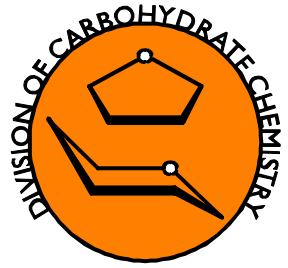
American Chemical Society
Division of Carbohydrate Chemistry



Newsletter

Spring 2010

2009–2010 Division Officers

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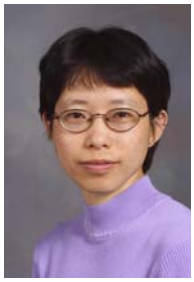

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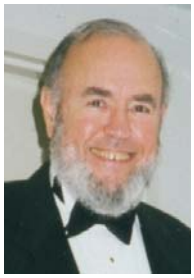

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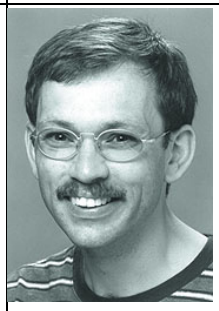

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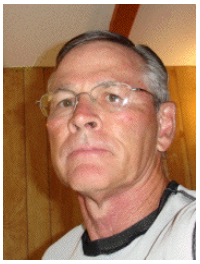
2009–2010 Division Officers



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Future Newsletters

The Carbohydrate Division Newsletter is published twice a year, just before the two annual National ACS meetings. If you have items for inclusion in future newsletters, please send this information to: Xuefei Huang, Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA, Phone: 517-355-9715, ext 329, Fax: 517-353-1793, Email: xuefei@chemistry.msu.edu.

Future Divisional Symposia

If you have ideas for future Carbohydrate Division symposia, these can be directed to Todd L. Lowary, Department of Chemistry, E2-52A Gunning-Lemieux Chemistry Centre, The University of Alberta, Edmonton, AB, T6G 2G2, Canada, Phone: 780-492-1861, Fax: 780-492-7705, Email: tlowary@ualberta.ca.

Solicitation of Nominations for Division Awards

The Division is soliciting nominations for the 2010 Melville L. Wolfrom Award, Horace S. Isbell Award and New Investigator Award, which will be awarded at the Fall 2011 National meeting in Denver.

- ***The Melville L. Wolfrom Award*** acknowledges outstanding service to the Division and to the field of carbohydrate chemistry.
- ***The Horace S. Isbell Award*** acknowledges excellence in and promise of continued quality of contribution to research in carbohydrate chemistry. The winner must be under the age of 41 at the time of the award.
- ***The New Investigator Award*** acknowledges and encourages outstanding contributions to research in carbohydrate chemistry by scientists in their first independent faculty position.

Visit membership.acs.org/C/CARB/awards.html for nomination forms.

NOTE: NOMINATION DEADLINE IS SEPTEMBER 15, 2010

Upcoming National ACS Meeting

240th National Meeting

August 22nd–26th, 2010, Boston, MA

Scheduled Carbohydrate Division Symposia Include:

Petite and Sweet: Glyconanotechnology as a Bridge to New Medicines

Recognition of DNA: Recent Advances

Synthetic Oligosaccharides and Glycoconjugates for Preventing and Combating Disease

Wolfrom-Isbell-New Investigator Award Symposium

General Papers: Computation

General Papers: Glycobiology

General Papers: Polysaccharides

General Papers: Synthetic Chemistry

General Posters

The deadline for Carbohydrate Division abstract submission is March 29th, 11 pm CT, 2010

Other Upcoming Meetings

XXV International Carbohydrate Symposium

August 1–August 6, 2010 – Tokyo, Japan

Visit http://www.bilingualgroup.co.jp/ics2010 for more information.

Program Sponsors

A big "Thank You" to the sponsors of our program.

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239th National Meeting

American Chemical Society

Division of Carbohydrate Chemistry

T. Lowary, *Program Chair*

SUNDAY MORNING

Section A

The Moscone Center
Esplanade Ballroom 310

Symposium in Honor of Ernest L. Eliel

M. Manoharan, *Organizer, Presiding*

8:30 Introductory Remarks.

8:40 1. RNA Interference and chemical modifications: Importance of conformation and stereochemistry. **M. Manoharan**

9:10 2. Origin of prebiotic homochirality on earth. **R. Breslow**

9:40 3. Origins of biological homochirality and asymmetric autocatalysis. **K. Soai**

10:10 4. Stereochemistry of reactions of nucleoside (2-thiono-1,2,3-oxathiaphospholane)s with phosphoric and polyphosphoric acids. **W. J. Stec**

10:40 Intermission.

10:55 5. Reactions of cationic iridium(III) silane complexes with halides, ethers, and carbonyl compounds. **M. Brookhart**, J. Yang, S. Park

11:25 6. Asymmetric organocatalytic reactions. **E. Juaristi**, J. L. Olivares-Romero, J. Vargas-Caporali

11:55 7. Ernest L. Eliel's connection with carbohydrates. **J. I. Seeman**

SUNDAY AFTERNOON

The Moscone Center
Esplanade Ballroom 310

Symposium in Honor of Ernest L. Eliel

M. Manoharan, *Organizer, Presiding*

2:00 8. Considerations of intramolecular hydrogen bonding and conformational preferences of simple molecules of the type X-CH_2-CH_2-Y derived from the use of NMR spectroscopy. **J. D. Roberts**

2:40 9. Enantiopure P-stereogenic triarylphosphines. **K. M. Pietrusiewicz**, K. Dziuba, M. Lubanska, A. Flis, A. Szmigielska

3:10 10. Stereochemical aspects of the tandem iminium cyclization and smiles rearrangement in pyrrol-1-ylpyrimidine systems. J. Xiang, T. Zhu, **X. Bai**

3:40 Intermission.

3:55 11. Promoting illiteracy in epigenetics: Discovery of small molecule MBT domain antagonists. **S. V. Frye**, M. Herold, T. Wigle, B. Janzen, D. Kireev

4:25 12. Investigations of *Mycobacterium tuberculosis* cell wall glycolipids. **C. R. Bertozzi**

4:55 13. Synthesis and evaluation of short antisense oligonucleotides containing 2',4'-(*N*-methoxy)aminomethylene and 2',4'-(*N*-MOE) aminomethylene bridged nucleoside analogs. **T. P. Prakash**, A. Siwkowski, B. Bhat, S. Lee, A. Berdeja, H. J. Gaus, E. E. Swayze

5:15 Concluding Remarks.

MONDAY MORNING

Section A

The Moscone Center
Esplanade Ballroom 310

Sustainability of the Sugar and Sugar-Ethanol Industries

Cosponsored by AGFD, CELL and FUEL
G. Eggleston, *Organizer, Presiding*

8:30 Introductory Remarks.

8:35 14. Major challenges and changes in the European sugar sector. **G. Parkin**, J. M. de Bruijn

9:10 15. Sustainability in the sugar and sugar-ethanol industries: The South African and southern African regions. **B. M. Muir**, P. M. Schorn, C. Kruger, M. Ewig, R. Rhodes, S. Peacock

9:45 16. Technical developments in ethanol production from energy crops. **G. M. Aita**, D. A. Salvi

10:05 17. Cultural practices for the sustainable production of sugarcane for sugar and bioenergy. **R. P.**

Viator, P. White, R. M. Johnson

10:25 Intermission.

10:40 18. “Cracking the Nut”: Integration of enzyme and microbial systems in the depolymerization and utilization of lignocellulose for sustainable production of ethanol and co-products. **S. Shoemaker**

11:05 19. Success and sustainability of the Brazilian sugarcane-fuel ethanol industry. **H. Amorim**, J. M. Borges Gryschek

11:35 20. Analysis of mannitol as a deterioration marker in sugarcane and sugar beet factories. **G. Eggleston**, J. Gober, C. Alexander

Modeling and Experimental Determination of Polysaccharide Structure and Properties

Anselme Payen Award Symposium Honoring Alfred D. French

Sponsored by CELL, Cosponsored by CARB

MONDAY EVENING

Section A

The Moscone Center
Hall D

Sci-Mix

T. Lowary, *Organizer*

8:00 - 10:00

21, 23, 25, 34, 36, 37, 39, 40, 42, 43, 45, 46, 49, 50, 51, 52, 56. See subsequent listings.

MONDAY AFTERNOON

Section A

The Moscone Center
Hall A

General Posters

T. Lowary, *Organizer, Presiding*

12:00 - 2:00

21. Development of ligands for the capture of bacterial toxins. **D. M. Lewallen**, J. Morrison, S. Iyer

22. Structure/activity relations of immunomodulating pectic polysaccharides from Malian medicinal plants. **K. T. Inngjerdingen**, C. S. Nergard, M. Inngjerdingen, D. Diallo, T. Michaelsen, B. S. Paulsen

23. On-resin synthesis of N-linked glycoconjugates and glycopeptides. **R. Chen**, **T. J. Tolbert**

24. New appraoches to stereocontrolled glycosylation. **D. J. Cox**, A. J. Fairbanks

25. Novel chemical biology approaches to modulate cancer heparanome and elucidate their role in cancer. **K. Raman**, K. Balagurunathan

26. Using chemical biology to investigate fungal transglycosidation. **J. Saha**, M. W. Peczuh

27. Acharan sulfate affinity chromatography for one-step purification of human ceruloplasmin. **Y. Park**, I. S. Lee, E. J. Joo, B.-S. Hahn, Y. S. Kim

28. Chondroitin sulfate and heparan sulfate from earthworms *Eisenia andrei*. **Y. Park**, A.-R. Im, J.-S. Sim, Z. Zhang, Z. Liu, R. J. Linhardt, Y. S. Kim

29. Purification and characterization of chondroitin sulfates from marine sources. **Y. Park**, A.-R. Im, J.-S. Sim, B.-S. Hahn, T. Toida, Y. S. Kim

30. Chemoenzymatic synthesis of Neu5Gc derived sialosides. **Y. Chen**, H. Yu, J. Cheng, L. Zhang, L. Ding, X. Chen

30.5. Molecular dynamics simulation of prion peptide: the effect of glycosylation. **H. Kim**, K. Jeong, S. Jung

31. Cloning, expression, and characterization of a recombinant human sialyltransferase ST6GalNAc I. **J. Qu**, Y. Li, H. Yu, X. Chen

32. Interaction of bacterial periplasmic glucans with tobramycin. E. Cho, Y. Kwon, **C. Kwon**, Y. Jeon, B. Lim, S. Jung

33. Solubility enhancement of luteolin by sulfobutylether β-cyclodextrin. Y. Kwon, E. Cho, **C. Kwon**, S. Jung

34. Design and synthesis of sulfotransferase inhibitors of heparan sulfate biosynthetic pathways. **V. Sorna**, T. K. N. Nguyen, D. J. Lee, B. Kuberan

35. Creating glycodendrimers via maltose and an amino tris-core. **R. Blackeye**, K. McReynolds

36. Convergent synthesis of two *N*-acetylglucosamine terminated dendrimers. **M. L. Watterson**, K. McReynolds

37. Fractional extraction and structural characterization of *Forsythia suspensa* hemicelluloses. J. Mao, F. Xu, F. Peng, **R.-C. Sun**

38. Gas phase structures and energetic of 2'-Deoxycyitidine radical cations by DFT study: How acidity of [dC $^{\bullet+}$] changes during deprotonation?. **Z. Aliakbar Tehrani**, A. Abedin, A. Fattahi

39. Solution geometry and long-range coupling in carbohydrate mimetics from glycal dimerization. **A. H. Franz**

40. Synthesis of unlocked nucleic acid derivatives and thermal denaturation studies. **T. B. Jensen**, J. Wengel

41. Modified Xyloglucan used to improve cellulose fibers. **A. Ek**

42. Chemo-enzymatic synthesis of mucin-type glycopeptides using sugar-protective groups and ppGalNAcT-2. **Y. Yoshimura**, T. Matsushita, N. Fujitani, F. Haruhiko, Y. Takegawa, N. Manri, A. Kaneko, T. Sakamoto, X.-D. Gao, H. Hinou, S.-I. Nishimura

43. Dilute solution properties of four natural chitin in NaOH/urea aqueous system. G. Li, **Y. Du**

44. Novel analogs of UNA (Unlocked Nucleic Acid): Synthesis and structural analysis. **N. Langkjær**, J. Wengel

45. Amino acids attached to 2'-amino-LNA: Synthesis of DNA mixmer oligonucleotides with increased duplex stability. **M. W. Johannsen**, L. Crispino, M. C. Wamberg, N. Kalra, J. Wengel

46. Structure-property relations in cellulose sulfates. **N. Normakhamatov**, K. Churkina, A. Turaev, P. Mischnick, I. Mukhamedov

47. B-cell targeting using nanoparticles bearing high affinity CD22 glycan ligand. **G. C. Completo**, W. C. Chen, N. Bovin, J. C. Paulson

48. Double-headed nucleosides in zipper constructs. **C. S. Madsen**, L. J. Nielsen, A. Lauritsen, P. Nielsen

49. Expanding the scope of protecting and leaving groups in chemical sialylations. C. De Meo, **B. N. Harris**, M. J. Stark

50. Synthesis and evaluation of carbohydrate based 1,2,3-lactosyl triazoles and carbohydrate-porphyrin conjugates as inhibitors of galectin-1: Two new classes of potential therapeutics for the treatment of cancer. **S. G. Miller**, **J. E. Tylko**, **C. J. Boisvert**, **T. P. Adams**, **P. F. Garrett**, **R. F. Rothbarth**, **N. L. Snyder**

51. Probing the enzymatic action of heparin degrading enzymes using chemical biology approaches. **P. Babu**, B. Kuberan

52. De novo asymmetric synthesis of mezzettiaside 8. **I. A. Townsend**, M. Li, G. A. O'Doherty

53. RGD-Xylosides inititate glycosaminoglycan biosynthesis. **V. M. Tran**, X. Victor, J. Yockman, K. Balagurunathan

54. Directed evolution of a thermophilic cellulase for biomass hydrolysis. **Z. Chen**, H. Tran, H. C. Chu, M. Hadi, P. Adams, B. Simmons, R. Sapra, K. Sale

55. Synthesis and evaluation of phenolic glycolipid immunomodulators as potential vaccine candidates for mycobacterial infections. **H. Elsaidi**, T. L. Lowary

56. Synthesis and conjugation of α-Gal and α-Rha saccharides for immunization experiments. **A. Pardo**, **R. Ashmus**, J. Vellucci, J. Khamsi, R. A. Maldonaldo, I. C. Almeida, K. Michael

57. One-pot multi-enzyme chemoenzymatic synthesis of LacNAc and its derivatives. **K. Lau**, V. Thon, R. Huang, X. Chen

58. Targeting Sialoadhesin using nanoparticles bearing high-affinity glycan ligands. **C. M. Nycholat**, W.

Chen, C. Rademacher, J. C. Paulson

59. Large-scale enzymatic synthesis and purification of a2-3- and a2-6 linked sialosides. **Z. Khedri**, X. Chen, H. Yu

60. Total synthesis of two new glycan derivatives based on the glycan component of the glycopeptide antibiotic vancomycin. **K. W. Graepel**, **G. B. Hone**, **L. C. Rono**, **G. M. Corneau**, R. H. Seewald, R. V. Myers, K. A. Alser, J. A. Pienkos, **N. L. Snyder**

61. Comparison of the binding affinities of Ricin and RCA_{120} using different glycan displays. **S. S. Mahajan**, S. S. Iyer

62. Functional studies of a viral α2,3-sialyltransferase. **G. Sugiarto**

63. Purification of hemicelluloses in hot water and alkali pre-extractives of mixed hardwoods using organic solvents. H. J. Youn, **H. Shin**, K.-J. Sim, S. Lee, H. L. Lee

64. Solid-phase "one-pot multi-enzyme" combinatorial synthesis of glycopeptides. **H. Malekan**, N. Yao, K. Lam, X. Chen

65. Glycan modification of natural products by chemoenzymatic approaches. **J. Hwang**, V. Thon, K. Lau, Y. Hai, P. G. Wang, X. Chen

66. Molecular cloning and characterization of a novel *H. hepaticus* a1–3 fucosyltransferase. **L. Zhang**, K. Lau, J. Cheng, H. Yu, G. Sugiarto, X. Chen

67. Synthesis of multiple sialic acid-terminated dendrimers with a poly(amidoamine) core for the study of the effect of generation and distance from sugar to core on protein binding affinity. **R. G. Clayton**, K. McReynolds

68. Synthsis of a library of trisaccharides involving regioselective glycosylation of mannose diol acceptor. J. Kalikanda, **B. C. Lainhart**, C. Lu, Z. Li

69. Stimulatory effect of glycoconjugates on nitric oxide and cytokine production by macrophages upon exposure of *B. cereus* spores. **M. H. Lahiani**, L. Soderberg, P. Alusta, O. Tarasenko

70. Quantification and characterization of carbohydrate compositions in microalgal biomass. **Y.-S. Cheng**, J. Labavitch, O.-U.-M. Tanadul, A. Powell, J. VanderGheynst

71. Characterization of a bacterial sialyltransferase Psp2,6ST for the synthesis of sTn Antigens. **L. Ding**, H. Yu, Y. Li, J. Qu, X. Chen

72. Enrichment of highly efficient thermophilic microbial communities active on switchgrass and corn stover in a high-solids environment. **A. P. Reddy**, M. Allgaier, J. M. Gladden, S. Singer, P. Hugenholtz, B. Simmons, T. C. Hazen, J. S. VanderGheynst

Section A

The Moscone Center
Esplanade Ballroom 310

Sustainability of the Sugar and Sugar-Ethanol Industries

G. Eggleston, *Organizer, Presiding*

2:00 73. Sweet sorghum hybrids and industrial processing of sweet sorghum into ethanol. **W. Nelson**

2:20 74. Opportunities and challenges of sweet sorghum as a feedstock for biofuel. **S. Lingle**

2:40 75. Liquid sugars produced in sugar refineries: Advantage of large central units serving the competitive and sustainable needs of the food industry. **F. Rousset**

3:00 76. Value-added products for a sustainable sugar industry. **M. A. Godshall**

3:20 Intermission.

