

support increases compared to the slowly evolving genomic regions alone, but quite similar to that obtained with the rapidly evolving genomic regions alone. Therefore, this study shows that rapidly evolving genomic regions provide more phylogenetic signal for resolving relationships among the rosids than the traditionally used slowly evolving regions.

HYDROPHILIC AND LIPOPHILIC ANTIOXIDANT CONTENT IN FIVE TROPICAL SPICES. Rachel E. Pence and Michael H. Renfro, Dept. of Biology, James Madison Univ., Harrisonburg, VA 22807. Dietary sources of antioxidants are important as part of healthy diets because antioxidants are thought to help prevent various chronic diseases and provide multiple health benefits. We analyzed the antioxidant content of five tropical spices: allspice, cinnamon, cloves, ginger and nutmeg. Antioxidant content was measured using the ABTS/H₂O₂/HRP decoloration method, and means were compared using a one-way analysis of variance followed by Dunnett's T3 test for significance of differences of means. Cloves had the greatest hydrophilic antioxidant content but the least lipophilic antioxidant content. Lipophilic antioxidant content was greatest in allspice, while the hydrophilic antioxidant content of allspice was second only to cloves. Ginger was relatively low in antioxidants compared with the other spices. Total antioxidants was greatest in cloves. Studies of antioxidant content in spices can provide information helpful to planning healthy diets.

ISOLATION AND CHARACTERIZATION OF LEAF ENDOPHYTES IN BETULA UBER AND BETULA LENTA. Jessica D. Weaver & Kevin G. Jones, Univ. of Virginia's College at Wise, Wise VA 24293. Although originally described as a distinct species, *Betula uber* is now regarded as a variant of *Betula lenta*. A ubiquitous characteristic of angiosperms is that their healthy tissues show symptomless internal colonization by fungi called endophytes. The purpose of this research is to initiate a survey of the endophyte complement of *Betula uber* and *Betula lenta* and to investigate the effects of leaf shape on endophyte colonization since these trees differ markedly only in leaf form. Surprisingly, gross morphology of the fungi revealed that there were no common endophytes between *Betula uber* and *Betula lenta*. There is great diversity in endophyte populations within and between these species; but, our results may simply reflect the natural diversity of endophytes. Because there is such diversity, no conclusions about the effects of leaf shape can be made at this time, and more samples need to be collected and analyzed. (Supported by the Virginia Academy of Science).

Chemistry

THE ENZYMATIC ACTIVITY OF MshA: A FUNDAMENTAL ENZYME IN MYCOTHIOIOL BIOSYNTHESIS. T. W. Boshers & M. Hernick, Dept. of Biochemistry, Virginia Tech, Blacksburg, VA 24061. Mycothiol is the primary reducing agent used by mycobacteria to prevent against oxidative damage. Consequently, enzymes involved in mycothiol biosynthesis are targets for antibiotic development. MshA is a glycosyltransferase that catalyzes the transfer of GlcNAc from UDP-GlcNAc to

inositol-1-phosphate to form GlcNAc-Ins-1P and UDP, a key step in the biosynthesis of mycothiol. We are working towards the biochemical characterization of recombinant MshA from *M. smegmatis* and *M. tuberculosis*. MsMshA has been expressed in *E. coli* and purified using amylose resin. We have developed an HPLC-based assay to measure MshA activity, and have used this assay to demonstrate that the recombinant MshA from *M. smegmatis* is active. We will use this assay in the future to characterize the chemical mechanism of MshA.

HYDROXAMATE FORMATION IN SIDEROPHORE BIOSYNTHESIS. S.W. Chocklett & P. Sobrado, Dept. of Biochemistry, Virginia Tech, Blacksburg, VA 24061. The proliferation of many microorganisms depends heavily on their ability to scavenge nutrients from their host and extracellular spaces. Since iron is an essential nutrient, microbes have developed a tightly regulated system to sequester iron and utilize this element for its metabolic needs. Like many other pathogens, *M. tuberculosis*, *P. aeruginosa*, *B. cepacia* and *A. fumigatus* synthesize and secrete low molecular weight ($M_r < 2000$) Fe^{III} chelators called siderophores under iron-limiting conditions. Pathogens then specifically take up the siderophores complexed with ferric iron, thereby increasing the concentration of iron to levels necessary for pathogens to proliferate during infection. The assembly-line process of siderophores has revealed that a critical step in siderophore biosynthesis involves the hydroxylation of the terminal amino group from an amino acid by a flavin-dependent monooxygenase at the expense of NAD(P)H and O₂. The hydroxylated product from this reaction is then incorporated into the backbone of the siderophore, where it directly coordinates ferric iron. Here, we report the characterization of two enzymes catalyzing the initial step in siderophore biosynthesis in the prokaryote *Mycobacterium smegmatis*, as well as the fungus *Aspergillus fumigatus*. This is the first report of members of the NMOs containing a bound FAD cofactor upon purification, assisting in the detailed biochemical characterization of this class of flavoprotein monooxygenases.

