Volume 5, Number 1 **Winter 2006**

Journal of Undergraduate Chemistry Research

ISSN: 1541-6003

CONTENTS

A COMBINED GAS CHROMATOGRAPHY/MASS SPECTROMETRY AND THERMOGRAVIMETRIC ANALYSIS STUDY OF THE THERMAL DECOMPOSITION OF BIS(DIBENZYLDITHIOCARBAMATO)- AND BIS(DIETHYLDITHIOCARBAMATO) COPPER(II)

Scott M. Brothers*, Michael J. Baird, Aloysius F. Hepp[a] and Norman V. Duffy† 1

REGULATION OF PYRIMIDINE CATABOLISM IN *PSEUDOMONAS LEMONNIERI* ATCC 12983

Elizabeth B. Burnette*, Randi L. Gant*, Gail M. Meyer, Manuel F. Santiago† 9

CHEMISTRY OF EPOXY ALCOHOLS. BIOMIMETIC 8-ENDO CYCLIZATION OF SCLAREOL EPOXIDE

Kevin M. Terry* and Thomas G. Waddell† 15

DEVELOPMENT OF CATHEPSIN D INHIBITORS WITH NEW HYDROXYETHYL PIPERAZINE DERIVATIVES

Rose M. McConnell†, Carol J. Michael-Trana*, Adam W. Green*, Nikki Myers*, Susan E. Hatfield*, Kelley L. Sayyar and Walter E. Godwin 19

A UV-VISIBLE SPECTROSCOPIC STUDY OF THE URANYL UO_2^{2+} ION UNDER STRONGLY ACIDIC CONDITIONS: EVIDENCE FOR PROTONATION OF UO_2^{2+}

Xiaoping Sun† and Clayton Samples* 29

HERBAL EXTRACTS FROM *CORTEX MOUTAN* EXHIBIT ANTIOXIDANT POTENTIAL, INHIBIT CELL-INDUCED APOPTOSIS, AND POSSESS ANTIMICROBIAL ACTIVITIES

Yang-Hsi Tsai*, Jaime L. Heimbegner*, John J. Beck, and James E. Turner† 33

ANALYSIS OF VOLATILE COMPONENTS OF WINES BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Carolyn Simmons* and Massimo D. Bezoari† 41

ANTHOCYANIN CONTENT IN HYDRANGEA SEPALS

Kathryn E. Pharr*, Kelly M. Mayhew*, and Henry D. Schreiber† 49

The *Journal of Undergraduate Chemistry Research* publishes papers of original research performed by undergraduates on all aspects of chemistry including analytical, organic, inorganic, physical, polymers and biochemistry. Articles about laboratory experiments to be used in the teaching of chemistry are not applicable. The *Journal of Undergraduate Chemistry Research* is issued quarterly and indexed once per year by Dr. Daniel Y. Pharr Editor, Chemistry Department, Virginia Military Institute, Lexington, VA 24450. Subscriptions price per year U.S.A.: institutional $ 120.00, individual $ 50.00 all other countries US $ 150.00. Claims for missing issues will not be honored after four months of issue date. Duplicate copies may not be sent due to the change of address when the publisher was not notified in a timely manner. The *Journal of Undergraduate Chemistry Research* can be contacted via phone (540-464-7244), fax (540-464-7261) or e-mail (PharrDY@vmi.edu) through Dr. Daniel Y. Pharr Editor. No responsibility is assumed by this journal, editor, reviewers or sponsors for any injury and/or damage from products, negligence, experiments, instructions or ideas contained in this journal that result in damage to persons or property. **POSTMASTER**: Send change of address to: Journal of Undergraduate Chemistry Research, Dr. Daniel Y. Pharr Editor, Chemistry Department, Virginia Military Institute, Lexington VA 24450.

A COMBINED GAS CHROMATOGRAPHY/MASS SPECTROMETRY AND THERMOGRAVIMETRIC ANALYSIS STUDY OF THE THERMAL DECOMPOSITION OF BIS(DIBENZYLDITHIOCARBAMATO)- AND BIS(DIETHYLDITHIOCARBAMATO) COPPER(II)

Bis(dibenzyldithiocarbamato)- and bis(diethyldithiocarbamato)copper(II), $Cu(S_2CN(CH_2C_6H_5)_2)_2$ and $Cu(S_2CN(C_2H_5)_2)_2$ respectively, have been examined for their suitability as precursors for copper sulfides for the fabrication of photovoltaic materials. Each complex was decomposed thermally and the products analyzed by GC/MS, TGA and FTIR. The dibenzyl derivative complex decomposed at a lower temperature (225-320°C) to yield CuS as the product. The diethyl derivative complex decomposed at a higher temperature (260-325°C) to yield Cu_2S. No Cu containing fragments were noted in the mass spectra. Unusual recombination fragments were observed in the mass spectra of the diethyl derivative.