3:35 77. Sugar beet pulp: A sustainable source of carboxy methyl cellulose (CMC) and other polysaccharides. **M. L. Fishman**, H. K. Chau, P. H. Cooke, D. R. Coffin, A. T. Hotchkiss, Jr

3:55 78. Aprroaches to raw sugar quality improvement as a route to sustaining a reliable supply of purified industrial sugar feedstocks. **J. R. Vercellotti**, S. V. Vercellotti, G. Kahn, G. Eggleston

4:15 79. Sustainability of low starch concentrations in sugarcane through short-term optimized amylase processing and long-term breeding strategies. **C. Kimbeng**, M. Zhou, S. Edme, A. Hale, G. Eggleston

4:35 80. Developments in sugarcane agriculture that affect cane and sugar quality. **B. L. Legendre**

Modeling and Experimental Determination of Polysaccharide Structure and Properties

Anselme Payen Award Symposium Honoring Alfred D. French

Sponsored by CELL, Cosponsored by CARB

TUESDAY MORNING

Section A

The Moscone Center
Esplanade Ballroom 310

Young Investigators in Glycoscience

T. Lowary, *Organizer, Presiding*

8:00 Introductory Remarks.

8:05 81. Metabolically-incorporated photocrosslinkers capture glycoconjugate complexes. **J. J. Kohler**, M. R. Bond, C. M. Whitman, S.-H. Yu, P. D. Vu

8:40 82. Nickel-catalyzed stereoselective formation of alpha-2-deoxy-2-amino glycosides. **H. M. Nguyen**

9:15 83. Chemical tools for studying fucosylated glycans. **P. Wu**

9:50 Intermission.

10:05 84. Glycoconjugates: Design, synthesis and evaluation. **S. J. Sucheck**

10:40 85. Chemical approaches to the investigation of protein-membrane binding interactions using synthetic probes. **M. D. Best**, M. D. Smith, M. M. Rowland, D. Gong, H. E. Bostic, E. A. Losey

11:15 86. Carbohydrate based biosensors: Rapid, one step, no wash assay for the detection of lectins and toxins. **S. S. Iyer**

Modeling and Experimental Determination of Polysaccharide Structure and Properties

Anselme Payen Award Symposium Honoring Alfred D. French

Sponsored by CELL, Cosponsored by CARB

TUESDAY AFTERNOON

Section A

The Moscone Center
Esplanade Ballroom 310

Young Investigators in Glycoscience

T. Lowary, *Organizer, Presiding*

1:45 87. Chemoenzymatic synthesis of N-linked glycoconjugates and their application to studies of the function of N-linked glycosylation. **T. J. Tolbert**

2:20 88. Entirely carbohydrate-based cancer vaccine constructs elicit selective cellular immunity. **P. R. Andreana**

2:55 89. Biointerfacial engineering and the carbohydrate microarray. **D. M. Ratner**

3:30 Intermission.

3:45 90. Defining roles on N-Glycans in endoplasmic reticulum-mediated quality control . E. Quan Toyama, E. H. Rodriguez, J. A. Read, J. S. Weissman, **D. Galonic Fujimori**

4:20 91. Insights into the structure and specificity of the mammalian neuraminidase 3 (Neu3) through site directed mutagenesis and kinetic studies. **C. W. Cairo**

4:55 92. Novel glycosylating agents inspired by Fraser-Reid and applications thereof. **R. B. Andrade**

Modeling and Experimental Determination of Polysaccharide Structure and Properties

Anselme Payen Award Symposium Honoring Alfred D. French

Sponsored by CELL, Cosponsored by CARB

WEDNESDAY MORNING

Section A

The Moscone Center
Esplanade Ballroom 310

General Papers

Glycobiology

T. Lowary, *Organizer*
X. Chen, *Presiding*

8:00 93. Metabolic profiling of *Helicobacter pylori* glycosylation. **D. H. Dube**, M. B. Koenigs, E. A. Richardson

8:20 94. Boronolectins for specific sensing of free sialic acid. **S. M. Levonis**, M. J. Kiefel, T. A. Houston

8:40 95. Investigating carbohydrate-carbohydrate interactions using fluorescent silica nanoparticles. **J. Zhao**, A. Basu

9:00 96. Structural, kinetic and mutational insights along the reaction coordinate of human UDP-glucose dehydrogenase. **S. Egger**, B. Nidetzky, A. Chaikuad, K. L. Kavanagh, U. Oppermann

9:20 97. Multiwell hydrogel saccharide sensor arrays. **B. Vilozny**, R. A. Wessling, A. Schiller, B. Singaram

9:40 98. Novel strategy for neuraminidase inhibitors using mechanism-based probe. **H. Hinou**, R. Miyoshi, Y. Takasu, H. Kai, M. Kurogochi, X.-D. Gao, S.-I. Nishimura

10:00 99. Neuraminidase substrate specificity studies for influenza viruses using chemoenzymatically synthesized sialosides. **X. Chen**, Y. Li, C. Cardona, N. Baumgarth, H. Cao, H. A. Chokhawala, H. Yu

10:20 Intermission.

10:35 100. Secret life of sugars: Using heteronuclear NMR to unveil molecular motion in carbohydrate TB-antigens. S. Vivekanandan, C. Rademacher, T. L. Lowary, **D. I. Freedberg**

10:55 101. Synthetic proteoglycan mimetics. **V. M. Tran**, V. Sorna, L. Duraikkannu, K. Balagurunathan

11:15 102. Fragmentations and rearrangements in the carbohydrate moiety of esperamycins: A possible mechanism of auto-resistance to natural enediynes antibiotics through conformational control?. **I. V. Alabugin**, A. Baroudi

11:35 103. Development of SL dye displacement assays and exploration of their competitive binding properties. **M. Harrell**

11:55 104. Bioprocess for the conversion of carbohydrates into bioisoprene™. **J. McAuliffe**, G. Whited, M. Cervin, K. Sanford, F. Feher, D. Benko

12:15 105. Stable isosteres of thio sugar templates as the new targets for galectin-3 inhibitors. **Z. J. Witczak**, N. Nguyen

WEDNESDAY AFTERNOON

Section A

The Moscone Center
Esplanade Ballroom 310

General Papers

Polysaccharides and Computation

T. Lowary, *Organizer*
D. Freedberg, *Presiding*

1:00 106. Preparation and physical properties of starch stearates of low to high degree of substitution. **R. L. Shogren**, A. Biswas, J. L. Willett

1:20 107. Study cellulase-cellulose interaction using FRET. **L. Wang**, Y. Wang, A. Ragauskas

1:40 108. Indicators of Maillard polymer formation in commercial moist snuff products. **J. Lauterbach**, D. A. Grimm

2:00 109. Interaction of cellulase enzymes with amorphous and crystalline cellulose. **M. Kent**, G. Cheng, S. Datta, J. Park, E. Kim, D. Tullman-Ercek, C. Halbert, J. Browning, M. Jablin, J. Majewski, R. Sapra

2:20 110. Enzymatic modification and characterization of pectin nanostructure. **R. Cameron**, G. A. Luzio, B. J. Savary, P. Vasu, M. A. K. Williams

2:40 Intermission.

2:55 111. Sugar, salt and sugar, salt-water complexes: Structure and dynamics. **M. Pincu**, B. Brauer, B. R. Gerber, V. Buch

3:15 112. Viscous dietary fibers as part of a healthy diet for the prevention and control of coronary heart disease and diabetes. **C. W. C. Kendall**

3:35 113. Towards the identification of ionic liquids that stabilize cellulases for sachharification of cellulosic biomass. **S. Datta**, K. Tran, B. M. Holmes, K. L. Sale, R. Sapra, H. W. Blanch, B. A. Simmons

3:55 114. Study on the chiral separation of some flavonoids with rhizobial oligosaccharides. **C. Kwon**, S. Jung

THURSDAY MORNING

The Moscone Center
Esplanade Ballroom 310

General Papers

Synthetic Chemistry

T. Lowary, *Organizer*
N. Snyder, *Presiding*

8:00 115. Effort towards the development of synthetic carbohydrate-based vaccine. **Y. Wang**, P. Wang

8:20 116. Glycosylation using alkynyl donors. **S. K. Mamidyala***, M. G. Finn

8:40 117. Synthesis and characterization of polyesters derived from linear sugar alcohols and citric acid. **D. G. Barrett**, M. N. Yousaf

9:00 118. Synthesis and metal-catalyzed decomposition of furanose-derived diazoesters. **P. Norris**, I. A. Sacui, A. M. Malich, J. L. Patton, C. A. Hartranft, M. Zeller

9:20 119. Nucleosides with 1,4-dioxane as sugar moiety. **A. S. Madsen**, J. Wengel

9:40 Intermission.

9:55 120. Synthesis of a “clickable” GPI anchor. **B. M. Swarts**, Z. Guo

10:15 121. Synthesis of carbohydrate-porphyrins conjugates via palladium-catalyzed cross-coupling approach. **N. L. Snyder**, P. F. Garrett, T. P. Adams, K. B. Fields, X. P. Zhang

10:35 122. Carbohydrate *C*-glycoside ketones: Introducing ketone chemistry into locked-ring aldose sugars. **C. A. Carpenter**, N. P. J. Price, J. A. Kenar

10:55 123. Kinetic study of oxidation of Glucose by N-bromophthalimide in the presence of ruthenium(III)chloride. **A. K. Singh**, N. Sachdev, Y. R. Katre

11:15 124. Study of Hantzsch synthesis reaction in the preparation of a novel dihydropyridine C-glycosylated compound. **S. Sedaghat**, E. Alipour, S. Majdpour

CARB 1

RNA Interference and chemical modifications: Importance of conformation and stereochemistry

M. Manoharan, mmanoharan@alnylam.com. Department of Drug Discovery, Alnylam Pharmaceuticals, Cambridge, MA, United States

A critical requirement for achieving safe and efficacious RNAi therapeutics is introduction of “drug-like” properties, such as stability, tissue bioavailability, cellular delivery, and target specificity, into synthetic siRNAs. Recently, we developed chemical modifications to improve the pharmacokinetic and pharmacodynamic properties of siRNA duplexes. The effects of particular modifications on siRNA properties and their biological activity are explained based on stereochemical, stereoelectronic, and conformational features of the chemically modified RNA nucleotides.

* This presentation is dedicated to the memory of Professor Ernest L. Eliel and his scientific contributions in the fields of stereochemistry, conformational analysis, and organic synthesis.

CARB 2

Origin of prebiotic homochirality on earth

R. Breslow, rb33@columbia.edu. Chemistry, Columbia University, New York, NY, United States

Ernest Eliel was a true pioneer in chemistry, and a major figure in the ACS and in world chemistry. In the spirit of his interest in chirality, I will discuss our work on the origin of homochirality of amino acids and sugars on earth. The story starts with neutron stars, and progresses through carbonaceous chondritic meteorites, decarboxylative transamination, and amplification of solution homochiralities.

CARB 3

Origins of biological homochirality and asymmetric autocatalysis

K. Soai, soai@rs.kagu.tus.ac.jp. Department of Applied Chemistry, Tokyo University of Science, Kagurazaka, Shinjuku-ku, Tokyo, Japan

The origin of biological homochirality of compounds such as D-sugars and L-amino acids has been a puzzle. The enantiomeric excess (ee) induced by previously proposed mechanisms, like effects of circularly polarized light, have been very low. We describe asymmetric autocatalysis with amplification of enantiomeric excess using pyrimidyl alkanol. When pyrimidyl alkanol with very low ee was employed as an asymmetric autocatalyst, the enantioselective addition of diisopropylzinc (*i*-Pr_2Zn) to pyrimidin-5-carbaldehyde afforded

pyrimidyl alkanol with significantly enhanced ee. Use of ^{13}C and ^{2}H substitution were also found to act as chiral triggers for asymmetric autocatalysis. Chiral crystals formed from achiral organic compounds also served as chiral initiators.

CARB 4

Stereochemistry of reactions of nucleoside (2-thiono-1,2,3-oxathiaphospholane)s with phosphoric and polyphosphoric acids

W. J. Stec, wjstec@bio.cbmm.lodz.pl. Department of Bioorganic Chemistry, Centre of Molecular & Macromolecular Studies, Poland

Nucleoside 3'-O-(2-thio-1.3.2-oxathiaphospholane)s (1) were demonstrated as convenient substrates for stereocontrolled automated solid phase synthesis of P-chiral oligo(nucleoside phosphorothioate)s of predetermined sense of P-chirality at each internucleotide phosphorothioate linkage. Recent attempts of separation of nucleoside 5'-O- (2-thio-1.3.2-oxathiaphospholane)s (2) into P-diastereomeric species appeared successful and allowed for the synthesis of nucleoside 5'-O-á-thiodi- and -polyphosphates as the results of OTP-ring opening condensation with dehydrated phosphorus oxy-acids . Surprisingly, reaction of 2 with PPi occurs with P-epimerization providing diastereomeric mixture of corresponding NTPáS, while similar reactions with methylene-bis-phosphonic acid is fully stereospecific. Most intriguing results were obtained during studies on reactions of 2 with O,O-dialkyl H-phosphonates providing P-diastereomers of nucleoside 5'-O-á-thiohypophosphates (3), so far undescibed in the literature analogues of nucleoside 5'-O-diphosphates (4). Their chemical properties and avidity towards selected enzymes involved in metabolism of 4 will be presented .

CARB 5

Reactions of cationic iridium(III) silane complexes with halides, ethers, and carbonyl compounds

M. Brookhart, MBrookhart@unc.edu, J. Yang, jiany@email.unc.edu, and S. Park, sehoonp@email.unc.edu. Department of Chemisty, University of North Carolina, Chapel Hill, Chapel Hill, NC, United States

The cationic iridium(III) pincer complex, $(PCP)Ir(H)^{+}$ binds silanes in an eta-1 fashion to yield complexes of the type $(PCP)Ir(H)(HSiR_3)^{+}$,**1**. The silyl unit is rendered highly electrophilic and is readily transferred to organic functional groups such as halides, ethers and carbonyl compounds. The remaining neutral $(PCP)Ir(H)_2$ is a hydride reducing agent which reacts with the silylated functional group, and thus **1** serves as an efficient catalyst for reduction of R-X and R-O bonds as well as for hydrosilation of carbonyl compounds. The synthetic and mechanistic details of these reactions will be described. In addition, under certain reaction conditions, **1** serves as a precursor to a catalyst which is able to rapidly

scramble alkyl and aryl groups among alkyl and aryl silanes. Application of this process in synthesizing polymers will be presented.

