Gustavus 2005 Summer Research Symposium Titles and Abstracts

8:30 am *A Computational and Spectroscopic Approach to Determining Protein Structure*
Mike Kamrath**,** Jonathan Smith

Computational and spectroscopic techniques have been combined to probe local protein structure. Experimental resonance Raman spectra were obtained for small fragments of the 29 amino acid glucose regulating protein glucagon. The Raman spectra for these fragments were also simulated computationally and were used to aid in the interpretation of the experimental spectra. Glucagon was then probed with experimental resonance Raman at a wavelength of 224 nm. Both the experimental and computational data from the smaller fragments were used to interpret the full glucagon spectrum.

8:42 am *Fluorescence Characterization of ATP Binding in γ-Glutamylcysteine Synthetase*
Becky Palermo, Brenda Kelly

γ-Glutamylcysteine synthetase is the first and rate-limiting enzyme in the production of glutathione, a biologically essential low molecular weight thiol. Previous studies have suggested that bound substrates/ligands affect ATP binding to γGCS; we have studied specifically the affects of glutamine, glutamic acid, α-aminobutyrate, and magnesium chloride. Our results using fluorescence spectroscopy indicate that the dissociation constant for ATP (K_d value where 50% of the ATP binding sites are filled) does not significantly differ in the presence or absence of these substrates. Further fluorescence and UV/Vis absorbance studies will be performed to probe for possible protein conformational changes in the presence of high concentrations of α-aminobutyrate.

8:54 am *Sulfur Cycling in the Marcell S6 wetland*
Brianna Vaa, Jeff Jeremiason

The purpose of our research was to begin examining sulfur dynamics in the S6 wetland at the Marcell Experimental Forest. A whole ecosystem sulfate addition experiment is being conducted on the S6 wetland to determine impacts of sulfate addition on mercury methylation and export from the wetland. Following sulfate additions we have been monitoring sulfate into dissolved sulfide. Porewater samples are taken at three depths and analyzed using a sulfide probe and ion chromatography. It is hypothesized that additional sulfate will stimulate sulfate reducing bacteria producing more dissolved sulfide. The process of the sulfate additions and collection of samples as well as the method of ion chromatography will be explained in detail. Data will be presented showing the relationship between sulfate and sulfide concentrations at 6 sampling sites on various days following sulfate additions.

9:06 am *The Synthesis of Two Amine Derivatives of Phenytoin*
Max Leither, Brian O'Brien

Para addition of a nitro group to benzoin with potassium nitrate (acidic conditions) was performed and reacted with ammonium chloride and an Indium catalyst to, then, selectively reduce the lone nitro functional group. The indium catalyst clumped and the very small yield of the desired product (*p*-aminobenzil) was attributed to this. Substituting benzil with *p*-aminobenzil in a standard benzylic acid type rearrangement using urea (basic conditions) yielded a very small amount of aminophenytoin. A second amine derivative of phenytoin with a tether link between the amine and phenyl group of phenytoin was pursued, but not yet accomplished. A variety of synthesized 4-iodophenol salts with *n*-bromopropylphthalamdie have shown considerable stubbornness in replacing the bromo group in an S_N2 reaction, regardless of repeated attempts under very reactive conditions, including methylethylketone and DMF solvents with catalytic sodium iodide as well as two varieties of crown ethers. A proposed synthesis of the desired product will be presented and further pursued in the future.

9:18 am *An Intramolecular Diels-Alder Approach to Natural Product Synthesis*
Amy McKeehan, Scott Bur

Many plant natural products, including those which have been shown to have biological significance in anti-viral, anti-fungal, and anti-microbial systems, have a common bicyclic core structure. The way in which many of these natural products interact with biological systems is not completely understood. If these macromolecules could be synthesized systematically, it would be possible to conduct specific studies in this area. One approach to synthesizing this type of molecule is by an intramolecular Diels-Alder reaction, in which the diene and the dienophile are part of the same molecule. In this research, the Krapcho decarboxylation of dimethylmalonate, reduction of the ester, and halogenation of the resulting alcohol, gave a haloalkyl chain. A haloalkene was attached to a siloxy-furan structure, resulting in a molecule with which the Diels-Alder reaction could be performed, giving a bicycle[4.3.0]nonane structure. Further studies will include using different substituents on the haloalkane to obtain various structural properties in the bicyclic product.

