American Chemical Society
22nd Annual Northern California
Undergraduate Research Symposium

California State University, Sacramento
Department of Chemistry

Sacramento, CA
May 8, 2010

(all events will be held in the University Union)

8:30a.m. – 9:00a.m.	Registration, Refreshments	outside the Main Ballroom
8:45a.m. – 9:00a.m.	Student Oral Presentation Set Up	presentation rooms (listed below)
9:00am – 9:10am	Conference Opening: Dr. Jill Trainer Dean, College of Natural Sciences and Mathematics Dr. Susan Crawford Chair, Department of Chemistry	Main Ballroom
9:15a.m. – 10:35a.m.	Student Oral Presentations	
	Session 1: Physical and Computational Chemistry	Foothill Suite, Auburn Room (3rd floor)
	Session 2: Biochemistry I	Orchard Suite (2nd floor)
	Session 3: Biochemistry II	Forest Suite (2nd floor)
	Session 4: Organic and Atmospheric Chemistry	Foothill Suite, Folsom Room (3rd floor)
10:35a.m. – 10:40a.m.	Poster Set Up	Main Ballroom
10:45a.m. – 11:35a.m.	Poster Session 1 (odd-numbered posters)	Main Ballroom
11:35a.m. – 12:35p.m.	Lunch (provided for registered attendees; please present lunch coupon)	Main Ballroom
12:35p.m. – 1:25p.m.	Poster Session 2 (even-numbered posters)	Main Ballroom
1:30p.m. – 2:30p.m.	Keynote Presentation: Dr. Robert M. Waymouth Stanford University "Catalysis: An enabling science for polymer chemistry"	Hinde Auditorium (1st floor)
2:30p.m.	Closing Remarks	Hinde Auditorium (1st floor)

Keynote Presentation

Catalysis: An Enabling Science for Polymer Chemistry

Robert M. Waymouth

Department of Chemistry, Stanford University, Stanford CA, 94305, USA

Polymers are ubiquitous and are highly useful modern materials. Catalysis has proven the enabling science for polymer synthesis, and the development of new families of catalysts continues to drive innovation in the generation of new polymeric materials. The catalytic polymerization of olefins constitutes one of the major technological achievements of the 20th Century. Olefin polymerization catalysis is a prototype of translational science, where new scientific insights and advances in catalyst developments have transformed industrial practice. In the first part of the lecture, I will describe our recent efforts to develop new families of polymerization catalysts to create new polyolefin structures with novel properties.

Catalysis is also a foundational pillar for sustainable chemical processes; the discovery of highly active, environmentally benign catalytic processes is a central goal of Green Chemistry. The widespread utility of plastics and their indiscriminate disposal has left an adverse and enduring environmental legacy. Biodegradable polymers derived from renewable resources provide an attractive alternative to many petrochemical thermoplastics, due to their attractive and improving cost/performance characteristics, their application as biomedical materials, and their potential to mitigate the environmental impact of discarded plastic waste in landfills. In the second part of the lecture, I will describe advances in a new family of environmentally benign organic catalysts for the synthesis of biodegradable and biocompatible plastics. Mechanistic and theoretical investigations have provided new scientific insights on the diversity of mechanistic pathways for organocatalytic polymerization reactions and the opportunities that these new insights have created for the synthesis of well-defined macromolecular architectures, including high molecular weight cyclic polyesters.

Robert M. Waymouth

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Robert (Bob) Waymouth was born on May 20, 1960 in Warner Robins Georgia. He obtained his B.S. in Mathematics and B.A. in Chemistry from Washington and Lee University in 1982 and his Ph.D. in Chemistry at the California Institute of Technology in 1987 with Professor R.H. Grubbs. He was a postdoctoral fellow with the late Professor Piero Pino at the Swiss Federal Institute of Technology (ETH) in Zurich in 1987 and joined the faculty at Stanford as an Assistant Professor in 1988. In 2000 he was named the Robert Eckles Swain Professor of Chemistry. His research interests focus on the development of novel catalysts for the synthesis of new polymers. Professor Waymouth teaches Freshman Introductory Chemistry, Organic Chemistry and graduate courses in Organometallic Chemistry and Polymer Chemistry. He received the Alan T. Waterman Award from the NSF in 1996, the Arthur C. Cope Scholar Award in 1995 and the Cooperative Research Award in Polymer Science in 2009. He has won several university teaching awards, including the Walter J. Gores Award, the Phi Beta Kappa Teaching Award administered by the students of the Stanford chapter, and was recently appointed as a Bass Fellow in Undergraduate Education.

(1) Kiesewetter, E. T.; Randoll, S.; Radlauer, M.; Waymouth, R. M. "Stereospecific Octahedral Group 4 Bisphenolate Ether Complexes for Olefin Polymerization" *J. Am. Chem. Soc.*, **2010**, *132*, 5566-5567.

(2) Kamber, N. E.; Tsujii, Y.; Keets, K.; Pratt, R. C.; Nyce, G. W.; Waymouth, R. M.; Hedrick, J. L. "Chemical Recycling of Poly(ethylene terephthalate) (PET) Bottles using N-heterocyclic Carbenes from Ionic Liquids" *J. Chem. Educ.*, **2010**, *87*, 519-521.

(3) Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth. R. M. "Organocatalysis: Opportunities and Challenges for Polymer Synthesis" *Macromolecules*, **2010**, *43*, 2093-2107.

(4) Jeong, W.; Shin, E. J.; Culkin, D. A.; Hedrick, J. L.; Waymouth, R. M. "Zwitterionic Polymerization: A Kinetic Strategy for the Controlled Synthesis of Cyclic Polylactide" *J. Am. Chem. Soc.*, **2009**, *131(13)*, 4884-4891.

(5) Lin, S.; Waymouth, R. M. "2-ArylIndene Metallocenes: Conformationally Dynamic Catalysts to Control the Structure and Properties of Polypropylene" *Acc. Chem. Res.*, **2002**, *35(9)*, 765-773.

Presentations: 9:15 a.m. – 10:35 a.m.

Session 1: Physical and Computational Chemistry Location: Foothill Suite, Auburn Room (3rd floor)
Session Chair: Dr. Benjamin Gherman (California State University, Sacramento)

9:15 a.m.	Nadezhda Korovina California State University, Sacramento Research Advisors: Dr. Benjamin Gherman and Dr. John D. Spence	1. Computational Study of the Cyclization Reactions of Naphthyl-Substituted Enediynes
9:35 a.m.	Victor A. Mendiola, Kris A. Pineda California State University, Sacramento Research Advisor: Dr. Benjamin Gherman and Dr. James A. Miranda	2. Prediction of Reduction Potentials from Electron Affinities for Metal-Salens and Application to the Reduction of Alkyl Halides
9:55 a.m.	Henry Wedler, Christian S. Hamann University of California, Davis Research Advisor: Dr. Dean J. Tantillo	3. Theoretical Hydration Energies of Biologically Relevant α-Keto Amides
10:15 a.m.	Andrew J. Ingram, Alexander G. Dunlap San Jose State University Research Advisor: Dr. Gilles Muller	4. The pKas and pH dependent lumiscence of N-(2-methylbutyl)-4-aminodipicolinic acid (MEBADPA)

Session 2: Biochemistry I Location: Orchard Suite (2nd floor)
Session Chair: Dr. Katherine McReynolds (California State University, Sacramento)

9:15 a.m.	John Kim San Jose State University Research Advisor: Dr. Roy Okuda	5. Gel Encapsulation Techniques of Corallina vancouverensis Acetone Powder (CVAP) containing the Enzyme Bromoperoxidase
9:35 a.m.	Frankie Robert Gonzales, Jennifer Pomponio, Kaitlin Fisher Sonoma State University Research Advisor: Dr. Jennifer Lillig	6. Determination of Binding Association of Mastoparan X to Liposomes by Isothermal Titration Calorimetry
9:55 a.m.	Samantha J. Carrington, Adam Dudik, Heather Turner, Nestor Francoleon Sonoma State University Research Advisor: Dr. Jon M. Fukuto	7. The Chemical Biology of Hydrogen Sulfide: Generation of Persulfides and Biological Implications
10:15 a.m.	Francine E. Park, Matthew Schombs, Suvarn S. Kulkarni University of California, Davis Research Advisor: Dr. Jacquelyn Gervay-Hague	8. Probing the Effects of Promoter Concentration on Yield in the One-Pot Synthesis of α-linked Glycolipids

Session 3: Biochemistry II Location: Forest Suite (2nd floor)
Session Chair: Dr. Tom Savage (California State University, Sacramento)

9:15 a.m.	Trinh Thai, Andrew J. Clifford, Hosea L. Matel University of California, Davis Research Advisor: Dr. Krishnan Nambiar	9. Bioconversion of α-Ionone to Hydroxy α-Ionone by a Streptomyces Strain
9:35 a.m.	Imad Sawaya, Hosea Matel, Andrew J. Clifford, Daniela Hampel, Susan Ebeler University of California, Davis Research Advisor: Dr. Krishnan Nambiar	10. Production of Zeaxanthin from Recombinant E. coli
9:55 a.m.	Thomas Gildea, Hosea Matel University of California, Davis Research Advisor: Dr. Krishnan Nambiar	11. Synthesis of 9'-Carboxychromanol, a Metabolite of Vitamin E
10:15 a.m.	Jonathan Grist, Heather Wright San Jose State University Research Advisor: Dr. Elaine D. Collins	12. Synthesis and Purification of TAR RNA and Tat Peptides from Bovine Immunodeficiency Virus

Session 4: Organic and Atmospheric Chemistry Location: Foothill Suite, Folsom Room (3rd floor)
Session Chair: Dr. James Miranda (California State University, Sacramento)

9:15 a.m.	Seham Afaghani Mills College Research Advisor: Dr. Beth Kochly	13. A Novel Ether Synthesis in Ionic Liquids
9:35 a.m.	Lauren E. Tracy, Conor P. Roche, Antje Echterhoff Santa Clara University Research Advisor: Dr. Thorsteinn Adalsteinsson	14. Synthesis of sub-micron poly(N-isoproopyl acrylamide) gel/oil capsules using polymerize-to method
9:55 a.m.	Michelle Nguyen, Matthew Greaney, Cheng-Chi Chang University of San Francisco Research Advisor: Dr. Lawrence Margerum	15. The effect of tethered dendrimer size on density and reactivity of immobilized metal chelate indicator displacement assays
10:15 a.m.	Lauren Ooka, Sampada Borkar, Andras Bodi, Thomas Gerber University of the Pacific Research Advisor: Dr. Bálint Sztáray	16. PEPICO Studies on the Energetics of Atmospherically Relevant $S_xO_yCl_z$ Ions

List of Presentation Abstracts

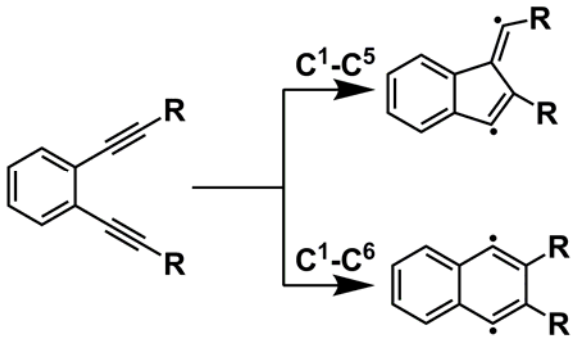
(Note: In each abstract, the presenting author is underlined and the faculty mentor(s) is denoted with an asterisk.)

1. Computational Study of the Cyclization Reactions of Naphthyl-Substituted Enediynes

Nadezhda Korovina, Benjamin F. Gherman, John D. Spence**

California State University, Sacramento, Department of Chemistry

Enediyne compounds, which upon Bergman cyclization produce diradical species, can be utilized as pro-drugs for DNA cleavage. The cyclization reaction can be initiated thermally or photochemically to produce the diradical. By introducing naphthyl substituents on the alkyne termini, the wavelength of light necessary to induce photocyclization may be extended into the near-UV region. Increased steric bulk, however, may allow direct C^1-C^5 cyclization to become competitive with C^1-C^6 Bergman cyclization. Computational methods applied to the thermal cyclization reaction have been used to understand the relative tendencies of C^1-C^5 versus C^1-C^6 cyclization. By appending electron-withdrawing and electron-donating groups to the naphthyl substituents, the electronics can be modulated to further affect the wavelength of light needed for photocyclization as well as the preference for the competing cyclization pathways. Using density functional theory (DFT) calculations, the kinetics and thermodynamics of the C^1-C^5 and C^1-C^6 cyclization reactions have been computed for enediynes with variously positioned and substituted naphthyl substituents under a range of reaction conditions. Time-dependent DFT calculations have been used to compute UV-Vis spectra for the enediynes. Results indicate that the favorability of the C^1-C^5 reaction increases through the inclusion of electron-withdrawing and electron-donating groups, whereas by strategic positioning of the naphthyl steric bulk, the preference for C^1-C^6 cyclization increases. In addition, while the absorption λ_{max} for the enediyne is not greatly affected by electron-donating groups on or repositioning of the naphthyl substituents, electron-withdrawing groups can potentially appreciably alter the absorption λ_{max}. These results suggest the ability to tune the cyclization reactivity of naphthyl-substituted enediynes.