CARB 6

Asymmetric organocatalytic reactions

E. Juaristi, juaristi@relaq.mx, J. L. Olivares-Romero, and J. Vargas-Caporali. Department of Chemistry, Instituto Politecnico Nacional, Mexico, DF, 07000, Mexico

Recently, we described the preparation of novel chiral diamine (S)-diphenyl-(pyrrolidin-2-yl)-methyl amine, (S)-1 [Olivares-Romero, J.L.; Juaristi, E. Tetrahedron 2008, 64, 9992-9998] from (S)-proline. In this presentation we will disclose application of (S)-1 in asymmetric organocatalytic reactions.

CARB 7

Ernest L. Eliel's connection with carbohydrates

J. I. Seeman, jiseeman@yahoo.com. Department of Chemistry, University of Richmond, Richmond, VA, United States

Ernest Eliel was not a carbohydrate chemist. But during the course of his work on stereochemistry and conformational analysis, he helped advance the field of carbohydrate chemistry. This talk will review those conbtributions.

CARB 8

Considerations of intramolecular hydrogen bonding and conformational preferences of simple molecules of the type X-CH_2-CH_2-Y derived from the use of NMR spectroscopy

J. D. Roberts, robertsj@caltech.edu. Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, United States

Ernest Eliel was a pioneer in conformational analysis with a very substantial contributions to understanding the factors which control the conformations of carbohydrates through applications of NMR spectroscopy. Recognition that different dihedral angles of rotation should be possible around the central C-C bonds of compounds, such as X-CH_2-CH_2-Y, was made clear by Bischoff ~;120 years ago, but it was not until much later that particular discrete gauche and trans arrangements were characterized is being more energetically stable with respective dihedral angles of about 60º and 180º, although normally interconverted so extremely rapidly that our experimental knowledge of the individual conformer properties are derived from averages usefully studied by NMR. Intramolecular hydrogen bonding leading to preferences of gauche conformations for monoanions of 1,4- dicarboxylic acids were extensively

investigated by Eberson(1963), McCoy (1967) and Kolthoff (1976). While this looks quite simple in terms of ratios of K_1/K_2 for the acids, interesting complexities and uncertainties will be discussed regarding whether the same reasoning can be applied to intramolecular hydrogen bonding of O-H--O with X = carboxylate, Y = noncarboxylate, neither X or Y being carboxyl or carboxylate; O-H--N, with or without carboxyl; and N-H--N with nitrogens of different characters.

CARB 9

Enantiopure P-stereogenic triarylphosphines

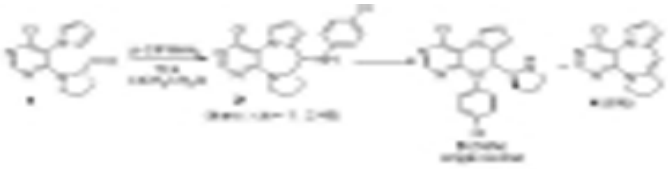
K. M. Pietrusiewicz, mstan@hermes.umcs.lublin.pl, K. Dziuba, M. Lubanska, A. Flis, and A. Szmigielska. Department of Organic Chemistry, Maria Curie-Sklodowska University, Gliniana 33, 20-614 Lublin, Poland

Chiral, non-racemic phosphorus compounds are ubiquitous in catalytic asymmetric synthesis, both as ligands in metal-based processes and as organocatalysts in their own right. Although a large number of such ligands have been tested, the great majority have their chirality located on the carbon backbone (C-stereogenic) rather than on the phosphorus atom (P-stereogenic). Although P-stereogenic ligands have proven to be effective, relatively few have been studied because they are difficult to synthesize. This is especially true for P-stereogenic triarylphosphines, which¾despite of their close relationship to the commonly used parent triphenylphosphine¾are not yet practically accessible in enantiopure forms. We now describe synthesis of a series of enantiopure P-stereogenic triarylphosphines via an efficient two-step procedure involving an oxidative resolution and a novel reductive process. The scope and the stereochemical aspects of the syntheses will be discussed.

CARB 10

Stereochemical aspects of the tandem iminium cyclization and smiles rearrangement in pyrrol-1-ylpyrimidine systems

J. Xiang, T. Zhu, and **X. Bai**, xbai@jlu.edu.cn. The College of Chemistry and The School of Pharmaceutical Sciences, Jilin University, The Center for Combinatorial Chemistry and Drug Discovery, 75 Haiwai Street, Changchun, China



We previously reported a novel tandem reaction consisting of iminium cyclization and Smiles rearrangement in pyrrol-1-ylpyrimidine[1] and pyrrol-1-ylpyridine[2]

systems. When substrate **1** with a stereo center was subjected to the similar process, ring closure intermediate **2** was obtained as an isomeric mixture, which led to rearranged product **3** as a single isomer and a small amount of aniline elimination product **4** after rearrangement. Further investigation revealed that only the *cis* isomer of intermediate **2** underwent Smiles rearrangement and the existence of equilibrium between the two isomers of **2**. The details of these studies and mechanistic hypothesis will be discussed in this presentation.

CARB 11

Promoting illiteracy in epigenetics: Discovery of small molecule MBT domain antagonists

S. V. Frye, svfrye@email.unc.edu, M. Herold, T. Wigle, B. Janzen, and D. Kireev. Department of Medicinal Chemistry and Natural Products, UNC Eshelman School of Pharmacy, Chapel Hill, NC, United States

The malignant brain tumor (MBT) repeat is a structural domain of ca. 100 amino acids and occurs in at least 9 human proteins which recognize mono- and dimethyl-lysine modifications of histones. MBT domains therefore ‘read’ the histone code. There are no known small molecule binders of MBT domains. This presentation will summarize our progress in assay development and the design and discovery of potent antagonists of methyl-lysine recognition by MBT domain containing proteins. The resulting chemical probes will permit exploration of the biological consequences of blocking this recognition in cell-based and in vivo models with relevance to normal and disease biology. Current understanding of the biological consequences of MBT domain antagonism would suggest that antagonists may be useful in de-differentiation, re-expression of silenced genes and cellular reprogramming.

CARB 12

Investigations of *Mycobacterium tuberculosis* cell wall glycolipids

C. R. Bertozzi, crb@berkeley.edu. Departments of Chemistry and Molecular and Cell Biology, University of California, Berkeley, United States

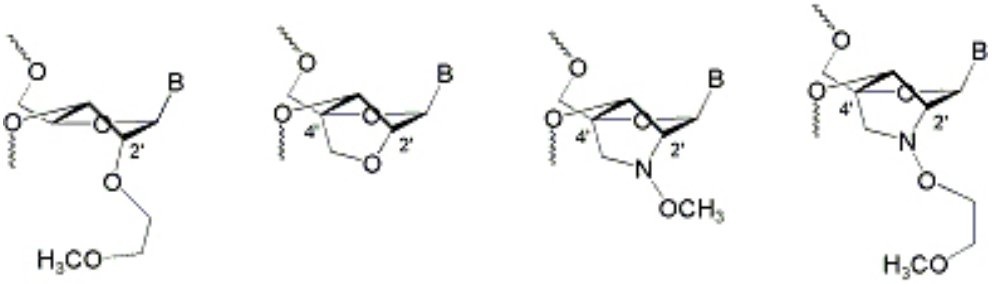
The *Mycobacterium tuberculosis* (Mtb) has a notoriously impenetrable cell wall that comprises a variety of exotic lipids, glycans, and glycoconjugates. We have been studying the biosynthetic machinery underlying sulfolipid-1, a tetraacylated trehalose-2-sulfate glycolipid that is unique to pathogenic forms of Mtb and whose abundance correlates with virulence of clinical isolates. This presentation will focus on our present understanding of the biosynthetic machinery underlying sulfolipid-1 and its functional significance with respect to host-pathogen interactions.

CARB 13

Synthesis and evaluation of short antisense oligonucleotides containing 2',4'-(*N*-methoxy)aminomethylene and 2',4'-(*N*-MOE) aminomethylene bridged nucleoside analogs

T. P. Prakash, tprakash@isisph.com, A. Siwkowski, asiwkowski@isisph.com, B. Bhat, bbhat@isisph.com, S. Lee, slee@isisph.com, A. Berdeja, aberdeja@isisph.com, H. J. Gaus, hgaus@isisph.com, and E. E. Swayze, eswayze@isisph.com. Medicinal Chemistry, Isis Pharmaceuticals, Carlsbad, California, United States

In order to improve upon antisense oligonucleotide (ASO) drugs, many different modifications to the core nucleoside monomer unit of the ASO have been evaluated. The most studied of these second generation antisense designs are MOE (**1**) and LNA (**2**) gapmer oligonucleotides. Currently there are multiple drugs employing various chemical designs in active development. We have synthesized 2',4'-(*N*-methoxy)aminomethylene (**3**) and 2',4'-(*N*-MOE)aminomethylene (**4**) bridged nucleoside analogs to combine the structural features of MOE and LNA. Biological evaluation of gapmer antisense oligonucleotides (ASO, 2-10-2 design) containing nucleoside analogs **3** and **4** was also carried out. These modifications provided increased thermal stability and nuclease resistance to oligonucleotides relative to MOE modification (**1**). Details from this study will be presented.



1 **2** **3** **4**

CARB 14

Major challenges and changes in the European sugar sector

G. Parkin, gparkin@britishsugar.co.uk, and J. M. de Bruijn. Research and development, British Sugar plc, Peterborough, United Kingdom

Over the last five years, a number of changes have taken place within the European Sugar Sector mostly driven by the reform of the European Sugar Regime. This Regime had been in place since 1968 and was designed to "maintain employment and standards of living for EU growers of beet sugar" by making the continent self-sufficient in sugar production. This presentation highlights the changes that have taken place to the Regime and how the Sugar Industry within Europe has altered to meet the new requirements. Sugar Beet Growers and Processors are examining alternative strategies, resulting in new

R&D initiatives, to ensure the stability and continuation of the industry in the future. These have included Biofuel production, greater power generation involving CHP plants, alternative fuel sources, product diversification, and refining of imported cane sugar. These initiatives will illustrate what a European sugar producer could be making and using in the near future.

CARB 15

Sustainability in the sugar and sugar-ethanol industries: The South African and southern African regions

B. M. Muir[1], bmuir@smri.org, P. M. Schorn[2], C. Kruger[3], M. Ewig[4], R. Rhodes[4], and S. Peacock[2]. [1]Sugar Milling Research Institute, Durban, Kwazulu Natal, South Africa, [2]Tongaat-Hulett Ltd (TEG), Glenashley, Kwazulu Natal, South Africa, [3]Sezela Mill, Illovo Sugar Ltd, Sezela, KwaZulu Natal, South Africa, [4]South African Sugarcane Research Institute, Mount Edgecombe, KwaZulu Natal, South Africa

The South African (SA) sugar industry is well established with strong infrastructure and support systems. The 14 sugarcane factories operate in the sub-tropical eastern and north-eastern regions; two research institutes are dedicated to the sustainability of the land, the manufacturing industry, and its people. While sugarcane cultivation is slowly on the decrease, SA sugar companies are rapidly expanding into southern and central Africa, already regenerating and reinforcing sugar establishments all the way to Kilombero in Tanzania, just north of the equator. Margins in the SA industry have declined and co-products such as ethanol, electricity and chemicals are attracting renewed attention. An oversupply of ethanol from oil-refineries and coal-to-fuel operations forced ethanol-from-molasses to maintain a low profile as potable bio-ethanol that is used mostly in the local beverage sector. However, the availability of fertile land, excellent climatic conditions, low cost labor and preferential international markets in other African countries are rapidly stimulating investment.

CARB 16

Technical developments in ethanol production from energy crops

G. M. Aita, gaita@agcenter.lsu.edu, and D. A. Salvi. Audubon Sugar Institute, St. Gabriel, LA, United States

The concept of energy crops, a renewable source of energy, has been around for decades. It was not until the discovery of fossil fuels, a non-renewable source of energy, in 1859 that agricultural and forestry crops and their residues stopped being the primary source of energy. Since then, fossil fuels have become the major source of energy generation and transportation fuels supplying 85% of the United States total energy demand. According to the National Renewable Energy Laboratory ethanol produced from energy crops could displace as much as 25%

of gasoline currently consumed in the United States. Ethanol produced from energy crops mitigates many of the limiting factors associated with corn-ethanol or sugarcane-ethanol production such as competition with the food supply, availability of feedstocks and transport costs. Nevertheless, the use of energy crops for ethanol production is still in the developmental stage. Available processing technologies suffer from relatively low sugar yields, severe reaction conditions, large capital investment, high processing costs and great investment risks.

CARB 17

Cultural practices for the sustainable production of sugarcane for sugar and bioenergy

R. P. Viator, ryan.viator@ars.usda.gov, P. White, and R. M. Johnson. USDA-ARS-Sugarcane Research Unit, Houma, LA, United States

Sugarcane (*Saccharum* spp.), while traditionally grown for sugar production, can also be grown as a biomass crop for biofuels production. Crop management practices will change depending on if sugarcane is grown for sugar or biofuels and will be influenced by climatic regions where the crop is grown. For example, artificial ripening may not be needed if cane is grown strictly for its fiber as an energy source. Degree of cultivation, dates of planting, date of harvesting, residue management, ratoon management, and land-use allocation may also need to be adjusted depending on the end-use product. If the entire plant including extraneous matter is harvested, harvesting logistics, soil fertility, soil health, soil compaction, and fertilizer application may be influenced. Producing sugarcane in climatic zones where cane is not traditionally grown for sugar will entail germplasm screening, water conservation, and crop rotation. Sugarcane cultural practices differ greatly from annual crops, such as corn and soybeans, because of its perennial crop cycle. For example sugarcane harvest date affects carbohydrate partitioning to underground buds. Any stress that affects these buds has the potential to reduce yields throughout the remaining crop cycle. Yield optimization must always take into account effects on the subsequent ratoon crops. We will discuss the similarities and differences in sugarcane and energy cane management and will highlight the need for managing this crop as a perennial and not as an annual crop.

CARB 18

“Cracking the Nut”: Integration of enzyme and microbial systems in the depolymerization and utilization of lignocellulose for sustainable production of ethanol and co-products

S. Shoemaker, spshoemaker@ucdavis.edu. California Institute of Food and Agricultural Research, University of California at Davis, Davis, CA, United States

This presentation reviews the enabling science that has advanced our understanding and use of lignocellulose as a feedstock for industrial production of ethanol and co-products. The phenotypic observations and experimental results of countless studies in past 40 years can assist in the rational design and interpretation of experiments using the tools of modern chemical biology, its “omic” approaches, multivariant analyses, high throughput screening and bioinformatics. A perspective of the past in the context of today and tomorrow, toward fully realizing cellulase-cellulose bioconversion in simultaneous-saccharification fermentation (SSF) systems is provided. The presentation is dedicated to the life and memory of Dr. Raphael Katzen.

CARB 19

Success and sustainability of the Brazilian sugarcane-fuel ethanol industry

H. Amorim[1], amorim@fermentec.com.br, and J. M. Borges Gryschek[2].
[1]Fermentec Ltda, Piracicaba, Sao Paulo, Brazil, [2]Brasmetano, Piracicaba, Sao Paulo, Brazil

Sustainability is a concept that basically integrates economical, environmental, and social aspects, that has frequently been applied to human activitivities in a changing world. Even for natural products such as sugar or renewable energy products such as bioethanol from sugar cane, a life cycle analysis can show how intensive and effective the processes are for their production. For this analysis, it is necessary to evaluate all the demands and relationships amongst the cycle components, e.g., soil occupation; water consumption and conservation; fertilizers, chemicals to control pests, and other sub-products applied as a fertilizer source, and residue destination. In the next step of processing the raw material, many others aspects have to be considered, e.g., type and quantity of energy and water consumption, characterization of many accessory products such as lubricants, antibiotics, detergents, and additives; liquid, solid, and gaseous emissions and their control and destinations; and the end-use of these products by consumers. When considering natural and renewable products, more than a hundred aspects may be considered if these products are to be environmental friendly, safe, potential solutions to reducing and controlling global warming, and sustainable in the market place.