METHOD DEVELOPMENT FOR THE DETERMINATION OF AMINO ACID IN SEXUALLY MATURE *Odocoileus virginianus* BY GAS CHROMATOGRAPHY MASS SPECTROMETRY. S. H. Clift, J. N. Watson, D. Swale, M. Houck, L. S. Webb, & G. C. Klein, Dept. Of Biology, Chemistry and Environmental Science, Christopher Newport University, Newport News VA 23606. The purpose of this study is to develop a method that can be used to quantify the amino acids present in a sample of muscle tissue from *Odocoileus virginianus* using Gas Chromatography Mass Spectrometry (GC-MS). Because amino acids are multifunctional, they are difficult to analyze by a single technique; however, they can be derivatized using *N*-tert-butyltrimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA). This derivatizing agent attaches to amine nitrogens and carboxylate oxygen sites on the amino acids, and create suitably volatile compounds for use with GC-MS. Fragmentation occurs at similar cleavage sites for all amino acids, allowing for quick and easy identification of each of the separated peaks in the gas chromatogram. Currently, data are being collected for derivatized standard amino acids at different concentrations in order to provide calibration data for the application of this method. These techniques will be used to

quantify amino acids extracted from the muscle tissue of sexually mature *Odocoileus virginianus*.

COMPETITION BETWEEN SUBSTITUTION AND ELIMINATION IN THE REACTIONS OF DIANIONS WITH SUBSTITUTED AND CYCLIC ALKYL HALIDES. Keyanna Conner, Renan Joviliano, Andrew Alexander & Scott Gronert, Department of Chemistry, Virginia Commonwealth University, Richmond, VA 23284-2006. The competition between substitution and elimination in the nucleophilic reactions of alkyl halides is an important testing ground for reactivity patterns in gas-phase organic chemistry. The dianions in the study employ sulfonates as inert, spectator ionic sites and phenolates or benzoates as the nucleophilic ionic sites. They were generated in the gas-phase by ESI in an LCQ ion trap mass spectrometer. Using a custom-built interface, alkyl chlorides or bromides were introduced into the helium buffer gas of the instrument. Reactions were monitored as a function of time at various flow rates (pressures) of the reagent gases and branching ratios were determined. Reactions were modeled computationally at the MP2/6-31+G** level and the results aid in the interpretation of the experimental data. Three groups of alkyl halides were examined. Alkyl chlorides with electron-withdrawing groups at the beta position produced strong activation of the elimination pathway. Investigations using cyclic alkyl bromides indicated the balance between substitution and elimination are sensitive to ring size with a large shift from substitution to elimination in the move from cyclopentyl to cyclohexyl bromide. A series of six bromopentanes produced widely varying substitution patterns at both the alpha and beta carbons.

DENSITY FUNCTIONAL THEORY STUDIES OF DIARYLAMINOSTYRYL CHROMOPHORES WITH HETEROCYCLIC AND VINYLENE BRIDGES. Courtney E. Dula & Edmund Moses N. Ndip, Chemistry Department, Hampton University, Hampton, VA 23668. Organic systems with large 2PA cross-sections have a broad spectrum of technological applications, i.e. Organic Light Emitting Diodes. Organic semiconductors, like the ones studied, show strong nonlinear optical properties due to the presence of delocalized electrons in the $\pi - \pi^*$ orbitals. These materials are ideal for fast processing of information and optical data storage applications. The linear absorption spectra, energy gaps, intensities and/or oscillator strengths, dipole moments, and other molecular properties have been computed at semi empirical and ab initio levels of theory. The computed λ_{max} for the thiophene compounds (423-437nm) are in good agreement with the experimental data (405-438nm). Additional calculations have been carried out for analogous compounds based on the success of the previous calculations. These are the first quantum mechanical studies that have been performed on these types of thiophene, furan, and pyrrole heterocyclic centrosymmetric systems. The data show reasonable agreement between Arguslab (ZINDO-CI) (398-420nm) and TITAN (DFT: B3LYP - 6-31G**) (421-512nm) λ_{max} . However, the band gaps that were extracted from the B3LYP calculations (1.16 - 2.02eV) are more consistent with experimental values (2.81-3.07eV) for the thiophene compounds.