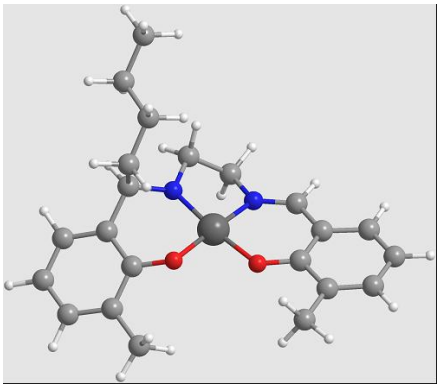


2. Prediction of Reduction Potentials from Electron Affinities for Metal-Salens and Application to the Reduction of Alkyl Halides

Victor A. Mendiola, Kris A. Pineda, Benjamin F. Gherman, and James A. Miranda**

California State University, Sacramento, Department of Chemistry

Reduced nickel(II)- and cobalt(II)-salen compounds can catalytically reduce alkyl halides. These reactions have environmental significance, as effective reduction of halogenated organic substrates facilitates the conversion of harmful herbicides and fungicides to more benign materials. The two processes involved here – reduction of metal(II)-salens and reaction of reduced metal-salens with alkyl halides – have yet to have their thermodynamics studied in detail. Computational chemistry can be used to obtain this information for not only nickel(II)- and cobalt(II)-salen, but for a wide range of other metal-salens. First, in order to establish a means of predicting reduction potentials for metal-salen compounds, electron affinities (EAs) for a training set comprised of 19 metal-salens, containing a variety of metal centers and electron-donating and electron-withdrawing substituents, are computed using density functional theory (DFT). Concurrently, E_{pc} values are measured for the metal-salens using cyclic voltammetry following two-step syntheses. E_{pc} for the training set metal-salens are effectively correlated to the computed EAs, forming a basis for predicting reduction potentials of new test sets of metal-salens. Second, the thermodynamics of the reaction of reduced forms of metal-salens from both the training and test sets with a variety of alkyl halides is determined using additional DFT calculations. Free energy changes are computed for reactions along pathways leading back to the metal(II)-salen plus an alkyl radical and the halide ion or leading to alkylation of the imino bond in the salen plus release of the halide ion. Results indicate that the thermodynamics of dehalogenation can vary appreciably with the identity of the metal-salen.



3. Theoretical Hydration Energies of Biologically Relevant α-Keto Amides

*Henry Wedler, Christian S. Hamann, Dean J. Tantillo**

University of California, Davis, Department of Chemistry

α-Keto amides are used in the pharmaceutical industry. Two drug molecules which contain α-keto amide functionality are Varespladib, a drug used for treating acute coronary syndrome, and Boceprevir, a drug used for treating hepatitis C. Our goal is to use hydration propensity as a lens through which we can predict what form of the α-keto amides is more active, i.e., the ketone or the ketone hydrate. All hydration energies were calculated using the B3LYP method using the 6-31+G(d,p) basis set using the Gaussian 03 suite.

In this investigation, we calculated the energies of hydration of numerous α-keto amides in vacuum. Next, these α-keto amides were optimized using water and chloroform as solvents. These solvent calculations employed the same method and basis set as above. Both UAKS and UA0 radii were investigated for all solvent calculations. Their energies of hydration were determined in both solvents. Thus far, analysis of the hydration reaction in vacuum suggests that the ketone form is favored for all α-keto amides. Aside from a few fluorine-containing compounds, this trend holds in water and chloroform using UAKS radii. However, when using UA0 radii many compounds both in water and in chloroform favored the hydrate.

Ultimately, our goal is to use hydration energy to investigate what form of these compounds is most active in the human body and hence what form (ketone or hydrate) should be expected in α-keto amide-containing pharmaceuticals.

4. The pKas and pH dependent lumiscence of N-(2-methylbutyl)-4-aminodipicolinic acid (MEBADPA)

*Andrew J. Ingram, Alexander G. Dunlap, Gilles Muller**

San Jose State University, Department of Chemistry

The effect of pH on the structure and luminescence properties of MEBADPA have been determined. The pKas of the molecule were determined by spectrophotometric titration using a custom peristaltic flow system to carry the titration solution to the spectrometer. In order to examine the luminescence of each of these species, the quantum yield of this molecule was measured as a function of pH. This data showed that the luminescence increases as MEBADPA is fully deprotonated, but then shuts down as the concentration of hydroxide increases. After a series of control experiments as well as luminescence, pH, and temperature studies, we have concluded that fully deprotonated MEBADPA is collisionally quenched by free hydroxide in solution via the Stern-Volmer model. This has allowed the luminescence spectra to be corrected for quenching and an absolute quantum yield for MEBADPA to be determined. Using the pKas and quenching constant the intensity has been modelled as a function of pH in order to determine the optimum pH for luminescence.

5. Gel Encapsulation Techniques of Corallina vancouverensis Acetone Powder (CVAP) containing the Enzyme Bromoperoxidase

*John Kim, Roy Okuda**

San Jose State University, Department of Chemistry

Gel encapsulation is a method that allows for the reuse of enzymes. Ideal encapsulation methods form matrixes that allow for the passage of substrates and products through the gel, but keeps the enzyme entrapped within the gel. In this project, sodium alginate and tetramethyl orthosilicate (TMOS) are used to encapsulate Corallina vancouverensis acetone powder (CVAP), which contains a bromoperoxidase. The encapsulation and re-use of the gels were verified qualitatively and semi-quantitatively using a colormetric phenol red assay. Both the sodium alginate and TMOS gels were found to successfully encapsulate CVAP and allow for the re-use of the bromoperoxidase enzyme.

6. Determination of Binding Association of Mastoparan X to Liposomes by Isothermal Titration Calorimetry

*Frankie Robert Gonzales, Jennifer Pomponio, Kaitlin Fisher, Jennifer Lillig**

Sonoma State University, Department of Chemistry

Background: This project focuses on studying the binding association of the anti-microbial peptide mastoparan X (MPX) to liposomes by isothermal titration calorimetry (ITC). MPX, found in wasp venom, is known to associate with lipid membranes. To better understand the features of binding, ITC is being used to determine an apparent association constant. Knowledge of this affinity will help to determine how MPX targets cells. These experiments will provide the foundation for studying the binding of anti-listerial bacteriocins to membranes by ITC. Listeria, a bacteria found in raw meats and processed foods, can cause many illnesses, including fetal miscarriages.

Methods: Mastoparan X peptide was purchased from Bachem. DMPC (dimyristoylphosphatidylcholine) and DMPG (dimyristoylphosphatidylglycerol) were purchased from Avanti and liposomes were prepared with varying compositions of each lipid. Sonication provided small unilamellar vesicles (SUVs) and extrusion provided large unilamellar vesicles (LUVs). The total heat of complete peptide binding was determined by titrating the peptide solution into a solution of excess liposomes and the binding isotherm was found by titrating the peptide solution with a liposome suspension. The background was determined by titrating liposomes into buffer without peptide, and buffer without liposomes into a peptide solution. Background was subtracted from the experimental data and analyzed using Origin 7.0 software.

Results: Binding has successfully been measured between MPX and DMPC:DMPG liposomes (1:1) by ITC. The total enthalpy of binding was found to be -7.35 kcal/mol, suggestive of an exothermic binding event. The molar ratio of binding was found to be 89 liposome sites per peptide site. The association constant was determined to be 8.76E5 M-1. Reproduction of this data was successful. Titrations with zwitterionic liposomes yielded less binding.

Conclusions: Results suggest that binding of MPX is stronger to anionic liposomes than to zwitterionic liposomes. This is possibly due to the electrostatic interaction between the positively charged peptide and the negatively charged liposomes. Further studies are currently being conducted to determine the association with liposomes of varied composition and in the presence of varied salt concentration.

7. The Chemical Biology of Hydrogen Sulfide: Generation of Persulfides and Biological Implications

*Samantha J. Carrington, Adam Dudik, Heather Turner, Nestor Francoleon, Jon M. Fukuto**

Sonoma State University, Department of Chemistry

Hydrogen sulfide (H_2S) has been reported to be an endogenously generated signaling molecule of significant physiological importance. For example, it can elicit smooth muscle relaxation and inotropy and can protect against ischemia-reperfusion injury. In spite of its important functions, the chemistry by which it acts is unknown. Considering that H_2S is a simple and potentially reactive thiol, it seems reasonable to speculate that its chemical biology will include redox reactions with other biological thiols. Thus, the study herein examines the redox chemistry of H_2S with thiols and thiol proteins. Specifically, the reaction of H_2S with oxidized thiol species to form persulfide (RSSH) intermediates is examined. We speculate that protein persulfide formation can impart significant and important changes in protein function. Moreover, we are developing methods for the facile generation of biological persulfides as a means of studying the effect this novel sulfur oxidation state can have on protein function.

8. Probing the Effects of Promoter Concentration on Yield in the One-Pot Synthesis of α-linked Glycolipids

*Francine E. Park, Matthew Schombs, Suvarn S. Kulkarni, Jacquelyn Gervay-Hague**

University of California, Davis, Department of Chemistry

In 1993, the first α-linked glycolipids were discovered from marine sponge. Subsequent SAR studies culminated with the development of α-linked galactosylceramide (KRN7000), which was found to elicit a significant immunological response in murine models. This created a need for access to diverse and anomerically pure sources of α-linked glycolipids to further investigate the immunological effects of these antigens. Although synthetic approaches for making cerebrosides were available, a more efficient model was desired. A major breakthrough came in 2007 when the Gervay-Hague Laboratory published an efficient protocol for the stereoselective, one-pot synthesis of α-linked glycolipids. Building on the success of their first generation process, the efficiency of the method lies in the thoughtful combination of glycosyl iodide donors, tetrabutylammonium iodide and careful selection of protecting groups. This second generation technology facilitates the use of fully functionalized ceramides. An area of study that had not been explored was the effect that catalyst concentration has on the stereochemical outcome of the glycosylation event. Described herein are the results of this study. Although the optimal TBAI concentration varies slightly, our findings can be applied to a wide variety of α-linked glycolipids, producing a consistent methodology for the synthesis of several biologically applicable glycoconjugates.

9. Bioconversion of α-Ionone to Hydroxy α-Ionone by a Streptomyces Strain

*Trinh Thai, Andrew J. Clifford, Hosea L. Matel, Krishnan Nambiar**

University of California, Davis, Department of Chemistry

The conversion of α-Ionone to hydroxy α-Ionone by an identified strain of Streptomyces was investigated at different culturing temperatures, length of time of culturing and initial pH of the culture medium. Conversion was higher at higher temperature. The bioconversion time for α-Ionone can thus be shortened by culturing the Streptomyces at higher temperature. But two other oxidation metabolites are being produced at higher temperature. The initial pH of the culture medium did not significantly affect conversion. The produced hydroxy α-Ionone is a single enantiomer based on derivatization with MOSHER's chloride.

10. Production of Zeaxanthin from Recombinant E. coli

*Imad Sawaya, Hosea Matel, Andrew J. Clifford, Daniela Hampel, Susan Ebeler, Krishnan P. Nambiar**

University of California, Davis, Department of Chemistry

Zeaxanthin is a yellow pigment carotenoid produced by plants and algae. In an effort to optimize the growth conditions for the production of zeaxanthin in recombinant E. coli engineered to overproduce this compound, the effect of the initial pH of the culture medium was examined. The E. coli were grown in Luria-Bertani (LB) broth containing ampicillin at 37°C at initial pH of 7.1, 7.6, and 8.04. Cell density was measured by taking absorbance at 660 nm at regular time intervals. The pH was also measured at regular intervals. Plots of the absorbance with respect to time revealed that the bacterium exhibited a biphasic growth. Results showed that a very basic medium encourages much more rapid initial growth (first phase) compared to neutral and slightly basic media. The organism in neutral pH medium and in the slightly basic medium had very similar initial growth rates. During the second phase, the organism in the neutral pH medium had the fastest growth rate. Samples from each culture were taken at different times, centrifuged to collect the cells, and extracted with acetone. The acetone extracts were concentrated and the primary product was isolated using HPLC on a C18 column using acetonitrile as the mobile phase. The chromatograms showed a predominant peak at a retention time of 13.6 minutes. The solution eluted at this time was collected and examined using NMR and mass spectrometry. The spectral data showed that the compound formed was not zeaxanthin. Because of the yellow color of the compound extracted from the cells, it is possible that the compound initially produced was zeaxanthin and underwent a reaction to give the final product. It is also possible that the initial compound was an intermediate of zeaxanthin.

11. Synthesis of 9'-Carboxychromanol, a Metabolite of Vitamin E

*Thomas Gildea, Hosea Matel, Krishnan Nambiar**

University of California, Davis, Department of Chemistry

Vitamin E is an essential nutrient which has been implicated in maintaining good health. Besides its role as an antioxidant, little is known about the physiological function of Vitamin E. As part of a human in vivo study of how the body metabolizes RRR-a-Tocopherol, the primary form of vitamin E absorbed by humans, it was necessary to synthesize its metabolites to use as standards for analyzing samples. One of these metabolites is 9'-carboxychromanol. 9'-carboxychromanol was synthesized using Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) and R-Citronellol (3,7-dimethyl-6-octen-1-ol) as starting materials. Trolox was reduced with borane and the resulting alcohol oxidized to the corresponding aldehyde after enzymatic resolution using lipase. R-Citronellol was subjected to regioselective allylic carbon oxidation and the resulting aldehyde protected as an acetal. Julia-Kocienski olefination reaction yields the alkene. Subsequent acetal deprotection, catalytic hydrogenation and oxidation of the aldehyde to the carboxylic acid yields 9'-carboxychromanol. Details of the synthesis and structural characterization will be the subject of this presentation.

12. Synthesis and Purification of TAR RNA and Tat Peptides from Bovine Immunodeficiency Virus

*Jonathan Grist, Heather Wright, Elaine D. Collins**

San Jose State University, Department of Chemistry

Bovine immunodeficiency virus (BIV) is an advantageous model system for studying human immunodeficiency virus (HIV) due to its similar structure and mechanism. The key to pathogenicity is the interaction between the transactivator response element (TAR) RNA and the trans-activating (Tat) peptide in both human and bovine infections. The interaction of the Tat protein and TAR RNA during the HIV life cycle causes viral RNA to transcribe more efficiently and accumulate in the nucleus of its host. We have cloned the cDNA for TAR RNA with a ribozyme, hepatitis delta virsus (HDV) ribozyme, and restriction sites through polymerase chain reaction (PCR)-assisted gene assembly. The cDNA was subcloned into the expression vector pUC-18 with the BamHI and HindIII restriction sites. The construct includes the cDNA for the hepatitis delta virus (HDV) RNA,a self-cleaving ribozyme at the 3' end of the TAR sequence. This allows the production of homogenous TAR RNA once transcription occurs whereas T7 RNA polymerase can add 0, +1, +2 or +3 nucleotides to the 3' end of the TAR RNA transcript. The ribozyme cleaves as the RNA is synthesized, and the TAR RNA is purified from a low-melting point agarose gel. We have also used PCR-assisted gene assembly to clone cDNA for the wild-type Tat peptide cDNA, as well as the two single mutants, R78G and K75G, and one double mutant, R78G/K75G. The Tat cDNA was subcloned into the expression vector, pTwin-1 (NEB) at the Pst I and Sap I restriction sites. The Tat peptides were then expressed in E. coli ER2566 cells and purified by affinity chromatography with chitin resin. Once each is produced,the interaction between TAR RNA and Tat peptides will be observed using Isothermal Titration Calorimetry (ITC). The goal is to develop therapeutic agents that interfere with the interaction between TAR RNA and Tat peptides.