CARB 20

Analysis of mannitol as a deterioration marker in sugarcane and sugar beet factories

G. Eggleston, gillian.eggleston@ars.usda.gov, J. Gober, and C. Alexander.
Commodity Utilization, USDA-ARS-SRRC, New Orleans, LA, United States

Better control of sugarcane and sugar beet deterioration will contribute to the sustainability of the sugar industry. Mannitol, formed mainly by *Leuconostoc mesenteroides* bacteria, is a sensitive deterioration marker of both sugarcane

and sugarbeet deterioration that can predict processing problems. An enzymatic factory method that is rapid, simple, accurate, and inexpensive is now available to measure mannitol in consignment juices at factories, and recently precision was improved to measure low mannitol concentrations in juices and other sugar products as well. A strong polynomial relationship (R^2=0.912) existed between mannitol and haze dextran (a-(1→6)-a-D-glucan) in sugarcane juices obtained across a 3-month processing season at a sugarcane factory. Mannitol concentrations are typically higher than concentrations of antibody dextran, which indicates (i) the usefulness and sensitivity of mannitol to predict sugarcane deterioration from *Leuconostoc* and other bacteria, and (ii) the underestimation by sugar industry personnel of the relatively large amounts of mannitol present in deteriorated sugarcane. Greater than ~;250 ppm/Brix of mannitol in sugarcane juice predicts downstream processing problems, but this threshold value may vary from region to region. The increasing awareness of how mannitol detrimentally effects processing, e.g., crystallization, is fully discussed.

CARB 21

Development of ligands for the capture of bacterial toxins

D. M. Lewallen, lewalldm@mail.uc.edu, J. Morrison, morrjt@gmail.com, and S. Iyer, iyersi@mail.uc.edu. Department of Chemistry, University of Cincinnati, Cincinnati, OH, United States

In order to infect a host, some microbial pathogens first use cell surface carbohydrates for recognition. This specific binding event is dependent on the composition, valency and topology of the carbohydrate. These carbohydrates can serve as a valuable tool to study cell-pathogen interactions because they are highly stable and are chemically well defined. Development of synthetic carbohydrates that mimic and bind with the same specificity and affinity as the natural carbohydrates could be used for *in vitro* detection and identification of the microbial pathogens. We have developed novel, synthetic carbohydrates that can bind microbial pathogens with specificity and high affinity.

CARB 22

Structure/activity relations of immunomodulating pectic polysaccharides from Malian medicinal plants

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Infectious diseases, gastric ulcer, wounds of different origin and fungal diseases are common ailments in Mali and contributing to the high degree of mortality in the country. An effective immune response is necessary to recover from these diseases, and it is therefore of interest to search for immunomodulating components in medicinal plants. Approximately 80% of the population in Mali rely on traditional medicine for their primary healthcare. We have compared immunomodulating activities of pectic polymer fractions obtained from different Malian medicinal plants, and it has became clear that the rhamnogalacturonan backbone of pectins with side chains of arabinogalactans is important for the expression of the bioactivities. This has been observed for both the complement fixing activity, the induction of B cell proliferation, and the intestinal immune system modulating activity. Proposed structures of pectic polymers will be presented.

CARB 23

On-resin synthesis of N-linked glycoconjugates and glycopeptides

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N-linked glycosylation plays a wide range of essential roles in nature[1], and is involved in such processes as signal transduction, cell-cell recognition, cell growth and immune responses. Therefore, it is important to have the access to N-linked oligosaccharides attached glycoconjugates and glycopeptides for various biochemical and structural studies to understand the effects of the N-linked glycosylation. Even though several strategies have been developed, it is still a challenge to synthesize glycoconjugates and glycopeptides containing large N-linked oligosaccharides.[2] By combining the advantages of solid phase synthesis with a convergent glycosylamine coupling strategy, we have utilized on-resin Lansbury aspartylation to synthesize glycoconjugates and glycopeptides which contain large N-linked oligosaccharides. This on-resin approach not only provides potent glycosylation reactions, but also allows high-yield recovery of the unreacted oligosaccharides, which are very valuablematerials. This approach has been applied to produce several useful glycoconjugates with different types of labeling that can be utilized to explore protein–carbohydrate interactions. Also, this strategy has been utilized to synthesize biologically active N-linked glycopeptides, such as the C34 HIV entry inhibitor.

(1) Dove, A. *Nature Biotech.* **2001**, *19*, 913-917.

(2) Kan, C.; Trzupek, J. D.; Wu, B.; Wan, Q.; Chen, G.; Tan, Z.; Yuan, Y.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2009**.

CARB 24

New appraoches to stereocontrolled glycosylation

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The control of anomeric stereochemistry during glycosylation remains a principal challenge in oligosaccharide synthesis. In particular, although 1,2-*trans* glycosidic linkages can usually be synthesised with high levels of stereocontrol by taking advantage of the classical neighbouring group participation (NGP) of 2-*O*-acyl protected glycosyl donors, the stereocontrolled synthesis of 1,2-*cis* glycosidic linkages is considerably more difficult. The use of new types of NGP to enforce the formation of 1,2-*cis* glycosidic linkages represents an attractive proposition. In our initial research a series of glycosyl donors possessing a 2-*O*-(thiophen-2-yl)methyl protecting group at the 2-position were synthesized. Reaction of a trichloroacetimidate donor with a range of glycosyl acceptors showed high selectivity for the 1,2-*cis* glycoside.1 Investigation into the use of other novel types of NGP is ongoing.

1 Cox, D. J.; Fairbanks, A. J.; *Tetrahedron Asymmetry* **2009**, *20*, 773-780

CARB 25

Novel chemical biology approaches to modulate cancer heparanome and elucidate their role in cancer

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Heparan and Chondroitin Sulfate proteoglycans modulate a myriad of biological processes in the tumor environment including growth factor binding, cell-cell communication, invasion, coagulation, and angiogenesis. Proteoglycans consist of a core protein attached to one or several glycosaminoglycan (GAG) side chains. Our lab has been developing chemical biology approaches to study the role of various GAG chains including heparan sulfate, dermatan sulfate, and chondroitin sulfate chains in tumor pathogenicity by modulating their glycome. These studies have revealed the role of tumor specific proteoglycans in various steps of cancer progression.

CARB 26

Using chemical biology to investigate fungal transglycosidation

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Dramatic increases in resistance to currently administered antifungal treatments require development of new therapeutics. For many of these pathogens, a crucial step in there life cycle is the biosynthesis of the cell wall. Targeting the appropriate enzymes, which are responsible for biosynthesis of the cell walls, should provide new targets for antifungal therapy. In our current research program, we aimed at development of new potential antifungal agents by two different approaches. One is aimed at identifying the protein or proteins responsible for transglycosidation of 1,3-β-D-glucan with chitin in the cell walls of *C.albicans*. A synthetic model of 1,3-β-D-glucan, labeled at the reducing end and a chitin pentaose labeled at the non-reducing end will be used for the study and the syntheses of these molecules are underway. The other approach is based on the inhibition of the chitin biosynthesis using seven membered 2-aminosugar analogues. Use of different 2-aminosugar analogues targeting chain termination of the chitin showed promises to rational designing of antifungal agents. With this motivation we have successfully synthesized different 2-aminoseptanosides derivatives and a general route to prepare more complex derivatives is currently underway.

CARB 27

Acharan sulfate affinity chromatography for one-step purification of human ceruloplasmin

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Acharan sulfate (AS) was first isolated and characterized from the body of the African giant snail *Achatina fulica* Bowdich. It has the repeating disaccharide unit of -4)-D-GlcNpAc (1[strike]-[/strike]4)-L-IdoAp2S(1- that is a novel structure, related but significantly different from heparin and heparan sulfate (GlcNpAc, N-acetylglucosamine; IdoAp2S, 2-O-sulfoiduronic acid). It has been reported to have important biological activities including anti-angiogenic, anti-tumor activities and anti-thrombotic activities *in vivo*. Human ceruloplasmin, a copper binding α2-glycoprotein, was purified by a single-step procedure using acharan sulfate affinity chromatography. Acharan sulfate was immobilized to amine-functionalized agarose matrix through carboxylic acids. Ceruloplasmin in human plasma was obtained from 0.4 M NaCl salt elution and characterized by SDS-PAGE (132 and 125 kDa), isoelectric focusing (pI 4.6), Western blotting, and MALDI-TOF-MS peptide mass fingerprinting. Ceruloplasmin was purified 106 fold with a specific oxidase activity of 0.53 U/mg protein.

CARB 28

Chondroitin sulfate and heparan sulfate from earthworms *Eisenia andrei*

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Acidic polysaccharides, especially glycosaminoglycans, of earthworms have not been reported previously in any detail. We extracted glycosaminoglycan-rich fraction from whole tissue of the earthworm (*Eisenia andrei*). Two fractions (1 M and 2 M NaCl fractions) eluted from an anion-exchange chromatography showed the presence of acidic polysaccharides on agarose gel electrophoresis. Monosaccharide compositional analysis showed that galactose and glucose were most abundant in both fractions. Liquid chromatography–electrospray ionization mass spectrometry (LC–ESI–MS) was performed to obtain disaccharide compositional analysis in 2 M NaCl fraction after chondroitinase digestion. The result showed that the chondroitin sulfate contained a 4-*O*-sulfo (76%), 2,4-di-*O*-sulfo (15%), 6-*O*-sulfo (6%), and unsulfated (4%) uronic acid linked *N*-acetylgalactosamine. LC-ESI-MS analysis showed the presence of *N*-sulfo (69%), *N*-sulfo-6-*O*-sulfo (25%) and 2-*O*-sulfo-*N*-sulfo-6-*O*-sulfo (5%) uronic acid linked *N*-acetylglucosamine after heparin lyase I/II/III digestion. Average molecular weight of 2 M NaCl fraction was 5,800 Da measured by high-performance size exclusion chromatography.

CARB 29

Purification and characterization of chondroitin sulfates from marine sources

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We investigated the by-products of marine organisms (giant squid, salmon, skate, flatfish, and yellow goosefish) to search for chondroitin sulfates (CS) as new marine sources. Depolymerization with chondroitinase showed that purified CS did not contain other glycosaminoglycans on agarose gel electrophoresis. The structure and purity of CS were confirmed by ^{1}H-NMR. The average molecular weight ranging from 22 to 116 kDa was determined by high-performance size exclusion chromatography. Strong anion exchange-high performance liquid chromatography (SAX-HPLC) was performed to obtain disaccharide compositions and purities after chondroitinase digestion. The purity (81.7±1.3 to 114.2 ± 2.5%) and the yield (1.3 to 21.6%) were varied on depending on sources. From all data, CS from giant squid cartilage, salmon

cartilage, skate cartilage, and yellow goosefish bone could be promising marine sources to substitute shark cartilage CS in commercial neutraceuticals.

CARB 30

Chemoenzymatic synthesis of Neu5Gc derived sialosides

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Sialic acids play important roles in many biological and pathological processes. Structural modifications on three basic forms of sialic acids: *N*-acetylneuraminic acid (Neu5Ac), *N*-glycolylneuraminic acid (Neu5Gc), and keto-deoxy-nonurosonic acid (KDN), lead to more than 50 sialic acid forms found in nature. Among these are Neu5Gc and its derivatives found in the animal kingdom, but humans are genetically unable to produce Neu5Gc and its derivatives. However, Neu5Gc accumulation has long been reported in many human tumors as well as normal adult human tissues. In order to study the function of Neu5Gc derived sialosides, the derivatives of *N*-glycolyl mannosamine (ManNGc) including *O*-acetyl and *O*-lactyl modifications at C-6 have been chemically synthesized. These compounds are precursors for synthesizing sialosides containing 9-*O*-acetylated or 9-*O*-lactylated Neu5Gc in an efficient one-pot three-enzyme system.

CARB 30.5

Molecular dynamics simulation of prion peptide: the effect of glycosylation

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We investigate in the conformational properties of the 108-144 peptide from the hamster prion protein. Molecular dynamics simulations of peptides (native, O-glycosylated, R136G peptide) are performed to investigate the effect of glycosylation on conformational behavior of prion peptide. The amyloid formation is characterized by an increase in β-sheet content and the kinetics was reported by C.-C Ho *et al.* (Proteins, 2009, *76*, 213). Random coil to b-sheet conformational transitions are observed in native and R136G peptide at 310K. There is no β-sheet transition of O-glycosylated peptide up to 15 ns in molecular dynamics simulations. We conjecture that this β-sheet formation is closely related to the amyloid formation. Highly retarded and facilitated amyloid formation of O-glycosylated and R136G peptide are analyzed and discussed based on the results of MD simulations.

CARB 31

Cloning, expression, and characterization of a recombinant human sialyltransferase ST6GalNAc I

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Tumor associated carbohydrate antigens (TACAs) are potential cancer vaccine candidates. Recent investigations show that unnatural analogs of these TACAs may have increased immunogenic properties. Sialic acids are terminal monosaccharides of many TACAs, making them important synthetic targets. *N*-Glycolylneuraminic acid (Neu5Gc) is a non-human sialic acid form which has been found to be presented on certain types of cancer cells and at a lower level in some normal cells. Here we report the cloning and characterization of a human sialyltransferase ST6GalNAc I which has been expressed in *Escherichia coli* BL21 (DE3). The substrate specificity of the enzymes is also presented. The enzyme can be used in chemoenzymetic synthesis of sialyl-Tn (Siaa2,6GalNAc-O-Ser/Thr) antigens containing natural and unnatural sialic acid derivatives.

CARB 32

Interaction of bacterial periplasmic glucans with tobramycin

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Periplasmic glucans are intrinsic component in gram-negative bacteria and classified by four families such as family I, II, III, and IV on the basis of the polyglucose backbone structure. These glucans have been investigated to see the interactions with tobramycin which is an aminoglycoside antibiotic used to treat gram-negative bacterial infection. 1D and 2D nuclear magnetic resonance (NMR) analyses of tobramycin and periplasmic glucans mixtures were carried out, and the results indicated that tobramycin interacted with the family IV glucan induces the largest chemical shift change, among peripalsmic glucans of all families. The stoichiometry of the complexe was determined to be 1:1 by Job plot, as the method of continuous variation. Through this work, a potential of antibiotic resistance by bacterial periplasmic glucans was suggested.

CARB 33

Solubility enhancement of luteolin by sulfobutylether β-cyclodextrin

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The slight water soluble flavonoid luteolin and its inclusion with β-CD and SBE(sulfobutylether)-β-CD were investigated. SBE-β-CD has been one of the most popular β-CD derivative to improved the ability to solubilize some poorly water soluble molecules. The stoichiometric ratios and stability constants describing the extend of formation of the complexes have been determined by phase solubility measurements, in all case of type-A_L diagram have been obtained(1:1 complex). The result shows that the inclusion ability of SBE-β-CD is better than β-CD. Nuclear magnetic resonance (NMR) spectroscopic analysis also showed that the chemical shift of the aromatic ring of the luteolin changed greatly by the complexation with SBE-β-CD.

CARB 34

Design and synthesis of sulfotransferase inhibitors of heparan sulfate biosynthetic pathways

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Heparan Sulfate Proteoglycans play a major role in various pathological and physiological processes. Heparan sulfate binds to and serves as co-receptor for a variety of growth factors and cell signaling molecules resulting in transduction of signaling across the cell membrane important for physiological process and pathological conditions including viral infections. Alteration of the sulfation pattern of HS might interfere with binding of various factors and thereby can mitigate the pathophysiological conditions. To unravel the role of individual sulfate groups in various physiological and pathological processes, we have synthesized and characterized a library of novel sulfotransferase inhibitors of heparan sulfate biosynthetic pathwyas. The synthesized compounds were then examined for their ability to affect the enzyme action in vitro and the results will be discussed.

