarylalkyllithiums in the coupling with chiral imines. All reactions produced chiral aziridines (ee≈99%) of *E* configuration except the α-chlorothiazolylethyllithium which afforded, on the contrary, the *Z* ariridine.

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