13. A Novel Ether Synthesis in Ionic Liquids

*Seham Afaghani, Beth Kochly**

Mills College, Department of Chemistry

It is the goal of this research to perfect a synthetic method for preparing a variety of bulky compounds by SN1 substitution in ionic liquids. Ionic liquids are a recyclable, non-volatile, aprotic class of solvents. This novel synthetic method allows SN1 type reactions occur in an aprotic solvent, a rare reaction type. The reaction under investigation is 1-adamantyl mesylate with methanol in 1-butyl-3-methylimidazolium bistriflamide (bmim NTf2). We have optimized reaction conditions and NMR data shows substitution occurs in solvent mixtures with as low as 13.73% methanol. Further research will explore the lowest concentration of nucelophile required for a reaction to occur. In the future, we hope to extend our research to other nucleophiles.

14. Synthesis of sub-micron poly(N-isoproopyl acrylamide) gel/oil capsules using polymerize-to method

*Lauren E. Tracy, Conor P. Roche, Antje Echterhoff, Thorsteinn Adalsteinsson**

Santa Clara University, Department of Chemistry and Biochemistry

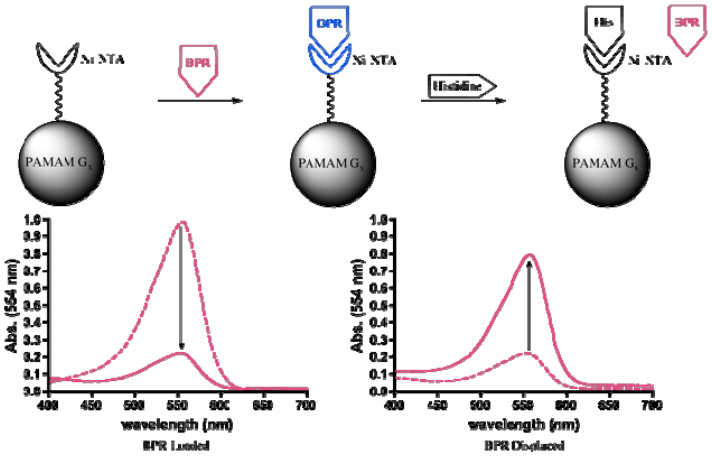
Sub-micron sized gel/oil capsules are synthesized using a polymerize-to method where a stable mini-emulsion is used as a scaffold for deposition of an ultra-thin porous gel-like polymer layer. Scaffolding, ranging between 100 and 200 nm is produced via sonication of a water, sodium dodecyl sulfate (SDS) and long linear alkane mixture. The polymer, N-isopropyl acrylamide, (PNIPAM), is deposited by direct free radical synthesis that is initiated from the micellar surface using a surface active initiator, tert-butylperoxy 2-ethylhexyl carbonate (tBEC). The capsules have a gel-like polymer shell of controllable thickness between 20-50 nm. The polymerize-to method produces capsules that are thermally stable and we have tested encapsulation of various types of oils, including octanol, tetradecane and Isopar-M. The deposition of the polymer does not appear to interfere with the composition of the oil phase, which may give us a pathway to directly encapsulate fragile oil-soluble molecules within the sub-femtoliter volume. These particles show significant potential for use as submicron containers for targeted drug delivery.

15. The effect of tethered dendrimer size on density and reactivity of immobilized metal chelate indicator displacement assays

*Michelle Nguyen, Matthew Greaney, Cheng-Chi Chang, Lawrence Margerum**

University of San Francisco, Department of Chemistry

Surface tethered dendrimers were used as platforms for colorimetric sensing of amino acids. Polyamidoamine dendrimers (PAMAM, Gx) were covalently attached to porous beads and the resulting surface tethered dendrimers were then modified with the metal chelating ligand N,N-bis[carboxymethyl]-lysine (NTA). The surface bound NTA's were loaded with Ni^{2+} followed by exposure to the metal indicator organic dye, bromopyrogallol red (BPR). Ternary complexes were formed between the chelated metal ion and the dye as indicated by the beads slowly turning blue. Indicator displacement assays were carried out on 20 different amino acids to gain insight into the surface bound dye release reaction. The Gx-NTA-Ni-BPR surfaces show selectivity for histidine among the amino acids tested. Surface modification was varied using dendrimer generations 3, 4 and 5 to gain insight into the effect of dendrimer size and surface charge on the sensing ensemble. Preliminary results suggest that the larger generations of dendrimers lead to a more sensitive and selective system.



16. PEPICO Studies on the Energetics of Atmospherically Relevant $S_xO_yCl_z$ Ions

*Lauren Ooka, Sampada Borkar, Andras Bodi, Thomas Gerber, Bálint Sztáray**

University of the Pacific, Department of Chemistry

Atmospheric sulfur chemistry has immense significance to the biosphere. In order to model interactions between the sulfur and halogen cycles in atmospheric models, reliable thermochemical data is needed for the various $S_xO_yCl_z$ neutrals and ions. TPEPICO and iPEPICO experiments were performed on SCl_2, S_2Cl_2, $SOCl_2$, and SO_2Cl_2 to derive the heats of formation of ions and their neutral counterparts to fill this gap. The iPEPICO experiments were performed on the VUV beamline of the Swiss Light Source. In dissociative photoionization, SCl_2 leads to SCl^+, the heat of formation of which is determined. In the iPEPICO experiment, S_2Cl_2 leads to S_2Cl^+ and then to S2+ in consecutive dissociation steps. In this case both the end product and the neutral precursor have reliable literature heats of formation. For $SOCl_2$, the picture is similar, except that the thermochemistry of SO^+ is much better known and is not consistent with the heat of formation of $SOCl_2$ for which a more reliable number is given. The heat of formation of SO_2Cl^+ is derived from the SO_2Cl_2 heat of formation. From our results, the sulfur-chlorine ionic bond energies are measured. Also, since the four systems are interconnected through a loss of oxygen, S=O bond energies are also determined indirectly.

List of Poster Abstracts

(Note: In each abstract, the presenting author is underlined and the faculty mentor(s) is denoted with an asterisk.)

1. Photoionization mass spectrometric studies of the 2-methyl-1-butanol + OH reaction

*Zhou Lu, David L. Osborn, Craig A. Taatjes, and Giovanni Meloni**

a. University of San Francisco, Department of Chemistry
b. Combustion Research Facility, Sandia National Laboratories, Livermore, CA

The hydroxyl (OH) radical oxidation of 2-methyl-1-butanol (2M1B) is considered to be a good substitute for petroleum fuels. The possible products are analyzed via multiplexed chemical kinetic photoionization mass spectrometer, using the third generation synchrotron light source from the ALS to photoionize the reaction species, reactants, products, and intermediates. The products were identified by the photoionization efficiency (PIE) curves. These curves are the plot of the ion signal versus the photon energy from the ALS. Also, the PIE curves of different molecules have different shapes due to their specific Franck-Condon factors. The reactions are initiated by hydrogen abstraction from the OH radical, followed by hydrogen loss (formation of a double bond), or carbon-carbon bond break to form more stable products.

2. Towards the synthesis of fluorinated sialic acids

*Leon Castaneda, Laila Dafik, Marc d'Alarcao**

San Jose State University, Department of Chemistry

Sialic acids are involved in numerous important biological processes including cell adhesion. Cancer cells metastasize through extravasation, the same mechanism macrophages use to exit the blood stream to gain access to infected tissue. Extravasation is a process requiring non-covalent interactions between sialyl Lewis X (SLe^x) present on cell surfaces with E-/P-selectins and integrins on the vascular endothelium to bring about rolling and firm cell adhesion, respectively. Dafik *et al*., has demonstrated that cultured cells incubated with fluorinated sialic acids exhibit decreased adhesion to fibronectin, E-, and P-selectin. However, the molecular mechanism of this reduced adhesion has not been established.

To determine whether the observed decrease in adhesion is due to diminished binding of the fluorinated SLe^x to the cognate lectin or to some other cellular compensatory mechanism, we are interested in performing binding studies with chemically homogeneous SLe^x analogues. To this end we are engaged collaboratively in the synthesis of various fluorinated SLe^x analogues. In this poster we report our progress in the synthesis of fluorinated and non-fluorinated sialic acid precursors that can be incorporated into the synthetic SLe^x analogues. Once synthesized, the chemical adhesion between these novel SLe^x analogues to E- and P-selectins will be measured.

3. A review on the inhibitory effect of ammonia on the photosynthetic oxygen evolution of the PSII protein complex

*Qi Mo, R. David Britt**

University of California, Davis, Department of Chemistry

The effect of ammonia (NH_3) on the photosynthetic oxygen evolution has been examined by the pulse electron paramagnetic resonance (EPR) technique of electron spin-echo envelope modulation (ESEEM). O_2-evolving Photosystem II (PSII) membranes (concentration ≈ 2.5 mg chlorophyll/mL) were prepared by the method of Berthold, Babcock, and Yocum. Both as-isolated and ammonia-treated samples were studied by EPR after being trapped in the S2 state of the oxygen evolution cycle. A change in the "multiline" Mn EPR signal was observed in the ammonia-treated sample, which indicated that the ammonia was indeed binding to the Mn ions in the PSII protein complex. This experimental result revealed that there is a direct coordination of an ammonia-derived ligand to the catalytic Mn complex during the S1 to S2 transition of the oxygen evolution S-state cycle. Our next goal is to determine if interactions of other ligands with the Mn complex—namely, putative histidine ligands—are also altered upon treatment with ammonia. These interactions will be measured by CW(Continuous Wave) EPR spectroscopy.

4. Synthesis and characterization of circularly polarized luminescence Ln(III)-containing probes

*Truman Jefferson, Andrew J. Ingram, Eliseo Quiroz, Alex Dunlap, Gilles Muller**

San Jose State University, Department of Chemistry

Chiral recognition is of utmost importance in the synthesis and characterization of novel pharmaceuticals and small molecules where a difference in chirality can determine the desired drug action and sometimes cause a drug to become effective or ineffective. Circularly Polarized Luminescence spectroscopy (CPL) has been shown to have the ability to characterize and potentially quantify the enantiomeric make-up of product mixtures. Luminescent chiral lanthanide(III) complexes have shown promise as potential molecular probes to use with CPL. In this study, a derivative of dipicolinic acid is being characterized in terms of pKas, luminesence properties, and complexation with Tb(III). Once the current complexation model is fully verified, the photophysical properties of various forms of the complex will be determined. The pKas of MEBADPA and the stability constants of each complex need to be determined by titration. Each system is aromatic and/or emissive, so spectrophotometric titrations were used as well as potentiometric after issues were encountered with the complexation data. An automatic pumping system was used to perform titrations, and the data were refined by the HYPERQUAD2006 package. In this study, a selected lanthanide(III)-based system is being developed and characterized in order to expand the tool set for CPL-based systems used as probes for biomolecules. The MEBADPA ligand was complexed with terbium(III) and the stability constants are found, which will allow the complete characterization of the ligand.

5. Adsorption and Phase Transition of Dipalmitoylphosphatidylcholine Liposomes via Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

*Mateo R. Hernandez, Terry C.H. Ng, Brian C. Walsh, Elyse N. Towns, Donald P. Land**

University of California, Davis, Department of Chemistry

Liposomes are becoming increasingly prevalent as an important part of drug delivery systems in modern medicine, however the need for a better understanding of the physical characteristics are needed. In this study we present our results on the stability and adsorption of liposomes formulated from dipalmitoylphosphatidylcholine (DPPC) via attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The phase transition temperature of pure DPPC liposomes, DPPC liposomes containing cholesterol, and DPPC liposomes containing cholesterol and polyethylene glycol (PEG) is determined using a temperature dependant study (25°C to 50°C) and been found to occur abruptly at approximately 41°C for pure DPPC liposomes, gradual changes between 35°C to 43°C for DPPC liposomes containing cholesterol, as well as the PEGylated liposomes. The rate of adsorption of these liposomes onto various hydrophilic and hydrophobic surfaces was also studied and is presented here. Knowing the stability and adsorption characteristics of these liposomes allow for a better understanding of their use in drug delivery systems.

6. Phosphorylation Effect of S151A/E on Known Cardiomyopathy Mutations found in Human Cardiac Troponin I

*Soyun Michelle Hwang, Susan Nguyen, James Shackelford, Aldrin Gomes**

University of California, Davis, Department of Biochemistry

Cardiomyopathy is a disease of heart muscle that is diagnosed in 1 out of every 500 individuals. In particular, Hypertrophic Cardiomyopathy (HCM) is the leading cause of sudden cardiac death in athletes and is characterized by abnormally thick left ventricle of the heart. Contrarily, Restrictive Cardiomyopathy (RCM) is a rare stiffening of the muscular walls of the heart. These conditions have been linked to genetic mutations in several proteins including Human Cardiac Troponin (Tn), a sarcomeric protein complex that regulates heart muscle contraction. The synchronized contraction of cardiac myocytes is initiated by the release of Ca^{2+} from sarcoplasmic reticulum and is followed by structural changes of Tn that reveal the actin-myosin binding site for force development. The latter is closely related to the Inhibitory subunit of Tn (HcTnI), which, in the absence of Ca^{2+}, blocks myosin binding sites on actin. Research shows that point mutations R145W and R145G in the inhibitory region of HcTnI are linked to RCM and HCM, respectively; both mutations impair the proper response of HcTnI to Ca^{2+} resulting in a significant increase in Ca^{2+} sensitivity. Phosphorylation sites on TnI have shown to decrease Ca^{2+} sensitivity. We hypothesize that phosphorylating Serine residue number 151 located in the inhibitory region of HcTnI to Alanine or Glutamic Acid (S151A/E) may counteract R145G/W mutations by modulating Ca^{2+} sensitivity. To test the functional outcome of S151A/E phosphorylation, we utilized several methods including site-directed mutagenesis, DNA purification, protein purification, reconstitution of Tn complexes, ATPase assays, and Calpain digestions.