RELATIVE STABILITIES OF C_{94} AND C_{94}^{2-} IONS USING QUANTUM AND STATISTICAL MECHANICAL FUNCTIONS. Tim Fuhrer, & Harry C. Dorn,

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA, 24061. C_{94} is one of many larger cage fullerenes being studied today. Previous experiments and calculations have found the C_{3v} symmetry empty cage for C_{94} to be unstable, but when $M@C_{94}$ ($M = Ca, Tm$) was synthesized in our lab and an independent lab in China, only the C_{3v} isomer is found. Quantum and statistical mechanical calculations show that the C_{3v} cage may be stabilized by the addition of the two electrons donated by the metal atom while the other more stable empty cage isomers are destabilized by the addition of those two electrons.

OXIDATION OF ALCOHOLS USING ALUMINA BOUND PCC UNDER HETEROGENEOUS REACTION CONDITIONS, Kristen Jobes, Heather Robinson, & Emma Goldman, Department Of Chemistry, University of Richmond, Richmond VA 23173. Our research project involves studying heterogeneous high temperature (100-200°C) gas/solid reactions. Previously substitution and elimination reactions using metal alkoxides have been studied. Our recent focus is specifically on oxidizing alcohols with PCC under the heterogeneous high temperature gas/solid reaction conditions. The successful oxidation of these alcohols provides data to support heterogeneous gas/solid reactions as a viable alternative reaction method. The adoption of the heterogeneous method in laboratories will reduce the wasteful use of solvents and help laboratories move towards the goals of Green Chemistry.

METHOD DEVELOPMENT FOR THE QUALITATIVE DETERMINATION OF PETRO-PORPHYRINS OF TWO GEOGRAPHICALLY DISTINCT CRUDE OILS BY UV-VIS SPECTROSCOPY. G.C. Klein, K.J. Anderson, R.G. Saller, & M.A. Beasley, Dept. Of Biology, Chemistry and Environmental Science, Christopher Newport University, Newport News VA 23606. Petroporphyrins are metal-containing biomarkers found in crude oils that are known to deactivate catalysts during the refining process. Quantification of petroporphyrins in crude oils will lead to efficient removal procedures increasing the overall production of petroleum products. Fractionation schemes were investigated to increase the overall recovery yield of the heavy crude oil. UV-Vis Spectrophotometry was used to screen each of the fractions for the presence of petroporphyrins. The use of the continuum-removal by division mathematical model assisted in the identification of these petroporphyrins by increasing the definition of the associated peaks. Petroporphyrins were found in 4 of the 6 fractions of our separation scheme. UV-Vis Spectrophotometry can be used not only as a means to screen fractions for the presence of petroporphyrins, but also can be used to potentially provide information on the type of crude oil (light vs. heavy).

POST-TRANSLATIONAL MODIFICATIONS OF MODEL PROTEINS WITH 4-HYDROXYNONENAL, A QUANTITATIVE ANALYSIS OF REACTIVITY AT SPECIFIC SITES. Qingyuan Liu and Scott Gronert, Dept. of Chemistry, Virginia Commonwealth University, Richmond VA 23284-2006. HSA was incubated with 4-hydroxynonenal (HNE) in PBS at molar ratios (HNE:HSA) ranging from 5:1 to 100:1 from 1 to 24 hours. The adducts were stabilized with sodium borohydride, digested with trypsin. The tryptic peptide mixtures were labeled with one of four iTRAQ reagents and then combined with other labeled samples. We performed two general