Scott M. Brothers*, Michael J. Baird, Aloysius F. Hepp[a] and Norman V. Duffy†, Department of Chemistry, Wheeling Jesuit University, Wheeling, WV 26003, nduffy@wju.edu, [a]Photovoltaic and Space Environments Branch, NASA Glenn Research Center at Lewis Field, Cleveland, OH 44135

REGULATION OF PYRIMIDINE CATABOLISM IN *PSEUDOMONAS LEMONNIERI* ATCC 12983

Pseudomonads are microorganisms that are found in fresh water and sediment.The fluorescent pseudomonads have been found growing on the *Agaricus bisporus*, a commercial mushroom, and are pathogens to other agricultural products. For this reason, it was of interest to investigate the effects of carbon and nitrogen sources on the pyrimidine reductive pathway in cells of *P. lemonnieri* ATCC 12983. The microorganism was grown in liquid medium containing glucose and succinate with various nitrogen sources. The three enzymes of the reductive pathway were measured in extracts from *P. lemonnieri* cells. It was shown that the degradative pathway enzyme activities can be regulated relative to the nutrient sources in the growth medium. The highest specific activity (*N*-carbamoyl-β-alanine amidohydrolase) was seen when ATCC 12983 was grown in glucose and β-aminoisobutyric acid as the carbon and nitrogen sources, respectively. In addition, dihydropyrimidine dehydrogenase specific activity was highest when the reduced form of nicotinamide dinucleotide phosphate was used as the cofactor.

Elizabeth B. Burnette*, Randi L. Gant*, Gail M. Meyer, Manuel F. Santiago†, Department of Chemistry, University of Tennessee at Chattanooga, 615 McCallie Avenue, Chattanooga, Tennessee 37403-2598, Manuel-Santiago@utc.edu

CHEMISTRY OF EPOXY ALCOHOLS. BIOMIMETIC 8-ENDO CYCLIZATION OF SCLAREOL EPOXIDE

The diastereomeric sclareol epoxides [4], prepared from the available labdane diterpene sclareol [3], were reacted with BF_3 etherate in CH_2Cl_2. In addition to minor dehydration products, the major product was the eight-membered ring ether [7]. Such an 8-*endo* epoxy alcohol cyclization is novel and represents a biomimetic reaction related to the biosynthesis of a marine natural product recently isolated by Vagias and coworkers from *Laurencia obtusa.*

Kevin M. Terry* and Thomas G. Waddell†, Department of Chemistry, University of Tennessee at Chattanooga, 615 McCallie Ave., Chattanooga, TN 37403, Thomas-Waddell@utc.edu

DEVELOPMENT OF CATHEPSIN D INHIBITORS WITH NEW HYDROXYETHYL PIPERAZINE DERIVATIVES

Cathepsin D, a lysosomal aspartic protease, clearly plays a role in the tumor processes and metastasis of several types of cancer. An increased incidence of relapse and metastasis of breast cancer has been associated with a high activated serum cathepsin D level. High levels of active cathepsin D have also been found in patients with uterine, ovarian, colon, and prostate cancers. In addition, cathepsin D may be implicated in Alzheimer's disease. Polymorphism of the cathepsin D gene has been isolated in patients diagnosed with Alzheimer's. Aspartyl proteases with substrate specificity similar to cathepsin D, such as the HIV-1 aspartyl protease, have demonstrated inhibition with the clinical use of hydroxyethyl isosteres with piperazine derivatives (cyclic tertiary amines). The design and the development of twelve new hydroxyethyl isostere inhibitors with piperazine derivatives is described, using hemoglobin as the substrate. The IC_{50} values and K_i (apparent) for these cathepsin D inhibitors are now reported.

Rose M. McConnell†, Carol J. Michael-Trana*, Adam W. Green*, Nikki Myers*, Susan E. Hatfield*, Kelley L. Sayyar and Walter E. Godwin, † School of Mathematical and Natural Sciences, Box 3480, University of Arkansas at Monticello, Monticello, AR 71656, mcconnellr @uamont.edu

A UV-VISIBLE SPECTROSCOPIC STUDY OF THE URANYL UO_2^{2+} ION UNDER STRONGLY ACIDIC CONDITIONS: EVIDENCE FOR PROTONATION OF UO_2^{2+}

The linear uranyl UO_2^{2+}, i.e. $[O{=}U{=}O]^{2+}$, ion in highly concentrated sulfuric acid has been characterized by UV-visible spectroscopy. The spectral data have shown that the magnitude of splitting (Δ, cm^{-1}) of the vibronic energy levels in UO_2^{2+} increases linearly as the molar concentration of sulfuric acid increases. This relationship is best represented

by Δ_{2-3} (difference between the highest vibronic peak and its adjacent lower-energy peak) in the equation of Δ_{2-3} (cm^{-1}) = 11.4 [H_2SO_4] +550 (with a correlation coefficient of 0.998). Such a quantitative relationship is unprecedented. The increase in splitting of the vibronic energy levels in UO_2^{2+} by acid corresponds to an increase in the U=O bond strength. The strengthening of the U=O bond by acid is due to formation of hydrogen bond(s), i.e. protonation, on the oxygen atom(s) in UO_2^{2+}. The protonation of UO_2^{2+} is believed to reduce the electron density in the highly negative oxygen atoms and decrease the electrostatic repulsion between the uranium and oxygen valence shell electrons making the U=O bond stronger. Based on the spectroscopic evidence, a model for possible protonation of UO_2^{2+} under strongly acidic conditions has been proposed. The results help us better understand and explore the oxidation-reduction chemistry of the uranyl ion.