7. A new hybrid enzyme for the selective hydroxylation of substrate unactivated C-H bond using light and water

*Phuong Ngoc, Mary E. Cooper, Ngoc Huynh, Misa Au, Lionel Cheruzel**

San Jose State University, Department of Chemistry

Cytochromes P450 are a superfamily of heme-thiolate monooxygenases, found in almost all living organisms, that play an important role in the biosynthesis and biodegradation of endogenous compounds. The classical P450 reaction is the introduction of an oxygen atom, derived from molecular oxygen, into a substrate unactivated carbon center. The mechanism involves the reductive scission of the O-O bond at the iron center, leading to the formation of a highly oxidative heme radical ferryl species, Compound I.

The long-term goal of this research is to develop hybrid P450 heme domain enzymes that will utilize light and water to perform selective hydroxylation of C-H bonds in various substrates under inert atmosphere. A photosensitizer Ru(II) diimine compound covalently attached to the heme domain enables the photo-oxidation of the resting state, heme Fe(III)-aqua complex, to generate high-valent Fe(IV)-oxo species. Substrate hydroxylation will occur through a novel oxidative pathway rather than through the reductive pathway involving molecular dioxygen used by the enzyme and the current studies. This new approach will provide enhanced activity of the heme domain as a result of 1) a better control of the electron flow and 2) a lack of rapid enzyme deactivation due to the absence of reactive oxygen species.

8. Novel Molecular Imprinted Polymer as P450 metalloenzyme active site mimic.

*Ruby Lo, Matthew T. Berry, Amandeep Nijjar, Lionel Cheruzel**

San Jose State University, Department of Chemistry

Cytochrome P450s are heme-thiolate enzymes that play an important role in the biosynthesis and biodegradation of endogenous compounds. The classical P450 reaction is the regio and stereo selective introduction of an oxygen atom, derived from molecular oxygen, into a substrate unactivated carbon center. Over the years, great advances have been made in mimicking P450 reactivity by utilizing metal (Fe, Mn, Ru) porphyrins and single oxygen atom donors (iodosylbenzene, peracids, hydrogen and alkyl peroxides). However, these models still lack 1) substrate recognition properties leading to regioselectivity of oxidation and 2) control of electron-proton transfer steps when oxygen is used as oxidant.

Molecular Imprinted Polymers (MIPs) are highly porous materials with template-shaped cavities. MIPs have had great success in the field of chemical sensing but only scarce examples of catalytic polymers are available. A MIP, which encompasses a small molecule catalyst and a templated cavity for a specific substrate would utilize the advantages of both enzymes and small molecule models with the incorporation of the active site within a defined geometry capable of performing reactions and a greater tolerance of pH, temperature, and organic solvents. We will present our recent findings in incorporating and characterizing a porphyrin moiety into a polymer matrix.

9. A Study of Substituent Effects on a Modified Ritter Reaction

*Daniel Vasilchuk, Cynthia Kellen-Yuen**

California State University, Sacramento, Department of Chemistry

The classic Ritter reaction involves the interaction of a nitrile with cation generated by either an alcohol or an alkene under acidic conditions to produce an N-substituted amide. Modified Ritter reactions have been developed which do not rely on the traditional cation sources. In this study, a modified Ritter reaction was undertaken in which various nitriles were allowed to react with an ester in order to generate the corresponding t-butyl amide products utilizing a novel, microwave-driven synthesis. Substituent effects on the nitrile were examined in order to understand the reaction outcome and assess the versatility of this reaction.

10. Synthesis of Fe_3O_4/Polystyrene Core-Shell Nanoparticles Using Atom Transfer Radical Polymerization

*Jake Abel, Steven Farmer**

Sonoma State University, Department of Chemistry

This work describes the use of atom transfer radical polymerization (ATRP) in the synthesis of Fe_3O_4/polystyrene (PS) core/shell nanoparticles. In this approach, oleic acid stabilized Fe_3O_4 nanoparticles were ligand exchanged with 2-bromo-2-methylpropionic acid, the initiator for ATRP. These Fe_3O_4 nanoparticles are soluble in styrene and were used as macroinitiators for ATRP. Well-defined Fe_3O_4/polystyrene core/shell nanoparticles were obtained. The synthesized core/shell nanoparticles were characterized by scanning electron microscopy (SEM).

11. Efficient & Environmentally Friendly Syntheses of Palladium Monomethyl Complexes

*Arturo Galano, Andrew Bolig**

San Francisco State University, Department of Chemistry & Biochemistry

Current PVC plasticizers are predominantly phthalate esters which are known endocrine disruptors. Although these plasticizers have been banned in children's toys, they are surprisingly still found in medical devices such as dialysis tubing and blood bags because general, suitable replacements have not yet been found. A promising newer strategy involves non-migrating plasticizers which cannot leave the polymer matrix. Current approaches involve polyesters which are prone to hydrolysis, which degrades physical properties and releases potentially hazardous small molecules. To avoid these pitfalls, we are exploring PE-PMMA co-polymers with polar ester groups and hyper-branched backbones as non-migrating plasticizers for PVC. These are best synthesized in controlled fashion with Pd Monomethyl Diimines which are unique in their ability to insert both ethylene (non polar) and polar monomers such as acrylates while introducing branches into the poly(olefin) which impart flexibility and processibility. Unfortunately, the current literature method to prepare these valuable catalysts requires tetramethyl tin, a volatile and highly toxic reagent whose byproducts are difficult to completely remove. The work presented here demonstrates a new, practical, and relatively 'green' synthetic route to these molecules which avoids these hazards. The merits and challenges of several alternative approaches will be discussed.

12. Approaches to regioselectivity in hetero-Diels-Alder reactions

*Erich Bowman, Jinsong Zhang**

California State University, Chico, Department of Chemistry

The Zhang group is working towards the total synthesis of neolignans isolated from Rodgersia podophylla A. Gray (Saxifragaceae). While model compounds have been successfully synthesized using an inverse electron demand hetero-Diels-Alder reaction, the regioselectivity of the method has been poor.

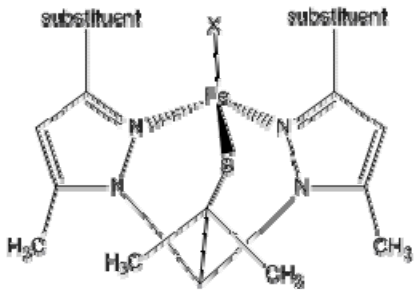
We have characterized compounds that have been synthesized with numerous methods; commonly used are nuclear magnetic resonance, both ^{1}H and ^{13}C, X-ray diffraction, high pressure liquid chromatography with UV-Vis detection, and gas chromatography/mass spectrometry.

13. DFT Computational Study of a Biomimetic Model for the Metalloenzyme Peptide Deformylase

*Darren Steele, Benjamin Gherman**

California State University, Sacramento, Department of Chemistry

The catalytic reaction of the metalloenzyme peptide deformylase, which involves the cleavage by hydroxide of the formyl group at the N-terminus of nascent proteins during peptide synthesis, has been suggested to be vital for eubacterial cell growth. As a potential antibacterial target it is imperative to study the catalytic process in detail. A computational investigation of the catalytic reaction using density functional theory was carried out using a biomimetic model consisting of a previously proposed heteroscorpionate ligand complexed to an Fe(II) center. The investigation was focused on altering the ligand through substitution of various electron-donating and electron-withdrawing groups and observing the immediate effects on the reaction thermodynamics and kinetics. It was found that the reaction free energy increased such that the product was more unfavorable as the added substituents shifted from electron-donating to electron-withdrawing. An electronic investigation suggests that the hydroxide-coordinated complex becomes further stabilized with electron-withdrawing substituents as the hydroxide ligand is pulled closer to the Fe(II) center. After determining the transition states, it was found that the activation energy of the nucleophilic attack step experiences a quadratic correlation with a rise in energy as the substituents' electronic donating or withdrawing abilities increase.



14. Synthesis and Characterization of Germanium-doped Silicotitanate Materials

*Corri L. Alexander, Jacqueline Houston**

California State University, Sacramento, Department of Chemistry

Inorganic ion-exchange materials have been used for decades as water softening agents, sorbents, and for the selective removal of radioactive isotopes. Titanosilicate is a structural analogue of the mineral pharmacosiderite, a non-aluminosilicate molecular sieve that is well suited as an ion-exchanger. Titanosilicate pharmacosiderites (TSP's) have a unique framework caused by the alternating titanium octahedra and silicate tetrahedra that create a three-dimensional tunnel system filled with exchangeable ions. This study presents the hydrothermal synthesis and solid-state characterization (XRD, FTIR, solid-state NMR) of various TSP's in the cesium phase, doped with 4-coordinate or 6-coordinate germanium. The substitution of germanium into these sites has been shown to cause distortions within the crystal structure that may effect the tunnel size and by default, ion-exchange selectivity. Future studies will focus on the ion exchange properties of these novel ion-exchange solids.

15. Effects of Ionic Strength on Aqueous Solutions of Xanthene Dyes

*Nina Huynh, Deena Sadeli, Silvio Rodriguez**

University of the Pacific, Department of Chemistry

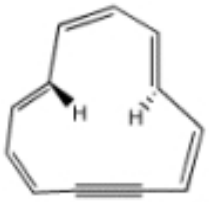
Xanthene dyes tend to aggregate even in dilute aqueous solutions causing dimer formation, or higher order aggregates, which are strongly affected by structure, concentration, ionic strength, temperature, and the presence of other organic molecules. Rhodamine 6G was studied as a function of temperature in the range of 10 - 75°C in the absence and presence of ~2.0 M aqueous sodium chloride. The presence of electrolytes clearly induces dimer formation. The DATAN (DATa ANalysis) 3.1 software was used to determine the relative amounts of monomer and dimer present in solution, and the equilibrium constant for dimerization, in the presence of electrolytes, is 8400. The Gibbs free energy of dimer formation is -22.4 kJ/mol and a van't Hoff plot gives a standard enthalpy of dimerization of -39.2 kJ/mol. Then the standard entropy of dimer formation is calculated to be -56.5 J/(mol*K).

16. Computational Analysis does not Support the Reported Synthesis of Dehydro[12]annulene

Vivian Huynh, Taylor S. Wood, Claire Castro, William L. Karney**

University of San Francisco, Department of Chemistry and Environmental Science

A computational study (ab initio and DFT) of numerous dehydro[12]annulene isomers reveals the most stable isomer to be **1** (CTCTC configuration). Two additional configurations of dehydro[12]annulene were located that were only 4 kcal/mol higher in energy, **2** and **3** (CCSD(T)/cc-pVDZ//BHHLYP/6-31G*). Computed energies along with computed ^{1}H NMR values and coupling constants are at odds with reports that different isomers of dehydo-[12]annulene have been synthesized.



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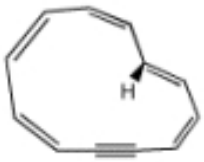

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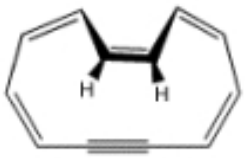

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17. Synthesis of Nucleobase-Calix[4]arene Conjugates via "Click" Chemistry

*Mikael Minier, Liang Xue**

University of the Pacific, Department of Chemistry

Calix[4]arene and its derivatives are an interesting class of molecules that can provide a hydrophobic "bowl" to interact with small molecules or metal ions in supramolecular host-guest chemistry. However, their potential as an artificial receptor for nucleic acid components (nucleobases, nucleosides, and nucleotides) has not yet been fully examined. We hereby report the synthesis and characterization of nucleobase-calix[4]arene conjugates using "click" chemistry. These molecules maintain a cone conformation as determined by 13C NMR. Their complexation with nucleobases in the gas phase using ESI mass spectrometry will also be discussed.

18. The Design and Synthesis of Novel Nitroxyl (HNO) Donor Molecules

*Christopher L. Bianco, Tyler A. Chavez, Jared Jackson, Jon M. Fukuto**

Sonoma State University, Department of Chemistry

Pharmacological administration of nitroxyl (HNO) has been shown to affect a number of physiological functions. Of its many functions, one of high importance is its ability to be used as a treatment of various cardiovascular disorders. Though very useful once within a physiological setting, HNO by itself is unstable and therefore must be administered using HNO-donor compounds. Some HNO-donating compounds include: Angeli's salt, Piloty's acid and, the one of increasing interest, acyloxy nitroso compounds. In our research, we have focused our efforts on creating a number of acyloxy nitroso compounds for comparison of release of HNO with other various donors. We have seen that by altering various molecular components of the acyloxy nitroso compound, we can affect the release of HNO from these donors. Furthermore, use of polar or charged oximes in the production of the acyloxy nitroso compound is also expected to produce a water-soluble species, which in turn, can be directly applied in a physiological setting.

19. Synthesis and Testing of Colloidal Nano-gels for Capillary Electrophoresis

*Shawn Khademi, Conor P. Roche, Thorsteinn Adalsteinsson**

Santa Clara University, Department of Chemistry and Biochemistry

Inverse mini-emulsions containing water-soluble acrylamide monomers were established. These free radical polymerization in these emulsions result in high molecular weight polymer particles of controlled size and composition. We have explored range of cross-linking densities and composition of poly(acrylamide-co-N-,N-dimethyl acrylamide) in the colloids. We study the swelling behavior of the particles as a function of pH and solvent conditions using dynamic light scattering (DLS) and zero-shear viscometry. We study these nano-gels as potential dense sieving matrices for stationary phase capillary electrophoresis. Result from the synthesis, purification and size analysis will be presented.

20. Synthesis of hollow poly(N-tert-butyl acrylamide) nano-capsules via meta-stable mini-emulsion droplet nucleation

*Elena Zavala, Thorsteinn Adalsteinsson**

Santa Clara University, Department of Chemistry and Biochemistry

This project has the overall goal of forming a biocompatible polymer shell around a nanometer-sized water droplet. These polymer shells are of interest as potential bio-molecule containing vesicles. In this project we have focused on: 1) Formulation of an inverse meta-stable emulsions that have sufficient stability to serve as capsule templates. 2) Construction of a thin polymer shell around the micelle droplets to freeze the capsule structure and stabilize them in a greater range of environments. A specific choice of polymer shell was made to form a semi-porous nano-gel layer rather than a dense plastic layer. 3) Isolation and purification of the capsules and dispersion in water. These particles may function as nano reactors, which may be of great interest to the medical field nano-drugs.