types of experiments to probe the kinetics of the reaction system. In the first, varying ratios of HNE/HSA were employed with a fixed reaction time of 3 hours. In the second, a high ratio (100:1) was used and measurements were taken at several times. The latter allowed us to probe slower processes. Kinetic data were obtained for 17 modification processes. The one free cysteine in HSA is highly reactive and in general, the histidines are more reactive than lysines. However, there is a large variation in reactivity among the histidines in HSA. Aside from the free cysteine, we find the following order of reactivity in the more reactive sites: His³¹² > His⁵³⁴ > Lys⁵⁴⁹ > His⁹¹ > His²⁶⁶/His²⁷¹ > Lys³⁷⁵ > His³⁹¹ (Swiss-Prot). The results suggest that reactions occur on multiple time scales, possibly including protein conformational changes, and this is a likely cause for the differences in previous reports.

A COMPARATIVE STUDY OF THE NON-LINEAR OPTICAL PROPERTIES OF A SERIES OF PUSH-PULL DIARYLAMINOSTYRYL CHROMOPHORES WITH HETEROCYCLIC VINYLENE AND AZO BRIDGES. Edmund Moses, N. Ndip & Courtney E. Dula, Chemistry Department, Hampton University, Hampton, VA 23668.

In the present study, a number of molecular descriptors (linear absorptions, dipole moments, transition dipoles, hyperpolarizabilities, etc.) have been computed for several series of diarylamino-styryl heterocyclic (thiophene, furan, and pyrrole-based) chromophores with vinylene and azo bridges at the semi-empirical (Arguslab ZINDO-CI) and ab initio (DFT/B3LYP using Gaussian98, Spartan06, and Titan) molecular orbital methods. The influences of terminal substituents on various molecular properties of the homologues were also examined. The HOMO/LUMO surface renderings show a greater population in the HOMO orbital stretching toward the terminal substituents in the azo compounds, the vinylene compounds show a decrease in the size orbitals on the benzene ring. The LUMO for the vinylene compounds show an increased population of the lobes around the benzene, whereas in the azo compounds the sizes of the lobes have decreased. When azo bridges were substituted for the vinylene bridges in the compounds an increase in the absorption maxima were observed (vinylene 421-512nm, azo 485-528nm). The increased electron density and electrostatic potential from the azo bridge suggests that the bridge substitution from vinylene to azo improves the conduction (exhibit stronger NLO properties) properties of these materials.

CHARACTERIZATION OF *Aspergillus fumigatus* UDP-GALACTOPYRANOSE MUTASE. Michelle Oppenheimer and Pablo Sobrado, Dept. of Biochemistry, Virginia Tech, Blacksburg, VA 24061. UDP-galactopyranose mutase (UGM) catalyzes the conversion of UDP-galactopyranose (UDP-Galp) to UDP-galactofuranose (UDP-Galf). UDP-Galf is then used for the addition of galactofuranose to the cell wall of *Aspergillus fumigatus*, where it plays a key structural role. Deletion of *A. fumigatus* UGM (AfUGM) results in attenuated virulence. In addition, Galf is absent in humans therefore AfUGM is considered an ideal therapeutic drug target for the treatment of aspergillosis. UGMs are also unique because of their novel chemical mechanism, in which the flavin must be reduced yet no net redox change occurs throughout the reaction. Studying the mechanism, as well as, the structure of AfUGM will provide valuable knowledge which can be used for the generation of new drugs for the

treatment of aspergillosis. Currently, we have been able to successfully recombinantly express and purify, crystallize, and initially characterize AfUGM, setting the stage for the future mechanistic studies and development of therapeutic drugs.

DIASTEREOSELECTIVE α -ALKYLATION OF CHIRAL β -BORYLATED ESTERS. Michael Perfetti & Webster Santos, Dept. of Chemistry, Virginia Tech, Blacksburg, VA 24061. The use of boron in the development of asymmetric methodologies and inhibitor synthesis has increased significantly over the last decade. Currently, the use of chiral boronic esters to enhance the stereochemistry of molecules through intramolecular diastereoselective alkylations is absent in the literature. We report the development and initial characterization of a novel intramolecular diastereoselective reaction for the α -alkylation of chiral β -borylated esters. We propose that standard deprotonation of chiral β -borylated esters with lithium diisopropylamide (LDA) leads to the formation of an intramolecular cyclic five-membered ring boron-“ate” complex. Upon treatment with an alkylation reagent, this complex will collapse to provide chiral α , β -substituted boronic esters with a high degree of diastereoselectivity. This reaction is powerful in that a wide range of chiral β -borylated ester substrates can be employed that possess varying degrees of substitution and steric bulk. Results show that yields up to 67% are achievable with diastereomeric ratios (DR) of (9.7:1), where alkylation products from bulkier tert-butyl esters provided higher DR values compared to methyl esters that possessed the same β -functional groups. Additionally, several ^{11}B NMR techniques were used to investigate and elucidate the mechanism of this reaction.