CARB 35

Creating glycodendrimers via maltose and an amino tris-core

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Dendrimers are branched macromolecules that are globular in shape and structurally well defined. Each point of branching leads to a different generation of molecules with an increasing number of reactive ends. The multiple termini give it the property of being multivalent, which make it capable of reacting with many receptors at one time. When carbohydrates are incorporated into the dendrimer structure, it is called a glycodendrimer. The overall goal of this research is to create two glycodendrimers, trivalent and hexavalent. A

commercially available amino tris-core was used as a foundation to build upon to create these compounds. The diasaccharide maltose will be added to the outer surface of each dendrimer after attaching linker molecules that have been created in our lab. Following this the glycodendrimers will be sulfated. In the end, this will yield multivalent glycodendrimers that have potential anti-viral properties.

CARB 36

Convergent synthesis of two *N*-acetylglucosamine terminated dendrimers

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Dendrimers are a remarkable class of polymers, characterized by their extensive branching. Each branch point is known as a generation, where the number of branches typically increases by a factor of 2. This results in a three dimensional, globular macromolecule that can be terminated with a variety of functional groups, allowing dendrimers to have a comprehensive range of physical properties.[1] The aim of this study was to synthesize two *N*-acetylglucosamine terminated dendrimers. This was done by first synthesizing an ethereal-carboxy-terminated core, using Michael-like addition. Next, an ethereal linker was coupled to *N*-acetylglucosamine using standard amide-coupling methods. Finally, the first dendrimer was completed, by amide-coupling the sugar-linker to the core. For the second dendrimer, the core was branched by amide-coupling a diamine to the core, concluded by a Michael-like addition. This dendrimer was then completed just as the first dendrimer.

[1] D. Tully & J. Frechet, *Chem. Commun.*, **14**, 1229 (2001)

CARB 37

Fractional extraction and structural characterization of *Forsythia suspensa* hemicelluloses

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The hemicelluloses in the cell walls of *Forsythia suspensa* were sequentially extracted with distill water, 70% ethanol, 70% ethanol with 1% NaOH, 1M KOH, 1M NaOH, 3M KOH, 3M NaOH under a solid to liquid ratio of 1:25 (g/ml) at 75° for 3 h, and each preparation was sub-fractionated in to hemicelluloses A and B. Their chemical composition, structural features and physico-chemical properties were clarified by sugar analysis, thermal analysis, nitrobenzene oxidation of

bound lignin, molecular weight, Fourier transform infrared, and 1H and 13C NMR spectroscopy. The results showed that xylose (74.6-96.9%) was the predominant sugar composition of alkali-soluble hemicelluloses, principally resulting from the $\beta(1\rightarrow4)$ xylans, and hemicelluloses A was less branched than hemicelluloses B. The sequential treatments under the conditions used were effective on the fractionation of hemicelluloses, and the extraction strength had a great influence on the chemical and structure features of hemcelluloses, such as content of associated lignin and molecular weight distribution.

CARB 38

Gas phase structures and energetic of 2'-Deoxycyitidine radical cations by DFT study: How acidity of [dC $^{\bullet+}$] changes during deprotonation?

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The radical cations of DNA constituents generated by the ionizing radiation initiate the alteration of the bases, which is one of the main types of cytotoxic DNA lesions. These radical cation spices are known for their role in producing nucleic acid strand break, and it is important to identify the radical cation formation at particular atomic site in these molecules so that the major pathway for the nucleic acid damage may be trapped. In this study, the gas-phase intrinsic chemical properties of the gaseous deoxycytidine nucleoside radical cation were examined by employing density functional theory (B3LYP) with the 6-31++G(d,p) basis set. Structures, geometries and relative energies of several deprotonation site of deoxcytidine radical cation were investigated. Theoretical calculations are also employed to gain an understanding of the factors that increase the stability of deoxcytidine radical cation, and these calculations predict that base stacking can stabilize the radical cation state and can have profound effects on its prototropic equilibria.

CARB 39

Solution geometry and long-range coupling in carbohydrate mimetics from glycal dimerization

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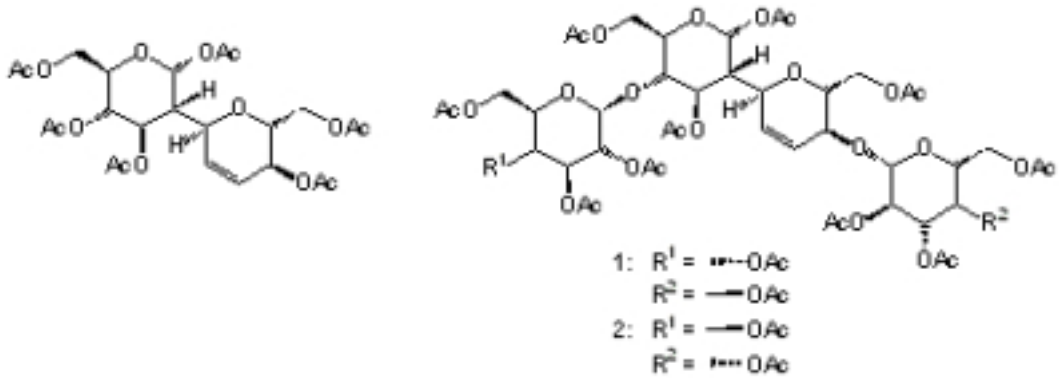
The solution structures of three carbohydrate mimetics with *gluco*-, *cellobio*- and *lacto*-configurations from glycal dimerization are discussed. NOE experiments were used to establish the conformation across the glycosidic bond for both

tetrasaccharide mimetics. J-resolved HMBC NMR experiments were used to measure long-range H,C coupling constants derived from iterative fitting of $\sin(\pi J_{HC}\tau)$. The structures were found to be rigid with very little conformational averaging across the direct C-C-linkage.



CARB 40

Synthesis of unlocked nucleic acid derivatives and thermal denaturation studies

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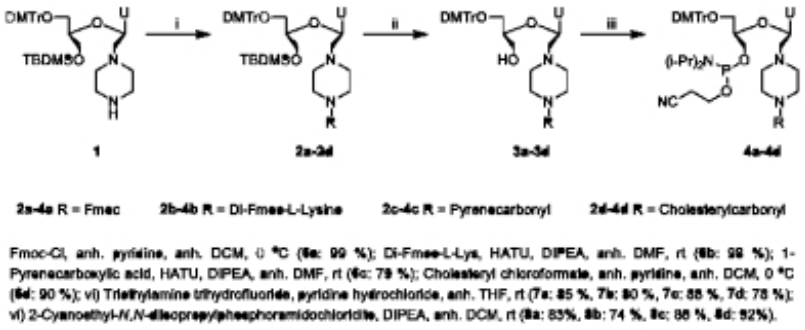
Herein we present the synthesis of unlocked nucleic acid derivatives.



Fmoc-Cl, anh. pyridine, anh. DCM, 0 °C (**6a**: 99 %); Di-Fmoc-L-Lys, HATU, DIPEA, anh. DMF, rt (**6b**: 98 %); 1-Pyrenecarboxylic acid, HATU, DIPEA, anh. DMF, rt (**6c**: 79 %); Cholesteryl chloroformate, anh. pyridine, anh. DCM, 0 °C (**6d**: 90 %); vi) Triethylamine trihydrofluoride, pyridine hydrochloride, anh. THF, rt (**7a**: 85 %, **7b**: 80 %, **7c**: 88 %, **7d**: 78 %); vi) 2-Cyanoethyl-*N*,*N*-diisopropylphosphoramidochloridite, DIPEA, anh. DCM, rt (**8a**: 85%, **8b**: 74 %, **8c**: 86 %, **8d**: 92%).

The synthesized phosphoroamidites were incorporated into 21-mer DNA oligoes and evaluated against complementary DNA and RNA. All the modified monomers causes a decrease in binding affinity towards DNA/RNA complements.

CARB 41

Modified Xyloglucan used to improve cellulose fibers

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SweTree Technologies develops and commercializes new biotechnological methods to improve cellulose-based fibers and products. One example is the use of the plant polysaccharide xyloglucan (XG), either in its native form or modified, for example by using chemo-enzymatic modification called “XET technology”. Briefly, the XET technology relies upon the use of a carbohydrate-active enzyme, xyloglucan endotransglycosylase (XET), to introduce chemically-modified xyloglucan oligosaccharides (XGO-R) into high molar mass xyloglucan (XG). This catalytic reaction thus produces a modified xyloglucan (XG-R), which bears the functional group (R). Importantly, the backbone of the xyloglucan molecule remains unmodified and retains its intrinsic high affinity for paracrystalline cellulose. XG-R is therefore readily adsorbed to e.g. wood or cotton fibers. This method has been proven to positively affect fiber properties and a multitude of properties can be introduced to renewable cellulose fibers without loss of fiber integrity or strength.

CARB 42

Chemo-enzymatic synthesis of mucin-type glycopeptides using sugar-protective groups and ppGalNAcT-2

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The UDP-GalNAc:polypeptide α-*N*-acetylgalactosaminyltransferase (ppGalNAcT) (EC 2.4.1.41) catalyzes the initial step of mucin-type *O*-glycan synthesis, which transfer α-GalNAc to Ser/Thr residue on polypeptide chain. Although ppGalNAcTs are attractive tools for enzymatic synthesis of mucin-type *O*-glycopeptide, ppGalNAcTs catalyze preferential glycosylations to specific Ser/Thr of multiple Ser/Thr residues on polypeptide chains. Therefore, synthetically available *O*-glycopeptides with ppGalNAcTs are restricted. To control the glycosylation sites by ppGalNAc-T2, we applied the several kinds of sugar residues except α-GalNAc as enzymatically removable protective groups for side chains of Ser/Thr in mucin-type *O*-glycopeptide synthesis. The ppGalNAc-T2 reaction to chemically synthesized peptide carrying partially sugar-protected Ser/Thr residues which are intrinsically glycosylated by ppGalNAc-T2 proceeded smoothly to generate artificial glycopeptides attached α-GalNAc to non-protected Ser/Thr. Furthermore, subsequent removal of protective sugar residues is also

accomplished by glycosidase-catalyzed hydrolysis. As a practical application, we demonstrated a novel type of chemo-enzymatic synthesis of MUC1 glycopeptides containing both Tn and sialyl-Tn structures.

CARB 43

Dilute solution properties of four natural chitin in NaOH/urea aqueous system

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Four kinds of natural chitin from crab, shrimp, silkworm chrysalis and flies shell were dissolved in 8 wt % NaOH/4 wt % urea aqueous solution with cooling. Dilute solution properties of chitin in NaOH/urea aqueous solution system was studied by laser light scattering and viscometry to give Mark-Houwink equation and the relationship between the *z*-average radius of gyration (R_g) and the average-weight molecular (M_w) for chitin in the solution. It indicated that chitin molecules existed as a flexible chain conformation in NaOH/urea aqueous. On the basis of the polymer solution theory, their conformation parameters were calculated, indicating the expanded flexible chains of chitin in the aqueous solution.

CARB 44

Novel analogs of UNA (Unlocked Nucleic Acid): Synthesis and structural analysis

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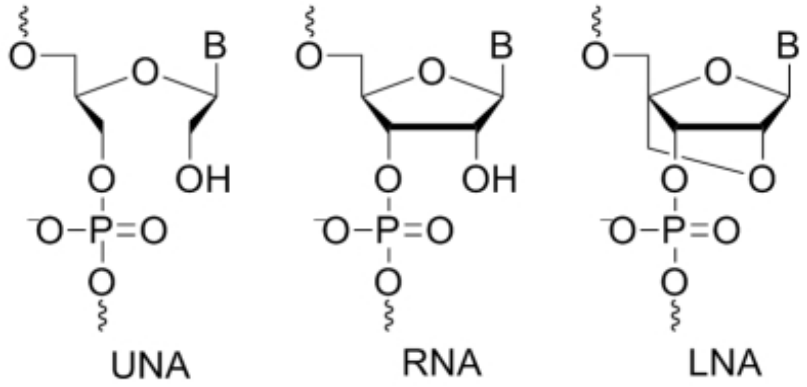
UNA (Unlocked Nucleic Acid) monomers are acyclic derivatives of RNA, missing the C2'-C3'-bond of the ribose ring. This chemical modification of RNA is known to decrease the thermal stability of duplexes in a predictable manner, thereby opposing the effect of LNA (Locked Nucleic Acid) (*BMC*, 2009, 17, 15, 5420-5425.).



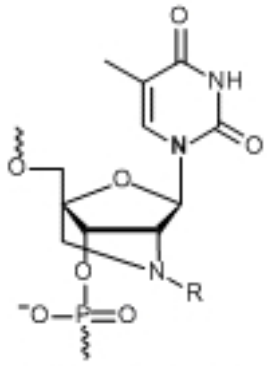
Synthesis of novel UNA analogs will be presented herein along with an evaluation of the resulting change in thermal stability.

CARB 45

Amino acids attached to 2'-amino-LNA: Synthesis of DNA mixmer oligonucleotides with increased duplex stability

M. W. Johannsen, mwj@ifk.sdu.dk, L. Crispino, M. C. Wamberg, N. Kalra, and J. Wengel. Department of Physics and Chemistry, The University of Southern Denmark, Odense M, NA, Denmark

The synthesis of 2'-amino-LNA (locked nucleic acid) opens up exciting possibilities for modification of nucleic acids by conjugation to the 2'-nitrogen (J. Org. Chem. (1998) 10035-10039). Incorporation of unmodified and N-functionalized 2'-amino-LNA nucleotides improve duplex stability compared to unmodified DNA. 2'-Amino-LNA nucleosides derivatized with amino acids have been synthesized and incorporated into DNA oligonucleotides. Following oligonucleotide synthesis, peptides have been added using solid phase peptide coupling chemistry. Modification of oligonucleotides with positively charged residues greatly improves thermal stability.



Modified 2'-amino-LNA-T
R = amino acid or peptide

CARB 46

Structure-property relations in cellulose sulfates

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Cellulose has wide application with its derivatives in industry, food, medicine, pharmaceutics and others. During the last years, sulfated cellulose derivatives (SCD) have been intensively investigated, as their salts depending on their molecular parameters, degree of substitution (DS) and molecular weight, show excellent physicochemical properties, such as high watersolubility(incl. its Ca and Mg salts), viscous solution (which applicable for drilling agent) and biological activities, such as non-toxic, antithrombic, antiparasitic, antivirus and antimicrobial (incl. HIV infections), anticancer and immunomodulator, which have increased their importance to use in petroleum industry, agriculture and medicine. In spite of the desirable properties, SCD have quite enough problems related their synthesis (intensive destruction of the macromolecule, low reproducibility) and properties such as some low-stability of product in various applications, i.e. in solution and soft-base forms; decreasing or even loss their biological activities when applied with soft-medicinal forms). This report focuses on the research of both the chemical modification of linear polysaccharides by the example of cellulose and its effect biological properties, on active reason and solution of above mentioned problems. It is observed, that microbes sensitivity depends on SCD macromolecular conformation and characteristics. Antimicrobial activity was increased with increasing DS of samples, but the sharp increasing was observed at DS from 2.0 till 2.25. Stability, reproducibility of the samples and the suitable soft-medicinal forms were chosen with studying the distribution of sulfate group by the anhydroglucopyranose units and macromolecule. Initial cellulose samples were activated and modified with random and regioselective sulfation methods for this purpose. A structure-property-application performance of SCD was investigated. A broad spectrum microbicide with high stability was obtained which can be widely used to treatment of pyoinfammatory diseases (pyodermatites) and esherichious, especially effective at klaebsielious infections.