21. Progress Towards the Total Synthesis of Gallicynoic Acids

*Ryan Barnes, Brandon Tautges, Christina McCulley, David Ball**

California State University, Chico, Department of Chemistry

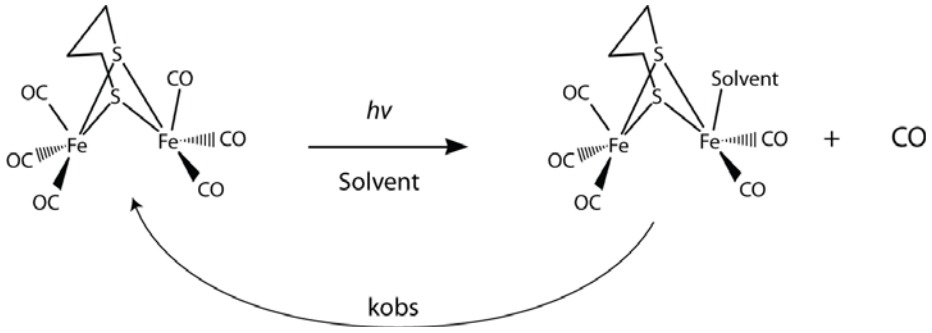
Recently a series of nine structurally related acetylenic carboxylic acids, gallicynoic acids, have been isolated from basiomycete Coriolopsis gallica. Some of these acetylenic metabolites exhibit diverse bioactivities, including cytotoxic, antimicrobial, enzyme-inhibitory, and anti-HIV activities. We have modified a previous synthetic scheme in our attempts to produce these acetylenic acids in a racemic fashion. Our previous scheme featured ruthenium catalytic conjugate addition of terminal acetylenes and Sonogashira cross-coupling of terminal acetylenes to unactivated alkyl bromides and iodides that failed to produce the desired hetero-coupled products. Our revamped synthetic scheme giving our desired racemic products will be presented. We are currently devising enantioselective an acetylide/aldehyde process that will lead to non- racemic gallicynoic acids with the desired stereochemistry.

22. Photochemical Studies of an Iron-Only Hydrogenase

*Melinda Pope, Melanie Lomotan, Haley King, Carmen Works**

Sonoma State University, Department of Chemistry

Photochemical studies of an iron-only hydrogenase model compound, $Fe_2(SCH_2CH_2CH_2S)(CO)_6$ (the model), was investigated. Photochemical and thermal reactivity were studied in acetonitrile (MeCN) for the model under air, nitrogen and CO. Results from both studies are consistent with the loss of CO from the model upon photolysis and the generation of a solvento species. Studies presented here are concerned with varying concentrations of CO, monitoring of the kinetics and measuring the observed rate constant for the reaction of the photo-product with CO in MeCN as well as $CNCH_3$ (tetrahydrofuran) at room temperature. These studies yielded second order rate constants of $2.0E^{-5}$ mM^{-1} s^{-1} and $9.0E^{-4}$ mM^{-1} s^{-1} respectively for the two solvents. Results suggest the formation of a solvento species that reacts with CO to reform the parent complex. Kinetics data at different temperatures will also be presented.

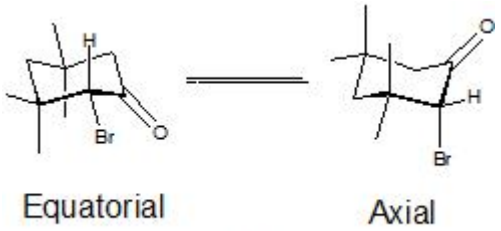


23. Experimental and Computational Studies of Bromocyclohexanone Systems

Sandra Blair, David Ball, Randy Miller**

California State University, Chico, Department of Chemistry and Biochemistry

Monobrominated cyclohexanones, like their unsubstituted parent compounds, readily undergo chair-chair interconversions. An example is 2-bromo-3,3,5,5-tetramethylcyclohexanone (1) shown below. The relative proportion of the axial versus equatorial conformations is strongly dependent on the polarity of the solvent. In previous work the ^1H NMR, IR and UV-Vis spectroscopic techniques have been applied to quantify the dynamical interconversion, but the validity of this approach is still under investigation. We will present detailed computational results that parallel the experimental ^1H NMR results on (1) and on model compounds to further our understanding of this system.



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24. Equilibrium Times and Partician Coefficients of Sesquiterpene, Monoterpene, Wound, Isoprene and MBO Standard Compounds Using Various Solid Phase Microextraction Fibers

*Niria Arellano-Jara, Brad Baker**

California State University, Sacramento, Department of Chemistry

Plants are the major source of volatile organic compounds (VOC) to the atmosphere and play a major role in the chemistry of the lower atmosphere. Of major interest is the contribution that biogenic VOCs make to natural background organic aerosol when they are oxidized in the atmosphere. Some VOC compounds are 'sticky' and have a short lifetime, some are polar and others are not, all of which make VOCs difficult to sample and quantify. Solid phase microextraction (SPME) fibers avoid much of the sample handling obstacles encountered with other gas sampling techniques. This study specifically focused on six different SPME fibers, each containing different coatings or film thickness, to determine which standard VOCs were observed, at what time they reached equilibrium, and what the partition coefficient was. The various fibers (100 and 7 µm PDMS, 65 µm PDMS/DVB, 85 µm PA, 85 µm CAR/PDMS, 50/30 µm DVB/CAR/PDMS, 60 µm PEG) were tested against various sesquiterpene, monoterpene, and wound compound standards as well as isoprene, and 2-methyl-3-buten-2-ol. Analysis was accomplished by gas chromatography mass spectrometry for identification and flame ionization detection for quantification of the VOCs.

25. Electroreductive Cyclization of Methyl Cinnamate in the Presence of Nickel(II) Salen: A Mechanistic Study

*Kellie R. England, James A. Miranda**

California State University, Sacramento, Department of Chemistry

The mediated electroreductive cyclization (ERC) reaction allows the substitution of an electrocatalyst as the stoichiometric source of electrons rather than the cathode, with the advantage of enabling chemoselectivity through the use of a more positive potential than necessary in the direct substrate reduction. Metal salens can play the role of electrocatalysts for mediated ERC reactions, provided that they operate within a specific potential window where electron transfer can take place. The mechanism of these reactions is unknown, but it has been postulated that inner sphere electron transfer is a likely pathway. Nickel salen can be used as an electrocatalyst for the ERC reaction. A study of cyclic voltammetric properties of reduced Nickel salen in the presence of an α,β-unsaturated carbonyl compound was employed to analyze the mechanism of Nickel salen's catalytic behavior in ERC reactions. Bulk electrolysis was also employed using methyl cinnamate in an attempt to isolate a modified electrocatalyst and verify the inner sphere electron transfer mechanistic pathway.

26. Determining the Rate of Water Substitution in Trinuclear Bi-Oxocapped Carboxylate-Bridged Metal Complexes Using ^{1}H NMR Spectroscopy

*Kris Pineda, Jacqueline Houston**

California State University, Sacramento, Department of Chemistry

The goal of this project is to determine the rate at which water ligands in the metal complex $[M_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^{+2}$ (M = Mo, W) are substituted by CD_3OD using ^{1}H NMR spectroscopy. The tetravalent metal ion was varied to determine the effect on ligand substitution. Rates of water substitution were determined by plotting the ^{1}H NMR signal area from the methyl group on the carboxylate bridge as a function of time. Preliminary data indicates that water substitution occurs faster for molybdenum complexes. Future work will focus on varying the functional group on the carboxylate bridge to investigate its effect on ligand substitution.

27. Tandem Cyclization Reactions Utilizing 3-Amino-1,2,4-triazole

*Joel Rivera-Pallares, Cynthia Kellen-Yuen**

California State University, Sacramento, Department of Chemistry

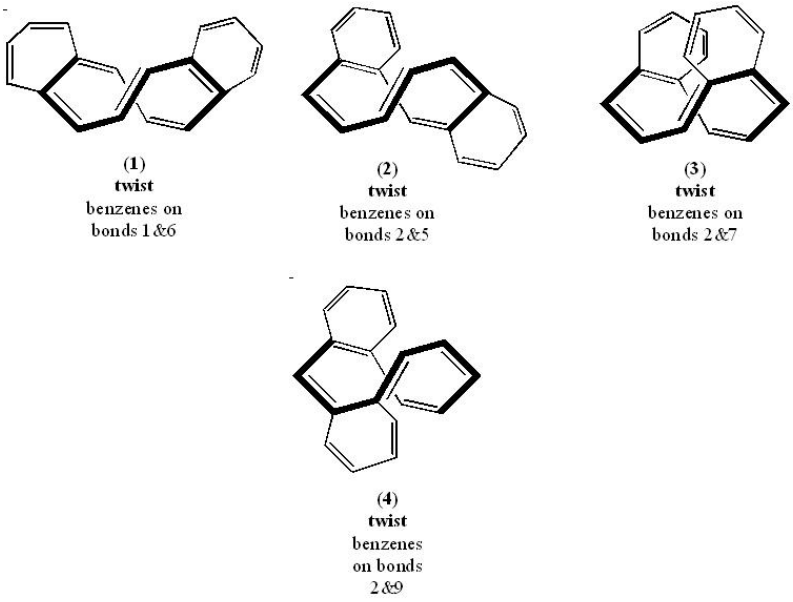
1,2,4-Triazoles represent an important structural element in a variety of useful molecules with applications varying from industrial (corrosion inhibitors) to medicinal (anti-bacterial, anti-inflammatory, anti-microbials). Triazoles are particularly interesting groups in pharmaceutical applications since they are more likely to be water soluble than other aromatic systems and are stable under biological conditions. With multiple nucleophilic sites, the 3-amino-1,2,4-triazole derivatives make for excellent candidates for tandem cyclization reactions. The fused heterocycles which are then produced can be studied as analogs to natural occurring bi-cyclic ring systems such as purines. In this study, the reactivity of aminotriazoles towards tandem cyclization reactions with a variety of difunctional electrophiles is explored.

28. Benzo-fused Twisted [10]Annulenes

Alyse Novoa, Claire Castro, William Karney**

University of San Francisco, Department of Chemistry

The purpose of this study was to computationally locate a [10]annulene minimum with a figure either (two-twist) topology. Two benzene rings were fused to the two twist core of [10]annulene to form four different isomers (1-4). At the CCSD(T)/6-31G*//BHHLYP/6-31G* benzo-fused (1) was lowest in energy, with species (2) only .7 kcal/mol higher in energy. Bond length analysis revealed that all structures displayed bond alternation (Δr= 0.15-0.16Å). The barriers for non planar pi-bond shifting for these species were all lower in energy than the barrier for the unsubstituted system. When a two-carbon bridge was also included (5), the barrier of the [10]annulene core of (5) was reduced to 3 kcal/mol.



29. Synthesis of an Array of Glyopeptides for Characterization of Aptamer Selectivity toward Post-Translational Modifications

*Ryan Murray, Gregory R. Stettler, Steven W. Suljak**

Santa Clara University, Department of Chemistry and Biochemistry

Our research is focused on the development and characterization of highly selective aptamers that can discriminate between peptides with variant post-translational modifications. As a method of modeling these modifications, we have begun to synthesize, using solid phase peptide synthesis, a panel of glycopeptides that vary in both the identity and location of their sugar moities. Our target peptides mimic a 32mer fragment of vascular endothelial growth factor (VEGF), which includes the asparagine residue that is glycosylated on the native protein. To enhance efficiency, we have replaced this asparagine residue with an unnatural amino acid that contains an N-alkylaminooxy side chain, which has been reported to be an effective nucleophile for chemoselective glycosylation. Herein we report our progress on constructing the array of VEGF glycopeptide mimics.

30. Evaluation of Hand Held Data Collection for General Chemistry Experiments

*Shirley Feng, Lawrence Margerum**

University of San Francisco, Department of Chemistry

The Vernier LabQuest is a stand-alone hand-held device with built-in data acquisition and analysis software. We investigated standard USF General Chemistry experiments using both manual data acquisition and with LabQuest to examine the efficiency of the device. Two experiments, "Kinetics of Dye Bleaching" and "Microscale Acid-Base Titration" were carried out using both methods. Our results indicate that by using LabQuest, accurate data can be obtained with time and chemical waste greatly reduced. Students should be able to obtain good data more quickly, generate less chemical waste and have time to repeat poor results that was not previously obtainable.

31. Novel Biopanning Method for Identification of Liver Cancer Protein-Ligand Interactions

*Laura Ramirez, Chun-Yi Wu, Kit S. Lam**

University of California, Davis, Department of Hematology and Oncology

The screening of one-bead-one-compound (OBOC) combinatorial chemistry libraries against a single target protein and the screening of phage display libraries against a single ligand have both been well developed. Recently, a novel multiplex screening method has been developed to screen an OBOC small molecule library against a phage display cDNA library to discover protein-small molecule binding pairs efficiently. The structures of the small molecules have been decoded and each identified compound has been re-synthesized on tentagel beads in large quantities for the convenience of biopanning. We panned the T7 phage-display liver tumor cDNA library onto the small molecules immobilized on the beads, washed out the unbound phages, and eluted the bound phages by infecting E. coli BLT-5403. The bound phage populations were amplified for another round of panning. Four rounds of phage panning and amplification were performed for each ligand to enrich the phage populations that carry proteins that bind specifically to the ligand. Single plaques from T7-infected E. coli were isolated, representing phage corresponding to each ligand. Polymerase chain reaction (PCR) amplification for DNA sequencing of phage plaques and protein BLAST was performed to identify target proteins. The protein-small molecule binding pair database has been established, and it may be useful for discovering novel protein inhibitors against cancers, developing novel diagnostic tools, or further proteomic studies.

32. Fluorescence Quenching of Tris(2,2'-bipyridyl)ruthenium(II) in 0.5 M Aqueous Sulfuric Acid by Copper (II) and Iron (III) at Room Temperature

*Deena Sadeli, Nina Huynh, Silvio Rodriguez**

University of the Pacific, Department of Chemistry

The fluorescence quenching of Tris(2,2'-bipyridyl)ruthenium(II) cation by copper (II) and iron (III) has been studied at room temperature in aqueous 0.5 M sulfuric acid. Under these conditions, the Stern-Volmer constants Ksv are determined to be 25.8 1/M for copper (II) and 734 1/M for iron (III). These are diffusion controlled processes, and the quenching rate constants and the self-exchange rate constants for the cations are analyzed in the context of Marcus theory.