GROUP 5 BACTERIAL MULTICOMPONENT MONOOXYGENASES. R. Robinson, M. Oppenheimer, J. Llanos-Velázquez, S.W. Chocklett & Sobrado, P., Dept. of Biochemistry, Virginia Tech, Blacksburg, VA 24061. Microbes that contain multicomponent monooxygenase systems can use organic compounds such as tetrahydrofuran (THF) or propane as the sole carbon and energy source. The ability to metabolize these compounds is related to the activity of the Group V Bacterial Multicomponent Monooxygenases (BMMs). Members of the Group V BMMs share the same operon orientation and conserved components, which consist of: *i*) a hydroxylase with an α catalytic subunit and a β structural subunit, *ii*) an oxidoreductase, and *iii*) a regulatory subunit to prevent futile cycling. The oxidoreductase is responsible for transferring electrons from NADH, through its FAD and 2Fe-2S cluster, to the diiron center of the hydroxylase. The reduced hydroxylase then reacts with molecular oxygen leading to the formation of a high-valent iron-oxo species, which is required for the hydroxylation of the substrate. We present the results of the cloning, expression, purification, and biochemical characterization of the recombinant forms of ThmD and PrmC from *Pseudonocardia* sp. Strain K1 and *Gordonia* sp. Strain TY-5. These are the oxidoreductase components of the *thm* and *prm* operons, for which the operon has been isolated from these organisms. Also reported is the expression, purification and crystallographic studies of ThmC and PrmD, the regulatory domains of each operon, respectively

MODIFICATION OF MACROPOROUS SILICA THIN FILMS VIA METAL NANOPARTICLE DEPOSITION. Amy E. Rue & Maryanne M. Collinson, Dept. Of

Chemistry, Virginia Commonwealth University, Richmond VA 23284-2006. Two methods were used to deposit metal nanoparticles into the cavities of sol-gel derived silicate thin films created from polystyrene sphere templates. The first method followed a bottom up electrochemical approach, where films were formed on glassy carbon electrodes from a 0.4 μ m polystyrene sphere doped sol prepared from the condensation of tetramethoxysilane (TMOS). Since pinholes in the film were filled by electrodeposition of TMOS, the only available surface for electrochemistry was at the bottom of the cavities. Copper was then electrodeposited into the exposed cavities. Changes in the deposition length resulted in variation in particle size. The second method used a top down approach for the electroless deposition of gold. Similar films were formed on glass, and the deposition occurred as a result of the attraction between prepared gold nanoparticles and a monolayer of (3-Mercaptopropyl)trimethoxysilane. To insure the placement of the gold only occurred in the cavities, the exposed film was blocked with octyltrimethoxysilane or trimethylchlorosilane before template removal. Films were characterized using atomic force microscopy. Measurements were taken before and after deposition, and showed the presence of copper particles ranging from 100 to 300 nm and gold particles ranging from 70 to 100 nm.