9:30 am *Optimization of Purification Techniques of γ-Glutamylcysteine Synthetase*
Andrea Putnam, Brenda Kelly

γ-glutamylcysteine synthetase is the first and rate limiting step in glutathione synthesis. Glutathione, γ-glutamylcysteinylglycine, is the predominant low molecular weight thiol in mammals and is responsible for protection against many reactive species both directly and with enzymatic catalysis. Current techniques for the isolation and purification of *E. coli* γ-glutamylcysteine synthetase using DE-52 anion exchange chromatography yield poor retention of enzyme activity. The following research demonstrates that γ-glutamylcysteine synthetase is isolated more efficiently using strong anion exchange resins.

9:42 am *Distribution and Mapping of the Cretaceous Tepee Buttes of the Western Interior Seaway*
Eleanor Bash, Russell Shapiro

The Tepee Buttes comprise the most aerially extensive seep carbonates in the world. They are found mainly in Colorado, but crop out from South Dakota south to Texas. A total of 106 buttes were studied in more detail at two sites in Colorado.
Six separate lithofacies were identified in outcrops of the Tepee Buttes and mapped at the meter scale: (I) vuggy facies; (II) articulated clam facies; (III) muddy clam facies; (IV) limestone concretion facies; (V) micrite facies; and (VI) microbialite facies. Previous studies of the Tepee Buttes described a concentric arrangement of facies within each butte that ringed an inner, central vent pipe.
Analysis shows that facies II dominates more buttes (39%) than any other facies, but the remaining 61% are dominated by other facies. If the buttes had a concentric arrangement of facies around a vent core, the same facies would be expected at the top and center of each butte. Our results show the presence of different facies at the center tops of different buttes. Therefore, these seep carbonates probably accumulated as vertical stacks of rapidly cemented carbonate that may or may not have had significant relief above the sea floor.

9:42 am *Petrology and Petrography of Cretaceous Methane-Seep Carbonates*
Julia Anderson, Russell Shapiro

The Tepee Buttes (~76 Ma) are ancient methane seep deposits of the Cretaceous Interior Seaway. They formed from methane-rich fluid seeping out of the underlying Pierre Shale and Niobrara formations during early Laramide faulting. Similar to modern seeps, these carbonates most likely formed from geochemical changes brought on by methanotropic bacteria (oxidation of methane) and sulfate reducing bacteria.
The Tepee Buttes carbonates consist of six different lithofacies: (I) vuggy intrapelsparite with complex cements and articulated and disarticulated clams; (II) dense coquina of articulated lucinid clams in vuggy intrapelsparite; (III) clams in micrite; (IV) limestone concretions; (V) micrite without shells; and (VI) vuggy peloidal intraclastic microbialite.
Samples were analyzed for petrographic fabrics and stable isotopes to determine a series of primary to late stage diagenetic features recording fluid diagenesis in each different lithofacies. Petrofabrics include pelmicrite, intrapelmicrite and intrapelsparite, and fringing, isopachous, botryodal and late stage spar cements. δ^{13} C isotope ratios for the microbial peloids range from -36.77 to -10.50 ‰ PDB. The primary micrite with siliciclastic grains range from -38.58 to -12.07. Values for the intraclasts within the primary micrite are -35.86 to -7.33. The primary cements include yellow calcite fringe with δ^{13} C values of -39.28 to -36.98, botryoidal and isopachous cements with δ^{13} C values of -48.73 to -34.95. During the latest stages, blocky calcite spar cement filled in the remaining void space and preserves a δ^{13} C ratio of -34.31 to -12.07.

10:00 am *A Representation of Finitely Additive Measures on the Natural Numbers*
Trevor Potter, Ron Rietz

A measure on **N,** the set of natural numbers, is a function which assigns a real number to each subset of **N**. A finitely additive measure has the property that the sum of the measures of a finite collection of disjoint subsets of **N** is equal to the measures of the union of the subsets. Two special types of these measures are full-valued measures and ultrafilter measures, which correspond to a notion of continuity and complete discontinuity for measures, respectively. We show that an arbitrary finitely additive measure on **N** can be represented as the sum of a full-valued measure and an ultrafilter measure.