33. Preparation and Structural Characterization of Peptoids with Biarsenical Dye Binding Motifs

*Myrna Mungal, Kanwal Palla, Lauren Sartor, Amelia Fuller**

Santa Clara University, Department of Chemistry and Biochemistry

Biarsenical dyes (e.g., FlAsH, ReAsH) are nonfluorescent until they bind covalently to tetra-thiol motifs in proteins. Although these dyes have been shown to be useful probes of protein secondary or tertiary structures, they have not been used to study abiological molecules. As part of a long-term effort to recapitulate complex protein structure and function wtih abiological molecules, we hypothesize that biarsenical dye fluorescence will correlate with secondary or tertiary structural features of peptoids (N-alkyl glycine oligomers). Peptoids containing potential biarsenical dye binding motifs have been prepared and structurally characterized. These include peptoids with varied helical propensities and peptoid amphipathic helices proposed to form a dye-binding motif upon self-association.

34. Development of an Economically Efficient Route to the Amino Acid Statine

*Michael Vu, James Miranda**

California State University, Sacramento, Department of Chemistry

The objective of this project is to develop an efficient, large scale synthetic route of the amino acid statine. Previous syntheses of statine suffer from lengthy routes and low diastereoselectivities in key steps. Additionally, these routes usually employed time consuming column chromatography. All of these factors contribute to the fact that the current technology is not amenable to a large scale (kilogram) synthesis of statine. This project seeks to develop a highly stereoselective and efficient synthetic route in which chromatography can be avoided completely. Our collaboration with American Peptide Company in Sunnyvale, CA seeks to develop a cost efficient synthesis. Our overall objective is to develop a synthetic route to that can lead to 1 kilogram of statine at a cost of $30/gram to produce.

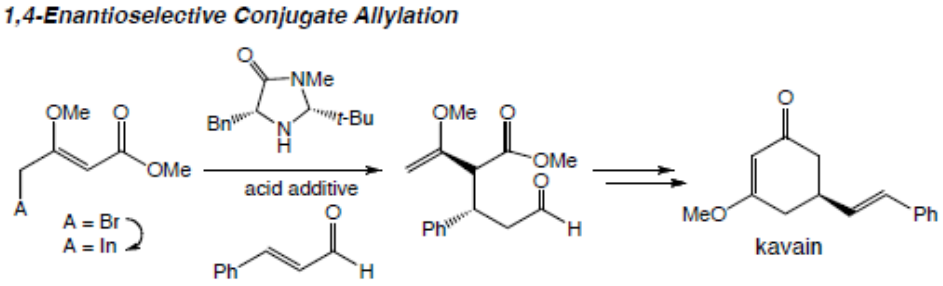
Our approach towards the synthesis of the unusual amino acid statine employs a combination of two earlier independent strategies by Li and Hoffman. Our strategy seeks to use a MgI_2 diethyl etherate-catalyzed Mukaiyama-type aldol reaction developed by Li and the use of a N,N dibenzyl protecting group (Hoffman) in the key coupling step. We are hopeful that these combined factors will serve to dramatically increase the observed selectivity in creating the 4S stereocenter in statine.

35. Total Synthesis of Kavain

*Namphuong Nguyen, Stella Plukchi, Claudia G. Lucero**

California State University, Sacramento, Department of Chemistry

The enantioselective conjugate allylation of α,β-unsaturated aldehydes for the synthesis of biologically active natural products will be investigated. The addition of nucleophiles to α,β-unsaturated aldehydes prefers to proceed in a 1,2-fashion rather than in a 1,4-fashion. Activation of the α,β-unsaturated aldehydes with chiral imidizolidinones, however, has proven to be successful in directing the addition in a 1,4-fashion. It is our goal to introduce the first enantioselective conjugate allylation of α,β-unsaturated aldehydes using substituted allyl indium reagents. This asymmetric approach will allow access to the natural product kavain, the principle constituent of the kava plant, reported to exhibit great promise in the treatment of ovarian cancer and leukemia.



36. Aryl-Aminations Strategies to Prepare Aza-Bridged Calixarenes

*Joshua Flynn, Chris Stains, John Spence**

California State University, Sacramento, Department of Chemistry

Heterofunctionalized calixarenes are a rapidly growing field in supramolecular chemistry. Heteroatoms may be introduced by replacement of phenol building blocks with heteroaromatic rings or through substitution of bridging methylene groups with heteroatoms. As part of a program to selectively replace methylene bridges with free amino groups, we recently described the synthesis of diazacalix[8]arene and triazacalix[12]arene methyl ethers via intramolecular Buchwald-Hartwig aryl amination of an open chain bromo-amino tetramer. In an effort to prepare smaller azacalixarene derivatives, we are currently examining intramolecular aryl aminations strategies of the corresponding bromo-amino dimer which can afford diazacalix[4]arene and triazacalix[6]arene as well as higher homologs. Following our previous work, the requisite amino-bromo dimer can readily be prepared in four steps from 4-tert-butyl-2-hydroxymethyl-6-nitrophenol. Our preparation of this key intermediate and our ongoing studies towards its cyclization will be presented.

37. Characterizing the Surface Chemistry Effects of Organically Modified Silica on Apomyoglobin

*Phillip Calabretta, Mitchell Chancellor, Daryl Eggers**

San Jose State University, Department of Chemistry

Encapsulation of a protein in silica gel is a useful technique for preparing a protein to be analyzed using spectroscopic methods, specifically circular dichroism which reveals the secondary structure of a protein. The silica gives a transparent medium for immobilization of the protein thus preventing aggregation under denaturing conditions. Also, the glass mimics macromolecular crowding, which occurs in vivo, by trapping proteins in the interconnected pores of the glass matrix which prevents the protein from diffusing out but allows buffers to be switched after a short equilibration period. The standard silica matrix denatures our marginally stable reporter protein, apomyoglobin (apoMb). However, on incorporation of organic modifiers, the glass becomes more "biocompatible" allowing the protein to regain some of its native helices. By varying the type (charged, polar uncharged, or nonpolar) and amount of the modifiers, a large range of effects can be seen on the structure of the encapsulated protein. Currently, focus is on low percentages (2.5-5 %) of each modifier to better characterize the effect of each reagent on apoMb. We hypothesize that the surface chemistry of the modified glass alters the average free energy of confined water, thereby influencing the secondary structure of the protein.

38. Intramolecular Vinylcyclopropane Radical-Cyclization Fragmentation

*Andrea Bailey, Maddy McCrea-Hendrick, James Miranda**

California State University, Sacramento, Department of Chemistry

Carbocyclic rings are common in biologically-active natural products. Paclitaxel, isolated from Taxus Brevifolia, is a powerful anticancer agent which contains an eight membered carbocyclic ring. Caryophyllenes, containing nine membered carbocyclic rings, are antileishmanials. Germacranes are a class of compounds that contain a ten membered carbocyclic ring. Germacranes can be found throughout nature; in plants such as caraway, liverworts; various arthropods; and fungi.

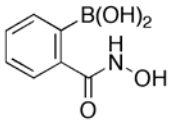
Entropic factors complicate the synthesis of these medium sized rings. In our approach, cyclization of a radical upon an appended vinylcyclopropane is followed immediately by a facile ring opening of the cyclopropylcarbinyl radical to give the eight, nine, or ten membered ring. Development of an appropriate test substrate is key to testing our mechanistic hypothesis. Additional investigation focuses on the addition of a cycloenolate to the natural product ethyl chrysanthemate. Our methodology can be applied to natural products containing medium sized carbon rings such as the anti-cancer compound paclitaxel.

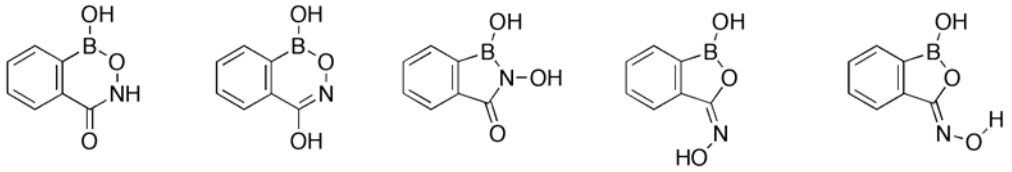
39. Progress Towards the Synthesis of a Novel Boron Heterocycle

*Dung N. Nguyen, Frank E. Cappuccio, Robin Baginski, Michael P. Groziak**

California State University East Bay, Department of Chemistry and Biochemistry

We report our progress in preparing a novel compound, 2-(hydroxycarbamoyl)phenylboronic acid. There is current interest in boron-based molecules as potential new molecular therapeutics. Efforts in our lab are currently underway to synthesize and study this target's structure in the solid state and in various solutions. Our goal is to investigate how a hydroxamic acid will interact with an ortho boronic acid. The multi-step synthetic route towards this new boron heterocycle is described, and the first four of the six steps have been accomplished. In addition, we have predicted a collection of potential cyclic structures which our target might form. We will investigate the final structure of our target by high field NMR and other analytic techniques.





40. Effects of Gel Encapsulation on Corallina vancouverensis Acetone Powder (CVAP) Bromoperoxidase Activity

*William Wung, John H. Kim, Ben Angunsri, Rei Hoang, Roy Okuda**

San Jose State University, Department of Chemistry

Gel encapsulation provides a convenient and effective means of enzyme reuse over the course of many reactions. This technique is especially useful given the limited resource of many biologically useful enzymes. To this end, we investigated the effects of encapsulating Corallina vancouverensis acetone powder (CVAP), which contains a bromoperoxidase, in sodium alginate and tetramethyl orthosilicate (TMOS) sol-gels of different shapes and sizes. Enzyme activity was tested using a colormetric phenol red assay. Preliminary results indicate varying degrees of enzyme activity, which in turn suggest that both enzyme distribution within a gel and total available gel surface area affect reaction rates of encapsulated enzymes.

41. Analysis of Chemical Degradation on Solid Adsorbent Cartridges

*Jason S. Fell, Bradly M. Baker**

California State University, Sacramento, Department of Chemistry

The use of solid adsorbent cartridges is a common method for sampling analytes that are in the gas phase. Sesquiterpenes (SQT) are biogenic volatile organic compounds emitted by trees into the lower atmosphere. SQTs react quickly in the atmosphere which makes analysis difficult. Using solid adsorbent cartridges for SQT analysis is ideal for both in the laboratory and in the field because they trap SQTs before they react. However samples taken in the field may not be analyzed for great lengths of time, which can cause sample degradation. In this study solid adsorbent cartridges containing Tenax TA and Carbopack B were stored with a standard of 10 SQTs for 8 weeks to analyze any sample degradation. 20 cartridges were stored and every 2 weeks 5 cartridges were analyzed on a Gas Chromatograph paired with Flame Ionization Detection. The results show that there appears to be no degradation of the SQTs sampled onto these solid adsorbent cartridges when compared to a known SQT standard.

42. Highly Conjugated Arenediynes: Phenanthrenyl-Substituted Enediynes

*Calvin W. Ruger, Michael L. Chang, John D. Spence**

California State University, Sacramento, Department of Chemistry

Over the past few years our group has been interested in the syntheses of highly conjugated enediynes to examine reactivity with ultraviolet and visible light. Towards this end, we have prepared a number of arenediynes possessing aryl substituents on the enediyne alkyne. In addition to increasing conjugation, incorporation of bulkier alkyne substituents also increases steric hindrance towards Bergman and the related C^1-C^5 cyclization. We are currently examining the photoreactivity of arenediynes possessing one or two phenanthren-9-yl substituents. Addition of two phenanthrenyl groups prevents enediyne cyclization at 300 nm, while excitation of the phenanthrenyl chromophore at 350 nm leads to a novel bis 2+2 photo-dimerization. The reactivity of this system, along with the synthesis and photoreactivity of the less hindered mono-phenanthrenyl derivative, will be presented.

43. Synthesis and Characterization of Nb-doped Silicotitanate Materials

*Nicholas P. Genovia, Jacqueline R. Houston**

California State University, Sacramento, Department of Chemistry

Recent studies of inorganic ion-exchange solids such as crystalline silicotitanate(CST) materials have shown them to be highly selective for the removal of radioactive ^{137}Cs in the presence of large amounts of brine. These studies have also shown that doping the structure with Nb metal ions increases the unit cell of the crystal lattice and as a result increases the solid's ion exchange affinity for large alkali metal ions. Undoped and doped crystalline silicotitanate materials with the formula $HNa_3Ti_4Si_2O_{14}\cdot 4H_2O$ and $HNa_2Ti_3NbSi_2O_{14}\cdot 4H_2O$, were synthesized hydrothermally and analyzed using solid-state techniques (XRD, FTIR, solid-state NMR).

44. Enhanced Photo-Bergman Cyclization of 1-Ethynyl-2-Phenylethynylbenzene

*Nicholas P. Genovia, John D. Spence**

California State University, Sacramento, Department of Chemistry

The Bergman cyclization of enediynes to produce 1,4-benzenoid diradical intermediates has been attributed to the potent ability of natural products like calicheamicin to cleave DNA. Photochemical Bergman cyclization of 1,2-bis(phenylethynyl)benzene derivatives is a common strategy employed to selectively activate enediynes towards cyclization by exposure to light. The overall yield for cyclization of the parent substrate, however, is very low as it suffers from significant polymerization due to long irradiation times. In an effort to improve cyclization yields of simple acyclic enediynes we have re-examined the photochemical reactivity of 1-ethynyl-2-phenylethynylbenzene, which we recently reported as the first example of a terminal arenediyne which undergoes photo-Bergman cyclization. In addition to affording C^1-C^6 cyclization products in higher yields compared to 1,2-bis(phenylethynyl)benzene, 1-ethynyl-2-phenylethynylbenzene requires significantly less exposure time and forms fewer byproducts. Our optimization studies for the photocyclization of this mono-substituted arenediyne compared to 1,2-bis(phenylethynyl)benzene will be presented.