CARB 47

B-cell targeting using nanoparticles bearing high affinity CD22 glycan ligand

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CD22 (Sialic acid binding Immunoglobulin domain containing lectin; Siglec 2) is a B-cell restricted surface receptor glycoprotein that recognizes glycans with the NeuAcα2-6Gal sequence as ligands. The restricted expression of CD22 on mature B-cells makes it an effective target for immunotherapy of B-cell malignancies. We have developed doxorubicin-loaded liposomal nanoparticles bearing CD22 ligands that target and kill CD22 expressing B-cells and significantly prolong survival in a murine model of human B-cell lymphoma. Current efforts are focused on ligand optimization by preparing the preferred sulfated human CD22 ligand for these liposomes to enhance B-cell targeting while also excluding other siglecs. Synthesized high affinity sulfated ligands were evaluated for their specificities towards human CD22 and to other siglecs. The use of specific human CD22 ligand is anticipated to enhance the targeting and delivery of cytotoxic cargo to B-cells potentially leading to a novel targeting approach for non-Hodgkin B-cell lymphomas.

CARB 48

Double-headed nucleosides in zipper constructs

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We investigate interactions with double-headed nucleosides in different zipper motifs. Previous studies show significant stabilization of (-3) zipper constructs containing 5'(S)-*C*-(thymine-1-ylmethyl)thymidine. We have synthesized the cytosine and adenine analogues and incorporated them into oligonucleotides. We here present the synthesis and evaluation of the homo- and heterozipper interactions.

CARB 49

Expanding the scope of protecting and leaving groups in chemical sialylations

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Sialic acids are present at the terminal position of glycoconjugates, where they exert important biological proprieties, ranging from cell-cell recognition/communication to mediators of bacteria and viruses. Thus, the efficient synthesis of these important biomolecules has become an essential synthetic tool for the design of viruses and vaccines. We previously reported the application of *S*-benzoxazolyl (SBox) leaving group in the synthesis of sialosides.

The main advantage of this leaving group is the opportunity to selectively activate it in the presence of alkyl/phenyl thioglycoside acceptors. However, the overall yields and stereoselectivities are not exceptionally high, partly due to the deactivation of triflates (silver and cupper) in the presence of acetonitrile. As a part of the program to improve the methodology, we screened other types of promoters in the presence of a wide variety of solvents. In addition, we synthesized and tested differently protected SBox sialosyl donors, for instance 5-N-acetylacetamido, 5-N-trifluoroacetamido, 4,5-oxazodlidinone.

CARB 50

Synthesis and evaluation of carbohydrate based 1,2,3-lactosyl triazoles and carbohydrate-porphyrin conjugates as inhibitors of galectin-1: Two new classes of potential therapeutics for the treatment of cancer

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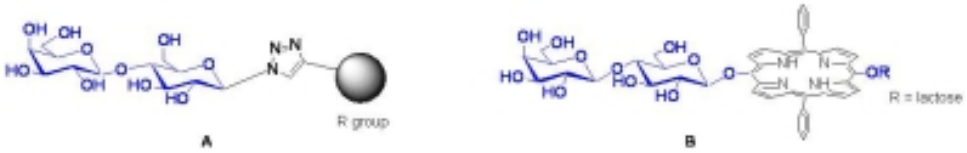
Galectin-1 is a protein that serves in many different biological functions including cell-to-cell communication, cell-matrix adhesion, cell growth regulation, and inflammation and immunity. The over-expression of Galectin-1 has also been implicated in cancer metastasis. For this reason, a considerable amount of research has been devoted to the design and synthesis of specific galectin-1 inhibitors. Research has shown that small molecules that mimic poly-N-acetyllactosamine, a ligand that shows high affinity for galectin-1, have the greatest potential to serve as reversible inhibitors of galectin-1. Here we present the synthesis of several 1,2,3-lactosyl triazoles (A) and carbohydrate-porphyrin conjugates (B) and the preliminary biological evaluation of these molecules using a human carcinoma cell line. Efforts are currently underway to evaluate binding of these molecules to human galectin-1 using ITC.



CARB 51

Probing the enzymatic action of heparin degrading enzymes using chemical biology approaches

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Heparan sulfate (HS) and heparin, are sulfated polysaccharides, composed of repeating hexuronic acid-glucosamine disaccharides, and are important for many biological functions. Heparitinase I, II and III are lyase enzymes are extensively used to obtain HS disaccharide signatures of biological origin. Very little is known about the exact mechanism of heparitinases, until recently. Furthermore, these lyases are thought to act differently on polysaccharide chains. We have developed a very sensitive fluorescent tagging approach to probe the exact mechanism of action these enzymes in real time. Our findings provide first direct molecular evidence for the generation of oligosaccharide intermediates from heparin like polymers. This robust strategy can be applied to deduce the enzyme action as well as harness oligosaccharides of sufficient sizes for various biological studies.

CARB 52

De novo asymmetric synthesis of mezzettiaside 8

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The development of a de novo asymmetric approach to the trisaccharide mezzettiaside 8 from acetyl furan is in progress. The synthesis of mezzettiaside 8 will be divergent, potentially leading to the syntheses of the related isomers, mezzettiasides 2,3,4,9, and 11. All six of these oligosaccharides display significant cytotoxic activity against a panel of human cancer cell lines, specifically those associated with lung and colon cancers (1). Our approach to the construction of these carbohydrate natural products has thus far consisted of a Noyori reduction, palladium-catalyzed glycosylation, Luche reduction, DCC coupling, and Upjohn dihydroxylation. Related reactions will be utilized to complete the mezzettiaside, along with the required regioselectivity to install the final acylation pattern.

(1) Cui, B.; Chai, H.; Santisuk, T.; Reutrakul, V.; Farnsworth, N.R.; Cordell, G.A.; Pezzuto, J.M.; Kinghorn, A.D. Novel Cytotoxic Acylated Oligorhamnosides from *Mezzettia leptopoda*. *J. Nat. Prod.* **1998.** *61,* 1535-1538

CARB 53

RGD-Xylosides inititate glycosaminoglycan biosynthesis

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Glycosaminoglycans (GAG) play many roles in various biological and pathological processes. Wide spread role of GAG chains in blood clotting, wound healing and tumor biology has led to the development of modified GAG chains. RGD peptides could be targeted to activated endothelial and cancer cells, which are known to express $\alpha v\beta 3$ integrin. Xylosides are known to induce GAG biosynthesis in various cellular systems. Therefore, RGD-conjugated xylosides is expected to be targeted to cells that express specific integrin and thereby, modulate the pathological processes by priming biologically active glycosaminoglycans. Our results demonstrate that RGD-conjugated xylosides are able to prime GAG chains in various cell types, and future studies are aimed toward evaluating potential utility of such xylosides in treating myocardial infraction as well as cancer-associated thrombotic complications.

CARB 54

Directed evolution of a thermophilic cellulase for biomass hydrolysis

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Lignocellulose is the most abundant biomass in the world and provides an abundant source of raw material for renewable production of biofuels. A key step in the production of biofuels from lignocellulose is the enzymatic hydrolysis of pretreated biomass to convert cellulose to glucose, which is carried out by cellulases, including endoglucanases (EC 3.1.2.4), cellobiohydrolases (EC 3.1.2.91) and beta-glucosidases (EC 3.1.2.21). Cellusases from thermophilic bacteria and archea, due to their higher temperature optima, are good candidates for industrial biofuels production; however, they often have lower than desired activity. Here we describe the directed evolution of an endoglucanase from a thermophilic bacterium, *Thermotoga maritima*, for its specific activity improvement. Mutant libraries were constructed using error-prone PCR and screened using a robotics-based high-throughput screening platform. Potential mutants from total activity screens were further confirmed by specific activity assays. Several mutants with 20-30% improvement in specific activity have been obtained and characterized.

CARB 55

Synthesis and evaluation of phenolic glycolipid immunomodulators as potential vaccine candidates for mycobacterial infections

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Leprosy and Tuberculosis are considered as two major life threatening health problems. For example, fifty million new infections with *Mycobacterium tuberculosis* occur annually, claiming 2-3 million lives from tuberculosis worldwide. The cell wall of pathogenic mycobacteria is abundant with complex glycolipids whose roles in pathogenesis are mostly unknown. One class of these glycolipids is phenolic glycolipids. Since the discovery of this family of glycolipid antigens, it was claimed that these compounds play a crucial role in the pathogenesis of mycobacteria as a key virulence factor. Also, it was claimed that these compounds could be potential vaccine candidates. This project aims at total synthesis of a full panel of all PGLs and then performing a complete immunological investigation of the synthesized compounds using cytokine induction ELISA to determine the immunological profile of these molecules. Also, the project aims at determining the possible Ag-Ab interactions using mass spectrometry. In this poster, I will describe recent synthetic work towards the target compounds as well as some of the immunological testing.

CARB 56

Synthesis and conjugation of α-Gal and α-Rha saccharides for immunization experiments

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Over 16 million people in Central and South America are infected with the protozoan parasite *Trypanosoma cruzi*, the causative agent of Chagas disease. It is known that *T. cruzi* contains cell surface glycoproteins with terminal α-galactosyl residues, and it is well established that they are highly immunogenic to humans. However, the exact structure of the immunogenic α-Gal epitopes remains unknown. To determine which α-Gal-containing epitopes are immunogenic we have synthesized α-Gal saccharides and conjugated them to carrier proteins for experimental immunization in mice that are knockout for the α-galactosyltransferase 1 gene (GalT1-KO). If these synthetic glycoconjugates prove to be capable of eliciting anti-α-Gal antibodies in GalT1-KO mice, they may help unravel the molecular details about the immunogenicity of *T. cruzi* and may be used for experimental vaccination. In some developmental stages of *T. cruzi* other unusual sugars that are foreign to humans are expressed, e.g. rhamnosides, which may also be immunogenic. Here we demonstrate syntheses of α-Gal and α-Rha containing glycosides, equipped with a thiol linker, and their

conjugation to the carrier protein KLH. Currently, immunization studies are on-ongoing.

CARB 57

One-pot multi-enzyme chemoenzymatic synthesis of LacNAc and its derivatives

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N-Acetyllactosamine (LacNAc) and its derivatives are common glycan motifs presented in glycoconjugates including glycoproteins and glycolipids. b1–4-Galactosyltransferases are the key enzymes that catalyze the formation of b1–4-galactosyl linkage in LacNAc and related lactose structures. They are expressed by many bacteria for the formation of capsular polysaccharides and lipooligosaccharides. In order to better understand the biological importance of LacNAc and its derivatives, a general, convenient, and efficient one-pot multi-enzyme chemoenzymatic approach has been developed. LacNAc and its derivatives with various modifications have been synthesized in efficient yields using a glucose-1-phosphate uridylyltransferase (GalU), a UDP-galactose-4-epimerase (GalE), and a b1–4-galactosyltransferases cloned from *Neisseria meningitidis* or *Helicobacter pylori*.

CARB 58

Targeting Sialoadhesin using nanoparticles bearing high-affinity glycan ligands

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Sialoadhesin (Sn, Sialic acid binding Immunoglobulin domain containing lectin; Siglec-1), is a surface receptor expressed solely on macrophages, involved in interactions with immune cells. Binding of cells and particles is based on recognition of glycan ligands terminating with the NeuAcα2-3Gal sequence. Due to its restricted expression, Sn is an effective target for development of a highly desirable macrophage-specific delivery system. To overcome the generally low intrinsic affinity of siglec-glycan interactions we have developed multivalent liposomal nanoparticles decorated with glycan ligands of Sn. Our results indicate that these particles bind specifically and are endocytosed by cells expressing Sn. In addition, we will describe our strategy for optimizing the affinity of the glycan ligand to enhance the binding of these liposomes. The rational design, synthesis and evaluation of second generation high-affinity Sn ligands will be presented.

(Supported by NIH Grant GM60938)

CARB 59

Large-scale enzymatic synthesis and purification of a2-3- and a2-6 linked sialosides

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Sialylated oligosaccharides are the major components of human milk oligosaccharides and are believed to be potential prebiotics that stimulate the growth and proliferation of beneficial bacteria whose colonization in human intestine can compete for the binding of pathogenic bacteria. In order to obtain sialosides in amounts large enough for prebiotic research, preclinical testing, and clinical trials, we here report an effective biosynthetic approach for large-scale production of Neu5Aca2,3Lac and Neu5Aca2,6Lac sialosides. With the highly efficient and convenient one-pot two-enzyme approach established in our group, the synthesis of these two sialosides in gram-scale was successfully achieved and the purification was achieved conveniently using anion-exchange chromatography. Pure forms of Neu5Aca2,3Lac and Neu5Aca2,6Lac were obtained in 72% and 90%, respectively and their structures were confirmed by NMR spectroscopy. The sialosides synthesized will be used for bacterial binding assays and prebiotic fermentation studies to identify the most suitable antimicrobial and prebiotic candidates.

CARB 60

Total synthesis of two new glycan derivatives based on the glycan component of the glycopeptide antibiotic vancomycin

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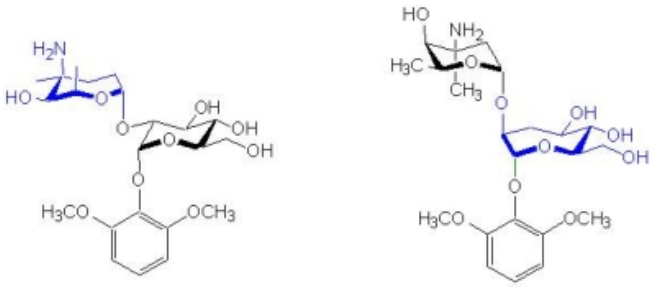
Vancomycin is a glycopeptide antibiotic used as a last resort for the treatment of methicillin-resistant *Staphylococci* and *Enterococci.* The development of bacteria resistant to vancomycin has prompted researchers to focus on the preparation of new and more potent derivatives of vancomycin. Recent attempts aimed at reversing vancomycin resistance have focused on modifying the glycan component of vancomycin, which is believed to play an important role in inhibiting bacterial cell wall biosynthesis by interacting with the glycosyltransferases that convert peptidoglycan precursors into mature peptidoglycan, although the exact nature of this event is not well understood. Here we present the total synthesis of two new glycan derivatives based on the glycan component of the glycopeptide antibiotic of vancomycin. Efforts are currently underway to evaluate the biological activity of these derivatives.



CARB 61

Comparison of the binding affinities of Ricin and RCA_{120} using different glycan displays

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Ricin toxin is considered as a potential biothreat agent. It enters the cell via specific glycan receptor on the cell surface and halts protein synthesis. This eventually leads to cell infection and death. Ricin is reported to bind to terminal galactose and *N*-acetylgalactosamine derivatives. Synthetic glycans that mimic these natural glycans can be used for capture of the toxin. The synthesis and development of biotinylated multivalent soluble glycans and their representation on different surfaces for precise binding with Ricin and the nontoxic surrogate, RCA_{120}, will be presented.

CARB 62

Functional studies of a viral α2,3-sialyltransferase

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Sialyl lewis x and sialyl lewis a are important sialic acid-containing carbohydrate epitopes involved in many biological processes such as inflammation and cancer. In the biosynthesis of sialyl lewis x and sialyl lewis, the sialic acid residue is transferred to a galactoside before the addition of a fucose. For their analog chemoenzymatic synthesis, it would be more beneficial if the structurally modified sialic acid residue can be transferred as the last step to the fucosylated galactosides. To date, there is only one sialyltransferase, a viral α2,3-sialyltransferase (v-ST3Gal I), that have been reported to be able to tolerate the fucosylated substrates. This paper describes the cloning, overexpression, and characterization of v-ST3 Gal I. The enzyme was overexpressed in *E. coli* origamiB^{TM} (DE3) as an MBP-fusion protein. The His_6-tag was added to the C-terminus to facilitate the purification in the Nickel affinity column. The purified enzyme was found to be active toward lactose, lacNAc, lewis x, and lewis a.