10:12 am *Steps Towards the Total Synthesis of Caulerpenynol*
Bruce Atwater, Matthias C. McIntosh (University of Arkansas)

The natural product caulerpenyne has shown great potential as an anticancer drug. This paper discusses advances towards the synthesis of a derivative of caulerpenyne using alkyne cross dimerization reactions with palladium (II) acetate.

10:24 am *Refreshments in Nobel Lobby*

10:54 am *Laboratory Curriculum Development*
Katherine Haynes, Scott Bur

New experiments were designed and tested for the Organic I, II and Inorganic I laboratories at Gustavus Adolphus College. The labs tested include the Bromination of Acetanilide, Preparation of chiraltris 1,10 phenanthroline cobalt (IIII), Preparation of Co(salen), a modified Wohler synthesis of urea, Bromination of methyl acetanilide of p-acetotoluidide, and the resolution of racemic phenylsuccinic acid with (-) proline as a resolving agent. An experimental procedure was designed for an acid/base extraction using Benzocaine as a base, Aspirin as an acid, and varying neutral compounds. The development and testing of these procedures will be discussed.

11:06 am *Methylmercury Formation in Marcell Experimental Forest after Sulfate Addition*
Lisa Raetz, Jeff Jeremiason

The anaerobic conditions of wetlands provide ideal habitats for sulfate-reducing bacteria to thrive. Laboratory experimentation has shown that sulfate-reducing bacteria are also the primary mercury methlyators. Methylmercury is the most dangerous form of mercury, possessing the ability to bioaccumulate in aquatic food chains. In order to understand the formation of methylmercury in a large-scale environmental setting, the S-6 wetland in the Marcell Experimental Forest was monitored for methylmercury and sulfate content after controlled sulfate additions. Porewater samples were collected at experimental plots receiving 4 times and 16 times the annual sulfate load. Samples were also collected from control locations receiving no additional sulfate. In general, methylmercury concentrations increased following each sulfate addition.

11:18 am *The cause(s) of reduced female fertility in a strain of Drosophila melanogaster*
Tanner Miest, Margaret Bloch Qazi

D. melanogaster females hemizygous for a small number of genes were tested to determine the cause of a documented reduction in fertility. Egg production, fertilization efficiency, and temporal sperm storage patterns for hemizygous and control females were tested as components of female fertility and quantified using egg, progeny, and sperm counts. Significant difference between genotypes for each variable will be determined by statistical analysis and used to further elucidate mechanisms of female fertility through the identification of an acting set of genes.

11:30 am *The effect of 5-5-diphenylhydantoin on the production or release of nitric oxide by mouse macrophage cells*
Britta L. Hansen, John Lammert

The drug 5-5-diphenylhydantoin, or phenytoin, with its anti-inflammatory properties has recently become the interest of many immunologists for its possible ability to relieve the symptoms of the auto-immune disease Rheumatoid Arthritis. In our study, mouse RAW 264.7 cells were induced to inflame by *E. coli* lipopolysaccharide (1 μg/mL), and following inflammation the cells were treated with differing concentrations of phenytoin (10 μg/mL, 30 μg/mL, 60 μg/mL, 90 μg/mL). Our results show a general trend of decreased nitric oxide production by cells treated with higher levels of phenytoin. While our data are encouraging for the alleviation of inflammation in Rheumatoid Arthritis patients, more studies are necessary to investigate the degree of side effects of phenytoin and also its optimum concentration for medical use.

11:42 am *A New Synthetic Route to Pyrrolizidine and Indolizidine Structures*
Aulaire M. Schmitz, Scott Bur

There are over 170 indolizidine-based and 560 pyrrolizidine-based structures found in the natural world. While many of these compounds are toxic, some may be of value in certain medical studies, including the study of cancer metastasis, immune response, HIV-1, and have shown anti-tumor activity. In the original reaction scheme, reduction of the imid was proving troublesome, so the process was abandoned and a new reaction scheme was developed. Nitro methane is deprotonated and added to methacrylate. The Nitro group will then be transformed into an aldehyde equivalent. This molecule can then be used to provide the key cyclization intermediate.