45. β-thujaplicin Production in Cupressus dupreziana Callus Cultures treated with Methyl Jasmonate

*Kulvir Sarai, Thomas Savage**

California State University, Sacramento, Department of Chemistry

β-thujaplicin is an antimicrobial tropolone synthesized naturally by Cypress trees. Understanding β-thujaplicin biosynthesis is required to enable genetic engineering of disease resistance into agronomically important plant species. Studies to elucidate the β-thujaplicin biosynthetic pathway require a tissue culture system that produces significant levels of β-thujaplicin. Methyl jasmonate has been used to elicit higher levels of plant natural product biosynthesis in other plant tissue culture systems. Here we evaluated the ability of methyl jasmonate to elevate β-thujaplicin production in cultures of Cupressus dupreziana. Production of β-thujaplicin was observed in both treated and untreated cultures; however no significant increase in production of β-thujaplicin was observed in methyl jasmonate treated cultures. These cultures may be unresponsive to methyl jasmonate, or higher levels of methyl jasmonate may be required to stimulate β-thujaplicin production.

46. Using a Yeast Screening to Identify SIRT Inhibitors from Marine-Derived Actinomycetes

*Van Pham, Jing Xiao, Erika Tada, Taro Amagata**

San Francisco State University, Department of Chemistry and Biochemistry

Class III HDACs (SIRTs) have been receiving global attention as anticancer target molecules. Currently, a dozen of classical HDAC inhibitors (classes I and II HDACs) are being evaluated as anticancer drugs in clinical trials. In 2006, one of the HDAC inhibitors, SAHA (Zolinza®), was approved as a drug for the treatment of cutaneous T-cell lymphoma (CTCL) by the FDA. Although SIRT inhibitors have great potential to be a new class of anticancer drugs, no potent SIRT inhibitors have been discovered from natural resources. The research focuses on: (1) indentifying marine-derived actinomycetes that produce SIRT inhibitors using yeast assay, and (2) dereplication of active-strain crude extracts. A crude extract library was developed from 70 different actinomycetes separated from deepwater and shallow-water marine sediments. This chemical library was applied to a yeast strain with Ura3 reporter gene in the telomere region. Active strains were screened for selective toxicity in media containing 5-Fluorooritic acid (5-FOA) against media without 5-FOA; in the presence of active strains, 5-FOA would consequently be converted into 5-Fluorouracil (5-FU), a toxic compound. This yeast assay provided several active strains. In this presentation, the results obtained from the yeast screening and dereplication of active hits by LCMS analysis will be shown.

47. Exploration of Class I and II HDAC Inhibitors from Marine-Derived Actinomycetes

*Erika Tada, Van Pham, Jing Xiao, Taro Amagata**

San Francisco State University, Department of Chemistry and Biochemistry

Epigenetic alterations (i.e. those that do not involve changes in the underlying DNA sequencing) of chromatin cause gene transcription and gene expression disorder connected to tumorigenesis. Class I and II histone deacetylases (HDACs) are a group of epigenetic enzymes. More than 10 classes of I and II HDAC inhibitors are in clinical trial for anticancer agents. In order to explore HDAC inhibitors with new structural motifs, a chemical library was screened prepared from 70 marine sediments-derived actinomycetes against a genetically modified yeast strain. This yeast strain possesses a reporter gene (Ura3) that converts 5-fluoroorotic acid (5-FOA) into the cytotoxic compound, 5-fluorouracil (5-FU), resulting in cell death. Several active actinomycetes were visually observed for selective activity in the media with 5-FOA (no growth = clear media) against in the media without 5-FOA (growth = cloudy media). The crude extracts of the active strains were dereplicated using a combination of LCMS analysis and database search. In the poster presentation, we will present the yeast screening results as well as potential HDAC inhibitors obtained by dereplication.

48. Isothermal Calorimetric Studies of Chromium (III) with Various Ligands

Nicole Trimble, *Carmen Works**

Sonoma State University, Department of Chemistry

Recent studies show that chromium (III) aids in weight loss, but consuming large amounts of Cr (III) is also potentially dangerous. In the body, there are proteins that bind to chromium, but the exact structure and make-up of these proteins are unknown. However, two chromium-binding proteins have been partially characterized in the literature, and these studies have determined the amino acid composition and molar masses. The goal of this project is to investigate the binding of various ligands and Cr (III) using an isothermal calorimeter. Preliminary results of the ligand nitrilotriacetic acid (NTA) with Cr (III) will be presented. Preliminary data from the NTA trials will be used to determine experimental parameters for the binding of biologically relevant ligands. NTA forms coordination compounds with metal ions, such as Cr (III), and will demonstrate possible mechanisms and binding schemes for peptide bonding. The calorimetric data will be used to yield both the enthalpy of the reaction and the equilibrium constant(s).

References:
1. Visser, H. G. (2006). Acta Cryst. E62, m3272-m3274.
2. Visser, H. G. (2007). Acta Cryst. E63, m162-m164.

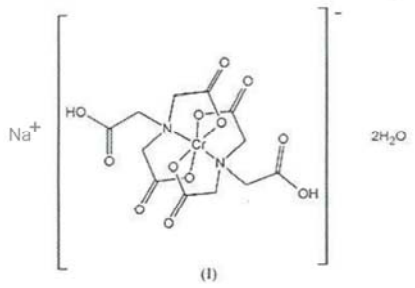
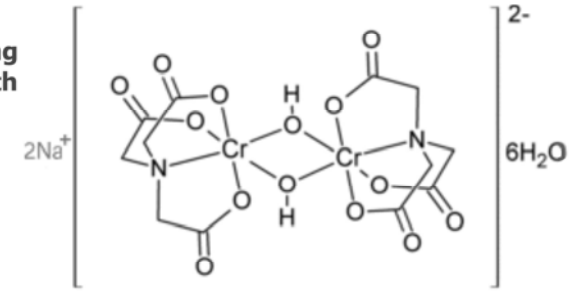


Figure 1:
Possible bonding scheme for Cr (III) with NTA[2]

Figure 2:
Possible dimer bonding scheme of Cr (III) with NTA[1]



49. Analysis of the formation of insoluble aggregates by the amyloid apolipoprotein variant L178H and WT

*Mustafa Safi, Mai Thao, Linda M. Roberts**

California State University, Sacramento, Department of Chemistry

There are many illnesses associated with the formation of amyloids, which are protein aggregates toxic to cells. Apolipoprotein A-I (apoA-I) is the major protein of HDL ("good cholesterol") which, in its normal function, exerts many beneficial effects that reduce the risk for heart disease. A number of naturally occurring amyloid variants of apoA-I have been identified. We previously characterized the amyloid variant G26R. Here, we report on the solubility properties of the amyloid variant of L178H. To analyze solubility, both wild-type (WT) and L178H proteins were incubated over a period of one month at temperatures ranging from 4 to 37 °C. Aliquots were removed periodically and centrifuged to separate insoluble aggregates from the soluble fraction and analyzed by SDS-PAGE. The experiment was conducted at pH 7.2 and at 3.8 to examine the influence of acidic pH on amyloid formation. Preliminary results indicate that WT protein remained soluble when incubated at either 4 or 25 °C but L178H, though soluble at 4 °C, became insoluble when incubated at 37 °C. Insoluble aggregates appeared at day 4 and increased throughout the month-long incubation period. These results confirm the amyloid propensity of L178H.

50. Investigations into Trapping Carbocationic Intermediates in Ionic Liquids

*Sara Jaka, Beth Kochly**

Mills College, Department of Chemistry

The ionic liquids 1-butyl-3-methylimidazolium bistriflamide and 1-butyl-2,3-dimethylimidazolium bistriflamide were used as solvents for the solvolysis of adamantyl mesylate. Investigations were made into doping the ionic liquid solvents with small amounts of heteroatomic nucleophiles in an attempt to trap the carbocation intermediates.

51. Fluorescent, solvatochromic peptoid side chain: Synthesis and utility as a putative structural probe

*Paul Bruno, Marisa A. Plescia, Amelia A. Fuller**

Santa Clara University, Department of Chemistry and Biochemistry

We have synthesized three primary amine submonomers for installation of a peptoid side chain functionalized with 4-N,N-dimethylamino-1,8-naphthalimide (4-DMN). These submonomers have varied chain length separating the naphthalimide core from the peptoid backbone. We have included these 4-DMN functionalized side chains into short peptoids, and have evaluated the peptoid fluorescence in solvents with a range of dielectric constants. For all peptoids, the fluorescence emission is highly responsive to solvent: the wavelength of maximum emission shifts, and emission intensity is roughly 100 times greater in 1,4-dioxane than in aqueous buffer.

Future studies will aim to use 4-DMN modified peptoids to probe their tertiary structural features as part of a long term goal to recapitulate complex biological structures with abiological, sequence-specific polymers.

52. Synthesis and Bergman Cyclization of Butadiynyl Arenediynes

*Nicola Clayton, John D. Spence**

California State University, Sacramento, Department of Chemistry

The naturally occurring enediynes, including calicheamicin and esperamicin, intercalate and cleave cellular DNA by formation of a 1,4-benzenoid diradical formed upon Bergman cyclization of their enediyne unit. The ability of arenediynes to undergo photo-Bergman cyclization offers an attractive method to increase specificity of enediyne pro-drugs by selective light exposure. Numerous synthetic enediynes derived from 1,2-bis(phenylethynyl)benzene have been demonstrated to undergo photo-Bergman cyclization. These substrates, however, typically require significant irradiation times at 300 nm affording low yields of cyclic adducts. We have prepared novel enetriyne and enetetrayne derivatives in an effort to improve cyclization yields and potentially extend the wavelength of light empoyed in photo-Bergman cyclizations. The synthesis of 1,2-bis(4-phenylbuta-1,3-diyn-1-yl)benzene and 1-ethynyl-2-(4-phenylbuta-1,3-diyn-1-yl)benzene, along with their solid state reactivity, thermal solution reactivity, and ongoing photochemical studies will be presented.

53. Cloning the Human Vitamin D Receptor into the pE-SUMOstar Expression Vector

*Lily Le, Aileen Espinoza, Amanda Rodriguez, Charae Gilbert, Elaine D. Collins**

San Jose State University, Department of Chemistry

Many of the actions of 1a,25-dihydroxyvitamin D3 [1,25(OH)2D3] are mediated by binding to the nuclear vitamin D receptor (VDR). VDR is a member of a superfamily of nuclear receptors that are ligand-dependent transcription factors. Ligand binding induces conformational changes in the VDR that enable the receptor to interact with other coactivators to modulate gene transcription. In order to better characterize the binding of the VDR to 1,25(OH)2D3 and to analogs of 1,25(OH)2D3, we have cloned the cDNA for the human VDR and several variants into the expression plasmid, pE-SUMOstar (Lifesensors). The full-length wild-type receptor (1-427), an isomeric form of the receptor (4-427), the C-terminal ligand binding domain of the receptor (118-427), and gold binding protein (4-27) receptor fusion were cloned using polymerase chain reaction (PCR) and subcloned into the BbsI and XbaI sites of pE-SUMOstar. The resulting plasmids will be transformed into E. coli ER2566 cells, and protein expression will be induced. Western blot analysis will be used to confirm the expression of target variants, and the purification of the proteins will be achieved through metal affinity chromatography. Once purified, the proteins will be used in microcalorimetry studies to determine thermodynamic parameters of ligand binding to the proteins. This information will assist in the rational drug design of vitamin D hormone analogs for therapeutic interventions.

54. Characterization of a Chromium Binding Protein

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Chromium(III) is a widely used dietary supplement and strong experimental evidence exists to support the use of chromium (III) for weight lost and relief of symptoms associated with type II diabetes. However, the mode of action in which chromium aids in glucose metabolism is not currently understood. There are two general hypotheses regarding the functional role of chromium binding proteins in biology. First, chromium binding proteins are thought to inhibit PTPase in the insulin glucose pathway in order to increase glucose metabolism. Second, chromium binding proteins could be used for chromium detoxification. If chromium does aid in glucose metabolism through an endogenous mode, it would be likely to occur through the structure-functional relationship of chromium binding proteins. Such proteins have been reported in the literature but very little data exists regarding the structure-functional relationship of chromium binding proteins. We have isolated a novel protein that has a high affinity for chromium. We suspect that this high affinity for chromium is directly related to the primary structure of the protein. The first goal in our research is to elucidate the primary, and secondary protein structure as well as explore the two general hypotheses regarding the functional role of chromium in biology.

55. Bioinformatic Identification of Nucleotide Sequences Possibly Encoding Enzymes in the Biosynthetic Pathway of Domoic Acid

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Cytochrome P450 monooxygenase may catalyze a three-step oxidation of gerayl sub-unit producing the intermediate isodomoic acid A in the biosynthesis of the marine neurotoxin domoic acid by the diatom Pseudo-nitzschia spp. Similar oxidation reactions participate in the synthesis of the plant hormone gibberellin in Gibberella fujikuror (fungus) and Arabidopsis thaliana (flowering plant). The synthesis of a defense molecule, diterpene resin acid, in Pinus taeda (pine tree) also utilizes a cytochorme P450 monooxygenase. These enzymes were used as queries in a homology search against the GenBank amino acid sequence database using Basic Local Alignment Tool (BLAST). Forty eight homologous amino acids sequences were recovered and used to perform a homology search against nucleotide sequence in an EST library derived from Pseudo-nitzschia multiseries. Eighteen sequences showed homology with an E-value range of 0.01 to 1e-5. These sequences were then used in a BLAST search against non-DA producing diatoms, Thalassiosira pseudonana and Phaeodactylum tricornutum. All 18 sequences showed some homology to non-DA diatoms genome sequences, suggesting these sequences my not encode enzymes unique to DA biosynthesis.

56. Syntheses and Photo-Reactivity of Methoxynaphthyl-Substituted Enediynes

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Over the past twenty years enediynes have been extensively studied since the discovery of the enediyne antitumor antibiotics including calicheamicin and dynemincin. While the natural products employ chemical activation of the enediyne, cyclic and phenylethynyl arenediynes are well documented to undergo photochemical Bergman cyclization. To examine the effect of extended conjugation on enediyne reactivity we have studied a series of naphthyl-substituted arenediynes that undergo C^1-C^6 or competing 2+2 cyclization. In the course of these studies we observed that incorporation of electron donating methoxy substituents on the naphthalene scaffold enhances the overall photochemical reactivity of the enediyne unit. To further examine this effect we have prepared a series of arylethynyl arenediynes containing 6-methoxynaphthalen-2-yl, 4-methoxynaphthalen-1-yl, 2-methoxynaphthalen-1-yl groups appended to the enediyne alkynes. The photochemical reactivity of these electron rich arylethynyl arenediynes will provide insights into the role of electronic as well as steric effects on naphthyl-substituted enediyne reaction pathways.