CARB 63

Purification of hemicelluloses in hot water and alkali pre-extractives of mixed hardwoods using organic solvents

H. J. Youn, **H. Shin**, heenai@naver.com, K.-J. Sim, S. Lee, and H. L. Lee. Department of Forest Sciences, Seoul National University, Seoul, Republic of Korea

Hemicelluloses as polysaccharides of C5 and C6 sugars are very useful natural materials. Despite its usefulness, about 50% of hemicelluloses are burn out in a boiler in kraft pulping process. Therefore, pre-extraction and isolation of hemicelluloses from wood is a requisite for further utilization of them. In this study, we pre-extract hemicelluloses from mixed hardwood chips using hot water and alkali prior to kraft pulping, and we intended to isolate hemicelluloses from pre-extractives by organic solvents. We conducted isolation treatment by precipitating hemicelluloses with 1,4-dioxane, ethanol, and isopropanol, respectively. We evaluated the isolation performance by analyzing the characteristics of isolated hemicelluloses. About 35% and 26% of the hemicelluloses were extracted from the initial wood chips for hot water and alkaline pre-extraction in this experiment. The yield of alkali precipitate was higher than hot water precipitate for all kinds of solvents in this experiment. Most precipitates were yellow colored, except hot water precipitate using 1,4-dioxane. The magnitude and purity of isolated hemicelluloses were affected by solvent types.

CARB 64

Solid-phase “one-pot multi-enzyme” combinatorial synthesis of glycopeptides

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In this study, an efficient solid-phase glycopeptide synthetic approach based on “One-Pot Multi-Enzyme” and “One-Bead-One-Compound” concepts is employed. Rapid formation of peptide bonds chemically and glycosidic bonds enzymatically can yield hundreds of compounds on beads by “split-mix” synthesis with each bead presents only one chemical identity. Our current synthetic effort focuses on a variety of short and biologically important glycopeptides containing a wide range of suitable glycosyltransferase acceptors for the formation of sialosides containing various natural and non-natural sialic acid forms and different sialosidic bonds. The combined strategy provides a highly efficient approach to synthesize a glycopeptides library on beads which can be directly used for high-throughput binding studies.

CARB 65

Glycan modification of natural products by chemoenzymatic approaches

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Puerarin is a natural product isolated from the kudzu plant and has shown to have the ability to suppress alcohol intake of animals with excessive drinking problems. It has been used recently to treat patients with coronary artery diseases. However, the poor solubility of puerarin has been a concern for its drugability. Here we introduce an effective chemoenzymatic approach for modifying the glycan moiety of puerarin. By introducing galactose and sialic acids to the glucose on puerarin via two one-pot multi-enzyme reactions, we are able to increase the solubility of the modified puerarin. Due to the importance of sialic acid in molecular recognition, glycan-modified puerarin may have alternative applications including being potential inhibitors for sialoside-protein recognition.

CARB 66

Molecular cloning and characterization of a novel *H. hepaticus* a1–3 fucosyltransferase

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Efficient chemoenzymatic synthesis of oligosaccharides and glycoconjugates requires fucosyltransferases (FucTs) with high activity and substrate promiscuity. Here we report molecular cloning and functional expression of a novel *H. hepaticus* a1–3-fucosyltransferase which shows good activity towards sialylated and non-sialylated Type II oligosaccharide acceptor substrates. It is a promising catalyst for chemoenzymatic synthesis of Lewis^X, sialyl Lewis^X, as well as other oligosaccharides and their derivatives.

CARB 67

Synthesis of multiple sialic acid-terminated dendrimers with a poly(amidoamine) core for the study of the effect of generation and distance from sugar to core on protein binding affinity

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Dendrimers are branched macromolecules that form spherical globular shapes. As a dendrimer is synthesized, the number of terminal groups doubles. These

terminal groups can be functionalized producing a multivalent molecule. The binding affinity to a receptor of a multivalent molecule is higher than that of a monovalent molecule. The goal of this work was to use the generations= -0.5, 0, 0.5, 1, 1.5, and 2 (poly(amidoamine) or PAMAM dendrimers and functionalize them with either sialic acid via an amide linkage, or by inserting a hydrophilic linker between the PAMAM and the sialic acid. The glycodendrimers were made then purified by a combination of size exclusion chromatography and HPLC. The glycodendrimers were then sulfated for future use in binding assays.

CARB 68

Synthsis of a library of trisaccharides involving regioselective glycosylation of mannose diol acceptor

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Oligosaccharides are among the most intriguing and useful classes of biologically active compounds. These compounds, which are sometimes integrated in more complex molecules, are often believed to be integral figures in cell-cell recognition, cell-cell adhesion, and other transmembrane activity. However, they are not found in homogeneous stereochemically pure form in nature. Synthetic routes to these molecules often involve many protecting and deprotecting steps to assure proper regioselectivity and stereoselectivity in the assembly process. A 2,3-mannose diol acceptor and donors of various base monosaccharides with various protections were fashioned using simple protection techniques and further coupled to examine regioselectivity. The results were highly regioselective. A library of trisaccharides was synthesized. Such a library could be very useful for future work in assembling natural and unnatural oligosaccharides.

CARB 69

Stimulatory effect of glycoconjugates on nitric oxide and cytokine production by macrophages upon exposure of *B. cereus* spores

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Both mammalian and bacterial cells express complex glycoconjugates (GCs). GCs are involved in recognition, adhesion, activation, and signaling processes. We have shown that GCs stimulate binding and inhibition of *B. cereus* spores and increase the resistance of macrophages. In present study, we studied the

stimulatory effect of GCs on nitric oxide (NO) and cytokines production by murine macrophages during phagocytosis of *B. cereus* spores. Macrophage viability, NO, lactate dehydrogenase (LDH), and cytokines production were measured after 24 hrs. NO was determined by Griess assay. Cytokines IL-12p70; TNF-alpha, INF gamma, MCP-1, IL-6, and IL-10 were determined using the BD™ Cytometric Bead Array. LDH was measured using CytoTox 96® kit. Results have shown that macrophages may become more prone to adhere to GC-treated spores, resulting in increased phagocytosis, NO production, spore killing, and cytokines release. The technique presented in this study may be helpful in finding GCs with bactericidal /antimicrobial properties.

CARB 70

Quantification and characterization of carbohydrate compositions in microalgal biomass

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Starch and cell walls are the two major carbohydrate sources in microalgal biomass. Cytoplasmic starch from microalgae could be a potential feedstock for biofuel production. Accessing starch for fermentation and efficient extraction of lipid require breaking algal rigid cell walls. Significant energy inputs are required for mechanical cell disruption. Biological treatments for the dissolution of cell walls may reduce the requirement for mechanical cell disruption. In addition, biological treatment may facilitate a more refined stream of cell wall carbohydrates amenable for fermentation. Understanding the composition and structure of polysaccharides in microalgae is important for the efficient hydrolysis of microalgal cell walls and cytoplasmic carbohydrates. Characterization of carbohydrates in the cell wall under different growth stages and environmental conditions will assist with the development of growth strategies to achieve efficient extraction and fuel production processes. A sequential approach was developed for quantitative analysis of the carbohydrate compositions of microalgal biomass. The cytoplasmic carbohydrates and cell wall compositions of four selected algal strains were analyzed and reported. The results demonstrate a significant effect of environmental conditions on starch levels and cell wall composition that vary with algal strain.

CARB 71

Characterization of a bacterial sialyltransferase Psp2,6ST for the synthesis of sTn Antigens

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Many sialic acid-containing carbohydrates are tumor-associated carbohydrate antigens (TACAS). Among numerous TACAs identified, sialyl Tn antigen (sTn) which is Siaa2–6GalNAc-a-O-Ser/Thr, is of particular interest. sTn is richly expressed on a number of tumors, such as breast, prostate, colorectal and ovarian cancers. Chemoenzymatic method is an promising and efficient approach for the synthesis of sTn containing different sialic acid forms. In this process, sialyltransferase is a key enzyme which transfers Neu5Ac from cytidine monophosphate *N*-acetylneuraminic acid (CMP-Neu5Ac) to GalNAc-containing Tn antigens. A recently reported sialyltransferase Psp2,6ST shows a great promise in accepting Tn-antigen as suitable acceptor substrate. The enzyme has been cloned, expressed, and characterized. Compared to a well studied a2–6-sialyltransferase Pd2,6ST cloned from *Photobacterium damsela*, the Psp26ST shows better activity in the synthesis of sTn containing different sialic acid forms. Site-directed mutagenesis has also been carried out to find mutants with improved activity.

CARB 72

Enrichment of highly efficient thermophilic microbial communities active on switchgrass and corn stover in a high-solids environment

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Compost microbial communities offer great potential for the discovery of enzymes that decompose plant cell walls. In this study compost was used as an inoculum source to enrich thermophilic microbial communities and associated enzymes that hydrolyze cellulose and hemicellulose in a high-solids environment. Decomposition of cellulose and hemicellulose by microorganisms is usually delayed by the presence of sugars; therefore ethanol and water extracted feedstocks were used for enrichment studies. To initiate the studies, extracted switchgrass and corn stover were wet with minimal media, inoculated with finished green waste compost from a commercial facility, transferred to solid fermentation reactor arrays, and incubated under aerobic conditions. Reactor arrays were incubated at 55^{o}C and the resulting enriched communities were transferred to fresh extracted material every two weeks. After each two-week incubation period, adapted communities reduced solids an average of 30% for switchgrass and 22% for corn stover. Respiration levels increased with successive enrichments. Overall, the changes for switchgrass were more pronounced than for corn stover; solids reduction between the first and second time points increased 4-fold for switchgrass while it remained relatively constant for corn stover. Also, enzyme activities significantly increased with each switchgrass enrichment, while activities remained relatively constant for corn

stover. Final samples will be included in a coordinated metagenomics and enzyme discovery effort.

CARB 73

Sweet sorghum hybrids and industrial processing of sweet sorghum into ethanol

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Genomics-based plant breeding and biotechnology offer the opportunity to make game-changing improvements to non-food, low-input energy crops being developed for next-generation biofuels and biopower. Combined with compositional analyses, this suite of technologies makes it possible to optimize not only yield-influencing traits such as plant architecture and flowering time, but also composition and conversion characteristics for various process technologies. Thus, improved cultivars have the potential to produce not only more biomass per acre, but more fuel or energy per ton for multiple downstream uses, including liquid transportation fuels, electricity, natural gas, and fine chemicals. Among the new crops being considered for next-generation biofuels, sweet sorghum has historically not received the same widespread attention as others, despite numerous advantages. It is a high-yielding seed-propagated crop that produces large amounts of sugar and biomass with relatively low inputs.

CARB 74

Opportunities and challenges of sweet sorghum as a feedstock for biofuel

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Sorghum (*Sorghum bicolor* L. Moench) is a grass crop with thick stalks adapted to warm climates. Sweet sorghum (SS) has a juicy, sweet stalk. The juice can be pressed from the stalks, directly fermented or boiled down to make syrup. The plant residue remaining can be burned to run the mill or cogenerate electricity, or used as feedstock for cellulosic ethanol. SS has wide environmental adaptation, rapid growth, high productivity, relative tolerance to marginal growing conditions, and high concentrations of the easily fermentable sugars glucose, fructose and sucrose. The sugars in SS start to deteriorate once the stalk is harvested. Leaves and leaf sheaths are difficult to remove from the stalk. They are a source of microorganisms, organic acids and starch. Microorganisms deteriorate the sugars, organic acids react with the sugars when the juice is heated, and starch thickens during boiling. Ideas for addressing these challenges will be discussed.

CARB 75

Liquid sugars produced in sugar refineries: Advantage of large central units serving the competitive and sustainable needs of the food industry

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In the present world economics, the prices of sugar have managed to remain very reasonable, thanks to continuous sugar availability from large producers such as Brazil, and sustained domestic sugar production in other producing countries. In comparison cereals, whose prices have been very volatile in 2008, are considered now as more questionable raw material for the production of liquid sugars such as high fructose corn syrups. The production of liquid sugars (Sucrose or Medium Invert) at the Sugar Refinery is gaining a new recognition for several reasons : · Raw material is available in large quantities at stable prices · Thanks to the proximity of the Sugar Refinery to the Food Industry, possibility to build large-cale efficient central units of Liquid Sugars · Saving energy usage by avoiding the costs of crystallization, when supplying directly a liquid product ready to use · Flexibility from the Sugar Refinery for supplying end-users with crystalline, or liquid sugar to fulfil the most cost-effective conditions

CARB 76

Value-added products for a sustainable sugar industry

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Sugar production, from both beet and cane, is energy and water-intensive. In today’s social and political environment, industries strive to be environmentally sustainable and “green,” while maintaining profitability. The sugar industry has three avenues for achieving these goals: improving the over-all efficiency of the process; expanding its market with a range of innovative edible products; and finally, entering into the 21st century’s bio-based economy by developing products to replace petrochemical-derived products. The industry has done well with the first two of these, but has found barriers to exploiting the latter possibility. This presentation reviews some of the industry successes with value-added products and the potential for further development in the area of bio-based products.

CARB 77

Sugar beet pulp: A sustainable source of carboxy methyl cellulose (CMC) and other polysaccharides

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It is estimated that the extraction of sugar from sugar beets in the U.S. produces about two million wet tons of sugar beet pulp yearly. The dry pulp of this sustainable material contains about 67% valuable polysaccharides. With the aid of microwave assisted extraction, we have extracted pectin, and two alkaline soluble polysaccharides. The presence of fibers in the insoluble cellulose residue was revealed by atomic force microscope (AFM) images (Kirby et. al., Food Biophysics 1, 163, 2006). The cellulosic fraction was solubilized by allowing the residue to react with monochloroacetic acid. Analysis of the solubilized residue (SR) revealed it contained a large fraction of CMC and a smaller amount of uronic acid. AFM revealed that the SR was comprised of linear strands interspersed with spherical particles. HPSEC of the SR with degrees of carboxy methyl substitution ranging from about 0.59 to 1.38 revealed linear molecules with molar masses ranging from about 1 to 1.6 x 10^5 Daltons.

CARB 78

Aprroaches to raw sugar quality improvement as a route to sustaining a reliable supply of purified industrial sugar feedstocks

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Demand for purified sugar is increasing while energy costs for a sustainable level of this product outstrips manufacturing technology. Agricultural commodity delivery of sugar as an adequately refined raw material for manufacturing value-added goods demands that the highest yields of purified crystalline sugar be realized to be competitive. Components in raw juice inhibiting the crystallization of sugar must be identified to achieve very low colorant values with highest pol of the crystals. Micro- and nanoparticulate materials can foul sensitive surface properties of adsorbents such as activated carbons or resins. Improved approaches to clarification, such as combined centrifugation/microfiltration or nanofiltration of sugar juices or syrups, permit more efficient decolorizing with solid adsorbents. Lower quality sugars can thus be upgraded to permit isolation of acceptable product while sustaining more favorable energy utilization.

CARB 79

Sustainability of low starch concentrations in sugarcane through short-term optimized amylase processing and long-term breeding strategies

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Starch negatively affects the quantity and quality of sugar produced. Starch increases juice viscosity, reduces crystallization and centrifugation rates, impedes refinery decolorization processes, and occludes into sucrose crystals. Alpha-amylase used to hydrolyze starch at the factory is a short-term solution as the enzyme is relatively expensive and not always efficient. A more long-term solution is breeding low starch sugarcane cultivars. We surveyed a large collection of cultivars and wild *Saccharum* species as a prelude to selecting and breeding for low starch content in sugarcane. Starch content varied among the cultivars and wild *Saccharum* species; it was generally higher among the wild non-sucrose producing species. Although starch values decreased as the cane matured or after exposure to freezing temperatures, their relative rankings among genotypes did not. Heritability values for starch were high and backcrossing from wild into cultivated germplasm lowered starch and increased sucrose content. Therefore, sugarcane cultivars developed to accumulate low levels of starch represent a more economical and sustainable strategy to mitigate the negative effects of starch.

CARB 80

Developments in sugarcane agriculture that affect cane and sugar quality

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Sugarcane quality and sugar yield and quality are interrelated. In many production systems, both agricultural and manufacturing, there is conflict between productivity in the field and sugar quality. High productivity and/or throughput many times compete with high product quality. However, quality can be influenced by ever-changing developments in sugarcane agriculture and manufacturing including the introduction of new cultivars, use of chemical ripeners, changes in cultural practices and harvesting systems and the introduction into an industry of new disease, insect and weed pests. These developments differentially affect cane and juice quality and have a direct bearing on sugar quality. Further, cane and sugar quality have taken on new meaning today with the vertical integration of many sugar operations from field to refinery to consumer. The new refinery today is seeking very high pol (VHP) sugar (>99.2 pol) and very low color (VLC) sugar (<2200 ICUMSA units).