11:54 am *The Biodiesel Project at Gustavus*
Zach Walgenbach, Jeff Jeremiason

Biodiesel is a clean renewable and domestically produced fuel that can be synthesized from any natural oil. Such fuels include, manure, animal fat, and waste/virgin vegetable oil. The process most commonly used is transesterification, which requires the use of three main ingredients: oil, alcohol, and a catalyst. The finished product has a plethora of positive environmental benefits. This summer we have begun construction of a large biodiesel reactor, tested different formulations, and done some preliminary chemical analyses of our products. Our goal is to utilize a waste product from campus (used grease from the cafeteria) and provide diesel fuel for our physical plant equipment.

12:06 pm *Development of a Molecular Dynamics Web-Interface for the Analysis of Biological Molecular Conformations*
Eddie Gorr, Jonathan Smith

Since the invention of computers, computational chemistry has become an increasingly important area of research for chemistry, biochemistry and molecular-biology. Our work has involved the concurrent computational investigation of protein conformations and the development of a graphical web-based interface. This interface allows users to carryout complicated molecular computations through a user-friendly setting. With this web-interface a detailed computational analysis of glucagon, a 29 amino-acid protein, was carried out. This preliminary analysis suggests that glucagon adopts three main conformations dependent on it's environment.

12:18 pm *Synthesis of Heterocyclic Rings Through 1,5-electrocyclization Reactions*
Ryan Schwiderski, Dr. Scott Bur

About two thirds of the drugs in the drug database contain heterocyclic rings and a majority of those have rings that contain nitrogen. 1,5-electrocyclizations to form 5-membered rings containing nitrogen could be an important method for the synthesis of heterocyclic molecules. To that end, vinyl glycine derivatives were reacted with aldehydes to form immine intermediates. Zwitterion formation should then lead to ring formation. Initial experiments with the primary amine in vinyl glycine were unsuccessful, but other N-Substituted derivatives are being investigated.

12:30 pm *Mercury in Lake Michigan*
Tara Lacoe, Jeff Jeremiason

Air and surface water samples were collected for mercury analysis in May and July from aboard the EPA *Lake Guardian* research vessel. Mercury concentrations in air were monitored on five minute intervals during weeklong cruises in May and July using a Tekran 2537 mercury vapor analyzer. Surface water grab samples were collected for analysis of total mercury, methylmercury, and dissolved gaseous mercury (DGM). DGM concentrations were measured on-board the ship using the Tekran, while total mercury and methylmercury concentrations will be analyzed at Gustavus. Preliminary results indicated higher mercury concentrations in air when winds were coming from the Chicago/Gary area, a water to air flux of elemental mercury, and no discernible spatial trends in total mercury concentrations in the lake.

Presentation given on 7/27/05
Correlation Between Color and Chemistry in Garnet with Implications for Diamond Exploration
Brian Goldner, James Welsh

Garnets are used as indicator minerals for diamond exploration because garnet-bearing mantle xenoliths are commonly associated with diamondiferous kimberlites, with the underlying assumption that these xenoliths must originate in the diamond stability field. Erosion of these diamondiferous garnet-bearing rocks by glaciers or other processes will leave a dispersal train containing the more abundant garnet. Garnets from mantle xenoliths have been categorized into 12 different groups (labeled G1-G12) based on parent rock type and CaO and Cr_2O_3 contents. These groups aid exploration in that some garnets, principally those with harzburgitic and eclogitic affinities, are more conducive to diamondiferous pipes than other mantle rock types such as lherzolite. If garnets from these groups can be distinguished by using color rather than chemical analysis the process becomes more economic. A microprobe mount containing 318 garnets from groups G1, G2, G7, G9, G10, and G11 whose chemistries have already been determined were then viewed microscopically and digitized for color using a red-green-blue (RGB) scheme. While there appears to be an indication that some groups can be separated by color, for example G1 and G2 groups tend to be more orange, while groups G7, G9, and G10 tend to be more pink-purple, the data suggest difficulty in separating G9 (lherzolitic) from G10 (harzburgitic) garnets.