57. The amyloid apolipoprotein variant L178H does not bind the beta-amyloid detecting dye ThT

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Apolipoprotein A-I (Apo-AI) is one of the major apolipoproteins present in High Density Lipoprotein (HDL) cholesterol. HDL is a "good" form of cholesterol due to its ability to transport cholesterol out of cells, which mitigates plaque buildup. ApoA-I also exerts cardio-protective anti-inflammatory and anti-oxidant properties. Naturally occurring variants of Apo-AI have been associated with amyloid deposits in a tissue specific manner. The mechanism of amyloid formation and the basis of tissue deposition are unknown. Previously, we characterized the variant G26R which acquires additional beta structure typical of amyloid proteins. Here, we examine the binding of the beta-strand detecting fluorescent dye Thioflavin T to the amyloid variant L178H in comparison to wild-type (WT) protein. L178H and WT proteins were expressed in E. coli, purified by nickel affinity chromatography, and then incubated at 37oC over a two week period. Aliquots of protein were removed at different time intervals and examined for binding to ThT. ThT bound to WT at a rate similar to what we previously observed. However, ThT did not appear to bind to L178H over the same time period, despite evidence of increased insolubility and fibril formation. These results suggest L178H forms an amyloid structure distinct from that of G26R. Differences in amyloid formation may underlie tissue-specific deposition.

58. Spectral Analysis of Polylysine Structure in Organically-Modified Silica Glass Pores

Gary Abel, Jr., *Daryl K. Eggers**

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The purpose of this research is to investigate the structural response of a model protein, polylysine, to changes in its local environment. This, in turn, provides insight into the factors that influence protein folding, including molecular crowding and hydration effects. The method used is encapsulation of the protein in the pores of a silica glass matrix using the sol-gel technique, in which the glass is formed around the protein under relatively mild temperature and pH conditions. In addition, the surface of the glass pores can be modified with positive, negative and neutral hydrophilic groups to alter its interaction with the peptide and surrounding water. The resulting glasses are not only permeable to water and small solutes, but also optically transparent, allowing for spectral analysis of the trapped biomolecules. Circular dichroism spectroscopy is used to compare the structure of polylysine in different glasses and under various solvent conditions.

Thus far, the most interesting results have been obtained in a glass modified with just 2.5% of a neutral hydrophilic reagent. The fact that polylysine is positively charged, yet its structure is significantly altered by the presence of a neutral group, suggests that hydration effects may dominate over direct electrostatic interactions in this system.

59. Diastereoselective acylation of 2-substituted cyclohexanols

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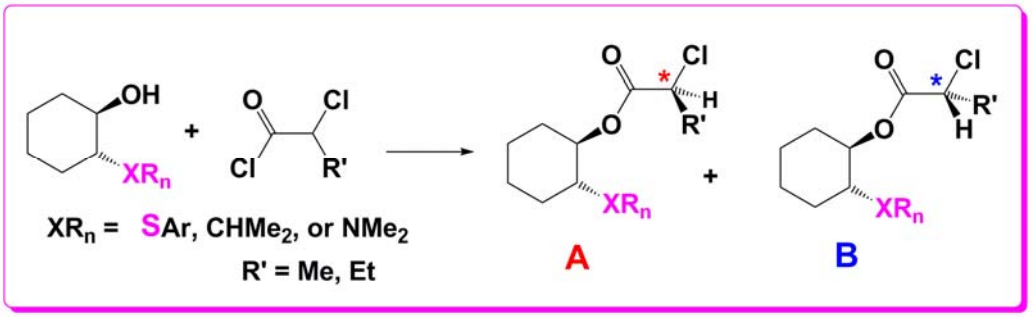
The ratio of diastereomeric products A and B in acylation of 2-substituted cyclohexanols was found to depend dramatically on the nature of substituents and solvents. Inversion of diastereoselectivity upon change of a solvent was found for certain combinations of reactants and conditions.



60. Hofmeister Series Analysis of Tryptophan Using the Non Interaction Model

*Melinda D. Mendolla, Daryl K. Eggers**

San Jose State University, Department of Biochemistry

The research from our lab is important because some diseases such as Alzheimer's are the result of a protein folding incorrectly. Using Dr. Daryl Egger's "Non-Interaction Model" which means that solute effects on protein conformation may be mediated through changes in the thermodynamic properties of water as opposed to the existing model that infers a preferential interaction between the reacting species (Ac-Trp-NH2) and the secondary solute (salt ions), we have been able to analyze salt ions in the Hofmeister series. Thus, to understand hydration as a driving force in protein folding, we used tryptophan to mimic the protein's backbone and analyzed the solute effects using an Anton Paar DMA 5000 Density Meter to calculate solubility points. Ac-Trp-NH2 was analyzed in a 2M TRIS control buffer and in 2M LiCl, TMAOAc, and LiOAc. LiCl and TMAOAc yielded solubility data that is not consistent with our hypothesis of the Non-Interaction Model.

61. Bioinformatic determination of the enzyme responsible for the double bond isomerization in the biosynthesis of domoic acid in Pseudo-nitzschia multiseries

*Kelli Walker, Tom Savage**

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Domoic acid (DA) is a marine toxin produced by diatoms of the genus Pseudo-nitzschia. Identifying genes encoding for DA biosynthetic enzymes allows for future cloning and enzymatic assays to confirm gene function and to enable research directed toward the molecular regulation of DA biosynthesis. Bioinformatic analysis was performed to identify nucleotide sequences potentially encoding the enzyme responsible for the double bond isomerization step in the postulated biosynthetic pathway. Literature searches were performed to identify enzymes that catalyze similar reactions which were then compared to the Pseudo-nitzschia multiseries EST cDNA library using Basic Local Alignment Search Tool (BLAST). The resultant sequence matches were compared to the non-redundant protein database to ensure they did not encode a previously well characterized protein not related to DA biosynthesis. They were also used as a query against the genome of the non-domoic acid producing diatom, Thalassiosira pseudonana, under the assumption that if present this protein would not be involved in the production of DA. A homology of isopentenyl-diphosphate delta-isomerase was identified that is uniquely found in the Pseudo-nitzschia library that may encode the enzyme responsible for the isomerization of isodomoic acid A.

62. Bioinformatic identification of nucleotide sequences encoding enzymes potentially catalyzing the initial reaction in the biosynthesis of domoic acid in Pseudo-nitzchia multiseries

*Meghan Paul, Tom Savage**

California State University, Sacramento, Department of Chemistry

Domoic acid (DA) is a neurotoxin produced by marine diatoms in the genus Pseudo-nitzschia. Understanding the biosynthetic pathway of DA may reveal regulation mechanisms important for future research in controlling environmental DA levels. Bioinformatics was used to identify candidate sequences from a Pseudo-nitzchia multiseries EST cDNA library that may encode the enzyme responsible for the condensation of geranyl diphosphate with glutamic acid in the proposed biosynthetic pathway of DA. Literature searches provided the amino acid sequences for proteins catalyzing reactions similar to the condensation of geranyl diphosphate and glutamic acid. The sequences were compared to the Pseudo-nitzchia multiseries EST cDNA library to identify homologous sequences in the diatom. Homologous sequences were then used as queries in a search of non redundant protein sequences using a Basic Local Alignment Tool (BLAST) to confirm that a non-DA function had not previously been characterized for a protein having a very closely related sequence. The candidate nucleotide sequences from the Pseudo-nitzchia multiseries EST cDNA library were also compared to the genome sequence of the non domoic acid producing diatom Thalassiosira pseudonana with the assumption that candidate sequences found in this organism are not likely to have a role in the biosynthesis of DA.

63. UV-Vis Spectroscopic Studies of Second-Coordination Sphere Interactions between Rutheniumamminepyridyl Complexes and Dissolved Polyvinylpyrrolidone in Acetonitrile

*Vanessa Cristina Yu, Zhu Li, Meng Shengnan, Jeff C. Curtis**

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We have used UV-Vis spectroscopy to characterize a novel form of metal-polymer binding in solution which is driven by favorable Lewis-acid/Lewis-base second-coordination interactions taking place between polyvinylpyrrolidone and ruthenium(II)pentaamminepyridine in acetonitrile as solvent. The relatively strong Lewis base pyrrolidone monomer units bring about a measureable redshift in the MLCT absorption band of the $(NH_3)_5$Ru(II)pyridine(2+) complex when they hydrogen bond to the Lewis-acidic ammine hydrogens. By following the spectral changes carefully as a function of metal:polymer ratio, we are able to discern a sequence of spectroscopically-distinct chromophore environments which we believe reflects the average number of metal-pyrrolidone contacts possible at a given metal loading (the extent of the observed redshift increases as the number of pyrrolidone monomer units available per each metal goes up). Surprisingly, the data suggest that at maximum loading there may be as many as 18-20 metal complexes associated with a single polymer chain containing only 45 (on-average) monomer units in its entire length. This would imply a highly-charged and probably very "rod-like" supramolecular assembly in solution. Efforts underway to quantitate the equilibrium binding constant will be described.

64. Intervalence Charge-Transfer Transtions in Binuclear Ruthenim Ammine Complexes as Probes of How Dissolved Salts Affect the Structure of Liquid Water

*Jerry W. Asuncion, Anthony G. Fabrizio, Bryant J. Blair, Zhiji Han, Jeff C. Curtis**

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Intervalence charge-transfer (IT) transitions of mixed-valence complexes such as $[(NH_3)_5Ru^{II}\text{-L-}Ru^{III}(NH_3)_5]^{+5}$ (where L=4,4'-bipyridine, or 1,2-bisbipyridylethene, bpe) have been measured in water as a function of various added electrolytes including simple alkali-metal halides.

The surprising result is that there is a qualitative difference in the direction of the spectral shift arising from the addition of different halide anions. Fluoride salts exhibit a spectral blue shift in contrast to the red shift obtained for added chloride, bromide, and iodide.

Even more surprising is the fact that there is a small but systematic effect due to the cation of the halide salt with more "structure-breaking" cations leading to lower IT band energies in the order $Cs^+ < Rb^+ < K^+ \sim Na^+ < Li^+$.

Thus we find that the position of the IT band in water for these decaammine mixed-valence ruthenium dimers turns out to be a sensitive new probe of the surrounding water structure as it is modified by the addition of various salts. Furthermore, the observed spectral shifts correlate with the Jones-Dole viscometric "B coefficient" which measures ion effects on water structure.

65. Analysis of Structure-Function Relationship in Taq DNA polymerase

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Taq polymerase is a thermostable DNA polymerase named after the thermophilic bacterium Thermus aquaticus. It is widely used in polymerase chain reaction (PCR). T. aquaticus was isolated from hot springs and Taq polymerase was identified as an enzyme able to withstand the thermal cycling conditions required for rapid amplification of DNA. Taq's optimum temperature for activity is 75-80°C, with a half-life of 9 minutes at 97.5°C.

In current research, we used Taq polymerase to study the relationship between its structure and function based on the hypothesis that primary structure (amino acid sequence) codes for it's folded 3D structure and in turn it's biological function. If the structure of protein is modified by substitutions of important amino acid residues, our hypothesis is that its structure and function are most likely altered.

To investigate this relationship, 25 single amino acid mutants of recombinant Taq polymerase gene were attempted using side directed mutagenesis. 23 of these mutants were successfully transformed into super competent cells. The wild type and all the mutant proteins were expresses and purified using ion-exchange chromatography. To observe the effect of mutation, we compare the melting behavior of the mutants with that of wild type protein. The protein denaturant guanidium hydrochloride was employed to generate denaturation profiles using circular dichroism spectroscopy to follow protein stability. 8 mutants have been analyzed so far.

66. β-Lactosyl Amine Glycodendrimer Synthesis by Means of Amide Linkages

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Dendrimers are spherical-shaped macromolecules with terminal polyfunctional endpoints that have been of increasing interest in the biomedical field since the latter part of the 20th century. Sugars may be placed at the end of a dendrimer to create a new category of macromolecules called glycodendrimers. The synthesis of glycodendrimers can be partitioned into two categories: divergent and convergent. The goal of this research is to manufacture ethereal hydrophilic glycodendrimers using divergent synthesis with great efficiency, reproducibility, and yield. This is achieved by comparing an array of synthetic pathways and purification techniques that combine to give the greatest yield, with brief turnaround periods. A β-lactosyl amine sugar was used to terminate the glycodendrimer through a BOP coupling reaction.

67. Preparation of Carbon Nanotube Based Device and Its Electrochemistry

*Khanh-Van Tu, Weiling Hsieh, Daniel Straus, Roger H. Terrill**

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The purpose of this research is to develop methodologies for the exploitation of carbon nanotube thin films as chemical and electrochemical sensors. In this study we prepared thin films of carbon nanotubes (CNT) by solution casting methods and then used a novel hybrid electrochemical-conductometric method to measure the CNT film electrical conductivity as a function of electrochemical bias and stimulus. The bias between the CNT film and the contacting electrolyte and the bias between the opposite ends of the CNT film (referred to as K1 and K2) were simultaneously controlled – analogous to a transistor with an electrolyte gate. A promising motif for sensing involved a cyclic voltammetric scan of K1 and K2 but with a 10 mVPP, 1 kHz AC signal summed onto the K2 potential, and thus generating a trans-film potential that was exploited, using a lock-in-amplifier detector, to monitor the CNT film conductance during the CV scan. In order to explore the chemical sensitivity of the CNT films in this setting, we examined blank electrolyte, dissolved ferrocene, and ultra-thin films of novel pyrene-modified iron(II)-terpyridine complex (Fe-tp-py) that binds to the CNT surface. Our principal finding is that this measurement method appears to discriminate between the CNT film trans-conductance and the interfacial electrochemical impedance because the iron(II)-iron(III) transition of the Fe-tp-py induced a clear change in the putative CNT film conductance that is distinct from blank or ferrocene control.