Xiaoping Sun† and Clayton Samples*, Department of Natural Science and Mathematics, University of Charleston, 2300 MacCorkle Avenue S. E., Charleston, West Virginia 25304, xiaopingsun@ucwv.edu

HERBAL EXTRACTS FROM *CORTEX MOUTAN* EXHIBIT ANTIOXIDANT POTENTIAL, INHIBIT CELL-INDUCED APOPTOSIS, AND POSSESS ANTIMICROBIAL ACTIVITIES

The therapeutic potential of traditional herbal medicines has started to draw attention from all corners of the world, especially from the Western countries where herbal constituents are being used more as over-the-counter supplements for treating conditions relating to lifestyle habits. Dietary intake of antioxidants is now believed to reduce the risk from several chronic diseases believed to be caused by oxidative stress induced by reactive oxygen species (ROS). Several traditional Chinese herbal medicines were studied and have proven to possess strong scavenging effects against ROS, as well as antimicrobial activities. Results from the present study, using the ferric reducing antioxidant potential (FRAP) assay, has confirmed that *Cortex moutan (*Family*)*, an herb used in Chinese traditional medicine and derived from the bark of the peony, possesses a high antioxidant potential. In addition, *Cortex moutan* aqueous extracts applied to Jurkat cells have been shown to significantly diminish the process of camptothesin-induced apoptosis in the tissue culture environment. In turn, *Cortex moutan* and WuHuang (an herbal combination) extracts were found to exhibit antimicrobial activity against several bacterial species. These results indicate that a chemical(s) in the *Cortex moutan* and WuHuang extracts could be significant in treating diseases which involve the apoptotic process initiated by ROS or microbial infection.

Yang-Hsi Tsai[1]*, Jaime L. Heimbegner[2]*, John J. Beck[2], and James E. Turner[1] †, [1] Departments of Biology Chemistry, Center for Molecular, Cellular, and Biological Chemistry, Virginia Military Institute, Lexington, VA 24450, turnerje@vmi.edu, [2] Department of Chemistry, Sweet Briar College, Sweet Briar, VA 24595

ANALYSIS OF VOLATILE COMPONENTS OF WINES BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

This paper describes the results of an undergraduate research project to determine the volatile components of several red wines using gas chromatography-mass spectrometry (GCMS) with the purge and trap concentration technique. The burgundy and merlot had similar profiles and showed a wider range of the lower-boiling alcohols and esters than the cabernet sauvignon. The presence of lower boiling alcohols and esters relate to the lighter odor and greater "bite" in taste of the burgundy and merlot, compared to cabernet sauvignon which is recognized as being richer in odor and taste, and has much less bite. Selected components of the wines were analyzed by nuclear magnetic resonance (NMR) spectroscopy, including two-dimensional techniques. This work can be adapted to teaching applied chemistry analysis methods in undergraduate chemistry laboratory courses.

Carolyn Simmons* and Massimo D. Bezoari†, School of Sciences – Chemistry Program, Huntingdon College, 1500 East Fairview Ave., Montgomery, AL 36106, bezoari@huntingdon.edu
***Currently at Spring Hill College, Mobile, Alabama.**

ANTHOCYANIN CONTENT IN HYDRANGEA SEPALS

The sepals {blooms} on hydrangea shrubs can be red for plants grown in basic soils and blue for those from acidic soils. The red pigment providing the color in the sepals is the anthocyanin delphinidin-3-glucoside, which can also form a blue complex with Al^{3+} in the sepals. A spectrophotometric procedure was developed to measure the anthocyanin content in hydrangea sepals from 15 commercial cultivars. This content ranged from 0.07 to 0.24 mg anthocyanin per g of fresh sepal, with the magnitude roughly proportional to the qualitative visual intensity of sepal coloration. However, the anthocyanin content was independent of the sepal color, being the same for red or blue sepals of the same cultivar. Bluing mechanisms other than the complexation of the anthocyanin with Al^{3+} may be operational in the hydrangea sepals.

Kathryn E. Pharr*, Kelly M. Mayhew*, and Henry D. Schreiber† Department of Chemistry, Virginia Military Institute, Lexington, VA 24450, HS@VMI.edu