SUBUNIT INTERACTION OF THE CLONED HUMAN GUANINE-7-METHYLTRANSFERASE. Jessica N. Skeeter, Jeanhee Chung & Thomas O. Sitz, Dept. of Biochemistry, Virginia Tech, Blacksburg, VA 24061. The 5'-end of eukaryotic mRNA is capped and the guanine base is methylated in the N-7-position generating a fully functional cap structure. If the cap is not methylated at the N-7 position, the mRNA is not translated. The enzyme that methylates the N-7 position, Guanine-7-methyltransferase, has been expressed as a His-tag protein in *E. coli*. and purified on a Nickel column. The full length enzyme, 476 amino acids long, and the deletion mutation, 120 amino acids removed from the N-terminus are about 80% pure after the nickel column. To further purify the enzymes, a positively charged ion-exchange column (Mono Q-Sepharose) was used. The elutants from the Nickel column were applied to Mono-Q columns and eluted with increasing concentrations of KCl. A major methyltransferase peak eluted at 0.1 and 0.15 M KCl and was over 95% pure as determined by SDS polyacrylamide electrophoresis. This purified guanine-7-methyltransferase was then applied to a FPLC-Superose 12 gel exclusion column to characterize the subunit structure. Two major peaks of protein were observed for both the full length and the deletion mutation enzyme which corresponded to about 90% homodimer and 10% monomer for each respectively. The purified enzymes were also analyzed by blue-native polyacrylamide gel electrophoresis and the deletion of 120 amino acids had no affect on the subunit interaction, i.e. about 90% dimer

IR AND NMR OF ALCOHOLS IN THE VAPOR PHASE: A COMPARISON BETWEEN EXPERIMENTAL RESULTS AND DENSITY FUNCTIONAL CALCULATIONS. C.C. White & T.C. DeVore, Dept of Chem. and Biochem., MSC 4501, James Madison University, Harrisonburg VA 22807. The observed IR and NMR spectra of the methanol, ethanol, 2-propanol and 2-methyl, 2- propanol (t-butanol) vapor molecules are compared to the spectra calculated for these molecules using the DFT-B3LYP method with the 6-311++G (3df, 3pd) basis set using the

Gaussian 03 software. NMR spectra were calculated using the GIAO method. IR spectra (4000 to 400 cm^{-1} at 0.5 cm^{-1} resolution) were obtained by injecting $10\text{ }\mu\text{L}$ of the alcohol into a 10 cm pathlength stainless steel vacuum cell placed in the sample compartment of a Nicolet 6700 FTIR. Vapor phase NMR spectra were obtained by placing 0.15 mL of the alcohol in the outer tube of a standard 5 mm OD double NMR tube. A Bruker Spectrospin 400 and a Bruker Spectrospin 600 NMR equipped with a variable temperature probe were used to collect the NMR spectra. D_2O was placed in the inner tube as the lock solvent. While the calculated chemical shifts were in qualitative agreement, the quantitative values varied by $\pm 0.2\text{ ppm}$ when adjusted to the same reference. The IR frequencies showed a decreasing error at the lower frequency. Since the calculations give the harmonic frequency, part of this difference may result from ignoring the anharmonic terms. The relative intensities generally agreed within a factor of 2.

SIZE TUNABLE HIERARCHICAL POROUS STRUCTURES BY DIRECT TEMPLATING. Bo Zhao, & Maryanne Collinson, Dept. of Chemistry, Virginia Commonwealth University, Richmond VA 23284-2006. Materials with bimodal porosity are of great interest in a diversity of applications of separation, catalysis, and sensing system. In this work, hierarchical porous materials were made by colloidal crystal templating with “raspberry” and “strawberry” shaped templates. These monodispersed hierarchical templates were prepared by simply coupling polystyrene beads of different sizes together. Both the “center” and “satellite” spheres can be varied, and the coverage of “satellite” spheres on the surface of the “center” sphere is tunable by reducing the coupling speed. Based on the templates, bimodal hierarchical porous silica monoliths and gold films were fabricated by sol-gel templating method and electrodeposition, respectively. The materials possess adjustable and well-defined bimodal pore sizes with interconnected windows. In this presentation, the synthesis and applications of these unique materials will be discussed.

Computer Science

USING SECOND LIFE FOR COMPUTER SCIENCE EDUCATION. Robert A. Willis Jr. Department of Computer Science, Hampton University. Over the past few years, I have noticed that our students are reluctant to approach learning computer science in the traditional ways. Computer science requires beginning students to learn the concepts of computer science and the art of programming. While disparate, both of these facets require a good deal of study using texts and practice. Second Life is used to implement a number of innovative interactive tutorials tailored for this generation of students. Furthermore, the environment is conducive for instruction in a number of other areas in computer science (and other disciplines). Second Life is a three dimensional virtual world. It is a social environment that allows people to “live” much as they do in real life. People (represented as avatars) can purchase land, build houses, work, play, and participate in many other activities. It is an ideal environment to reach all levels of students.