CARB 81

Metabolically-incorporated photocrosslinkers capture glycoconjugate complexes

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Glycan-mediated interactions constitute the underlying molecular bases for a wide range of biological processes. This class of interactions is particularly important in development, immunology, infection, and carcinogenesis. Yet glycan-mediated interactions are difficult to detect and characterize, due to their low affinities and rapid dissociation kinetics. To capture these ephermeral complexes, we make use of metabolic oligosaccharide engineering to incorporate photocrosslinking groups into cellular glycoconjugates. In this presentation, I will describe our strategy for introducing photocrosslinkers into a variety of glycoconjugates, how we characterize which glycoconjugates are modified and the degree of modification, and the use of these photocrosslinkers to discover glycan-mediated interactions.

CARB 82

Nickel-catalyzed stereoselective formation of alpha-2-deoxy-2-amino glycosides

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We have recently developed a novel method for the stereoselective synthesis of alpha-2-deoxy-2-amino glycosides utilizing C(2)-N-substituted benzylidene D-glucosamine and galactosamine trichloroacetimidates as the donors. This method relies on the nature of the nickel catalyst to control the alpha-selectivity at the newly-formed glycosidic bond. The current nickel method has been applied to a variety of primary, secondary, and tertiary alcohol nucleophiles to provide the desired glycoconjugates in good yields with excellent alpha-selectivity.

CARB 83

Chemical tools for studying fucosylated glycans

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Fucosylated glycans are widely distributed throughout eukaryotes and certain bacteria. On the surface of mammalian cells, they mediate a variety of physiological and pathological processes. In pathogenic bacteria and parasites, fucosides regulate adhesion and colonization of host tissues and modulate the host immune response. Despite the obvious importance of fucosylated glycans, delineating the molecular basis of their function is severely hampered by their structural complexity and heterogeneity. Currently, there is no facile and cost-

effective chemistry for synthesizing these glycans and their structurally related derivatives. In this talk, I will discuss the new chemical tools developed in my laboratory for preparing structurally defined fucosides and their derivatives and chemical tools for detecting fucosylated glycans in bacteroides, a human symbiont.

CARB 84

Glycoconjugates: Design, synthesis and evaluation

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Glycoconjuates are found in nature in a variety of forms, some of these include: glycoproteins, glycolipids, components of cell walls and as small molecule natural products. Unraveling the biological roles of glycoconjugates requires access to these complex materials. However, there are significant challenges to their preparation. We have been investigated new chemoselective amide-bond forming reactions useful for the preparation of glycoconjugates. In particular, we have investigated new methods for the efficient mixed-phase synthesis of glycopeptides. In parallel with these studies we have designed, synthesized, and evaluated a novel three component L-rhamnose-containing antitumor vaccine which contains tumor-associates carbohydrate antigens found on the MUC1 glycopeptide. In a third aspect of our program we have explored the synthesis and study of glycoconjugates that act as inhibitors of the enzyme antigen 85, an acyltransferase that acts on the cell wall *Mycobacterium tuberculosis.* The chemical and biological aspects of this program will be discussed.

CARB 85

Chemical approaches to the investigation of protein-membrane binding interactions using synthetic probes

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Signaling lipids present in cell membranes act as important regulators of biological processes, and have been implicated in the onset of numerous disease states. Such compounds commonly act as ligands for peripheral proteins that lead to their anchoring onto the cell membrane, processes that regulate protein function and localization. Herein, chemical strategies for the efficient characterization of protein–membrane recognition events will be presented. First, modular approaches for rapid generation of probes corresponding to important structures including diacylglycerol (DAG), phosphatidic acid (PA) and the phosphoinositides (PIP_ns) will be discussed. In addition, the utility of these analogs for probing and perturbing protein–membrane binding will also be presented. Here, microplate-based detection of protein–membrane binding

employing both isolated motifs and whole membranes has been performed towards the development of a multi-format high-throughput microarray system. In addition, progress towards the application of bifunctional probes for pulling down, identifying and characterizing cognate receptors from complex samples will also be discussed.

CARB 86

Carbohydrate based biosensors: Rapid, one step, no wash assay for the detection of lectins and toxins

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Carbohydrates are excellent recognition molecules as they are highly stable and immune to antigenic drift. Unfortunately, selectivity and sensitivity issues impede practical applications. We report a rapid, one step, no wash assay that detects carbohydrate binding proteins with high selectivity, sensitivity and minimal sample preparation. A dose-dependent increase in the transverse relaxation time (T2) was observed when carbohydrate encapsulated magnetic beads were incubated with target protein. Proteins that bind to the same carbohydrate displayed different binding kinetics and were readily differentiated by measuring the T2 values over time. Selectivity was further improved using two different recognition molecules. This technique was used to detect clinically relevant Shiga toxins, the virulence factor of *E.coli O157:H7,* in hamburger, lettuce and stool. The limit of detection was 1 picogram of Shiga toxin in spiked stool samples, a significant advancement over commercial ELISA kits, which uses several reagents and has a 1 nanogram detection limit.

CARB 87

Chemoenzymatic synthesis of N-linked glycoconjugates and their application to studies of the function of N-linked glycosylation

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N-linked glycoconjugates can be very challenging to study due to their heterogeneity and difficulties in obtaining sufficient quantities for biochemical studies. To overcome these obstacles we have taken a combined biosynthetic and chemoenzymatic approach to the synthesis of N-linked glycoconjugates. In this strategy high mannose N-linked glycoproteins are first produced in genetically engineered yeast and then *in vitro* chemoenzymatic methods are utilized to produce homogeneous high mannose, hybrid, and complex glycoconjugates. This approach allows the possibility of isotopic labeling, the rapid synthesis of N-linked glycopeptides, and incorporation of synthetic modifications onto expressed glycoproteins. Application of these synthetic

methods to the synthesis and study of biologically active glycoconjugates will be presented.

CARB 88

Entirely carbohydrate-based cancer vaccine constructs elicit selective cellular immunity

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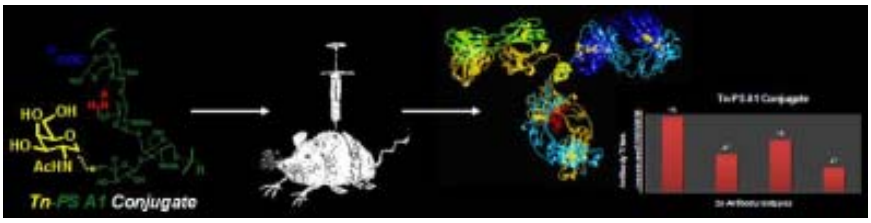
Vaccines are powerful tools for disease prevention and various cell surface carbohydrates are important templates for their development. However, as isolated single entities carbohydrates have only been known to invoke *T-cell-independent* immune responses. To elicit a strong and long-term immunity, a vaccine must target the class II major histocompatibility complex (MHCII) and $CD4^+$ T-cells in a *T-cell-dependent cascade*. Most recently zwitterionic polysaccharides were isolated from anaerobic bacteria and shown to modulate the cellular immune system by activating $CD4^+$ T-cells via MHCII. Based on this discovery and as an alternative approach for vaccine development, we hypothesize that chemically conjugating tumor associating carbohydrate antigens/haptens (TACAs) to zwitterionic polysaccharides (ZPS) will lead to *T-cell-dependent* vaccines. This talk will focus on the isolation, purification, chemical modification of PS A1 (a naturally occurring capsular polysaccharide) with tumor associated carbohydrate antigen (TACA) Tn. Subsequent *in vivo* mouse studies with our Tn-PS A1 construct will reveal a Tn specific MHCII mediated immune response characterized by a high IgG3 titer. Sera obtained from Tn-PS A1-primed mice will be used to target human cancer cell lines Jurkat, MDA and MCF-7 specifically with the IgG3 antibody. Finally we will argue for an unprecedented immune mechanism arising from the Tn-PS A1 construct that is characterized by a high IL-17 profile; complete switch from IL-2 and IL-6 from PS A1-primed mice.



CARB 89

Biointerfacial engineering and the carbohydrate microarray

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Advances in surface analysis have yielded a variety of tools that are revolutionizing interfacial science and engineering by quantifying composition, orientation and spatial distribution of biomolecules – including carbohydrates – on the surface of a material. This talk describes the glycoanalytical application of X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry and atomic force microscopy to characterize the biointerface of glycan-modified surfaces for biosensing applications. Analysis of these glycosylated surfaces focuses on identifying the extent of surface functionality occupied by carbohydrate, the nature of glycan accessibility and the capacity of immobilization strategies to tune surface functionality. These techniques are providing valuable insight into the design of a new generation of carbohydrate biosensors and glycan arrays.

CARB 90

Defining roles on N-Glycans in endoplasmic reticulum-mediated quality control

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Secretory and membrane proteins are co-translationally translocated into the lumen of the endoplasmic reticulum (ER), where they attain their correct three-dimensional structure. The high flux of proteins through the ER leads to terminal misfolding of a subset of folding intermediates. The nature of oligosaccharides, cotranslationally attached to the amide side chains of asparagines residues, play pivotal role in decision making process during the protein degradation. While properly folded glycoproteins are further exported to the Golgi, terminally misfolded proteins are removed from the ER lumen in a process collectively described as ER-associated degradation (ERAD). The mechanisms that the ER employs to distinguish terminally misfolded glycoproteins from folding intermediates is the central question in the field of protein degradation in the ER. Studies in *S. cerevisiae* demonstrated essential roles of several carbohydrate-recognizing proteins in ERAD. By their in vitro characterization, we aim to define molecular logic of substrate recognition in ERAD.

CARB 91

Insights into the structure and specificity of the mammalian neuraminidase 3 (Neu3) through site directed mutagenesis and kinetic studies

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The mammalian neuraminidase enzyme, Neu3, is known to act on plasma membrane glycolipid substrates. The enzyme appears to play a role in cancer progression, likely through glycolipid remodeling of the membrane. Specific inhibitors of the enzyme could be valuable tools for evaluating the enzyme's biological function. However, few potent, specific inhibitors of Neu3 are currently known. We propose that improved models of the Neu3 active site will be a useful tool for designing inhibitors. Towards this end, we have generated a series of site-directed mutants based on a revised homology model of Neu3, and tested the resulting mutants for activity. Several arginine-to-alanine point mutations have confirmed the expected catalytic residues of the active site. Also, the pH optimum, kinetics and inhibition of active enzymes by transition-state mimics will be reported. Together, these data will be used to refine our model and guide inhibitor design.

CARB 92

Novel glycosylating agents inspired by Fraser-Reid and applications thereof

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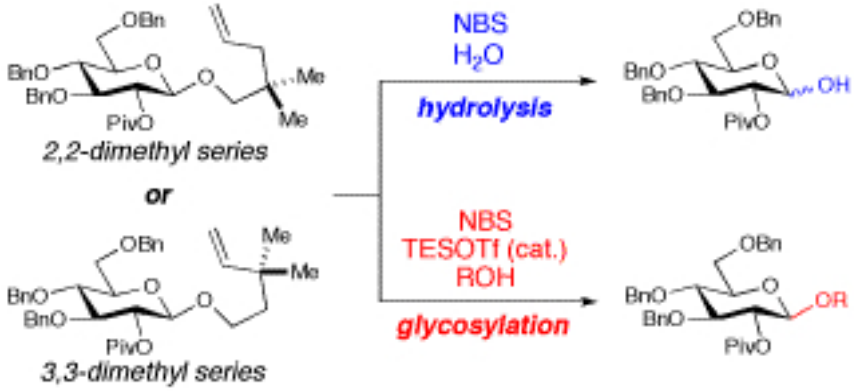
Two classes of gem-dimethyl 4-n-pentenyl glycosides (i.e., C2-series and C3-series) have been prepared and studied in both the glycosylation and hydrolysis manifolds utilizing NBS as the sole stoichiometric activator. These novel glycosylating agents, which are analogues of Fraser-Reid's 4-n-pentenyl glycosyl donors, show increased reactivity in side-by-side studies by virtue of the gem-dimethyl effect. Application of these donors will also be discussed.



CARB 93

Metabolic profiling of *Helicobacter pylori* glycosylation

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Virulence of the gram-negative bacteria *Helicobacter pylori* appears to be directly linked to the pathogen's ability to glycosylate proteins. Although *H. pylori's* glycans are linked to pathogenesis and are targets of therapeutic intervention, *H. pylori's* glycome remains poorly understood. Here we set out to inventory the glycoproteins synthesized by *H. pylori* using a chemical technique termed metabolic oligosaccharide engineering. We demonstrate that treatment of *H. pylori* with the unnatural, azide-containing sugar peracetylated *N*-azidoacetylglucosamine (Ac_4GlcNAz) leads to metabolic incorporation of azides into a large number of N-linked and O-linked glycoproteins. These data suggest that there are far more glycoproteins synthesized by *H. pylori* than the two glycoproteins previously characterized in this organism. Future experiments will be aimed at identifying these novel glycoproteins and the nature of the modifying sugar. This work sets the stage for providing further insights into bacterial glycobiology and the roles of glycans in pathogenesis.

CARB 94

Boronolectins for specific sensing of free sialic acid

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Concentration of the ubiquitous mammalian carbohydrate sialic acid as measured in plasma can be used as an indicator of malignancy in humans and detection of elevated levels of the carbohydrate could provide prompter diagnoses. Reversible boron-hydroxyl interactions can be demonstrated to have greater avidity at a lower pH when binding to α-hydroxyacids as compared to vicinal diols.(1) We will present the activity of a fluorescent boronolectin with specific sensing of free sialic acid that demonstrates a divergent response.(2) Development of boronolectins as well as synthetic methodologies will be discussed. Modification and improvement of carbohydrate binding boronolectins with other targets will also be presented.

(1) Houston, T. A.; Levonis, S. M.; Kiefel, M. J.; *Aust. J. Chem.* **2007**, *60*, 821.
(2) Levonis, S. M.; Kiefel, M. J.; Houston, T. A. *Chem. Commun.* **2009**, 2278.

CARB 95

Investigating carbohydrate-carbohydrate interactions using fluorescent silica nanoparticles

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Silica nanoparticles have been functionalized with carbohydrates using the copper promoted azide-alkyne cycloaddition. The loading of carbohydrates onto these particles has been characterized using a variety of methods, including elemental analysis and a colorimetric assay. The interaction of these particles with carbohydrate binding proteins has been visualized using transmission electron microscopy. The carbohydrate-carbohydrate interactions of these particles with glycolipids assay in microtiter plates have also been investigated.

CARB 96

Structural, kinetic and mutational insights along the reaction coordinate of human UDP-glucose dehydrogenase

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UDP-glucose dehydrogenase (UGDH (EC1.1.1.22)) catalyzes two successive NAD^+ dependent oxidations of UDP-glucose to yield UDP-glucuronic acid combining an alcohol and aldehyde dehydrogenase activity in one catalytic scaffold. The product serves as precursor for cell wall and capsular polysaccharides in bacteria, and in mammals for biosynthesis of glycosaminoglycans like heparin, hyaluronic acid and chondroitin sulphate (1). Inhibition of hyaluronan synthesis has been reported to restrict in vivo tumor growth (2,3). Therefore elucidation of the complex mechanism and detailed knowledge of structure-function relationships provide the tools for specific inhibitor design (1). Protein structures at every important step of the reaction including the trapped intermediate provide unique insights along the reaction coordinate. Separation of the ADH from ALDH reaction using transient kinetics, proton transfer studies and structure-guided site directed mutagenesis are used to dissect and understand the reaction mechanism.

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2. Simpson, M. A., Wilson, C. M., and McCarthy, J. B. (2002) *Am. J. Pathol.* **161**(3), 849-857
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CARB 97

Multiwell hydrogel saccharide sensor arrays

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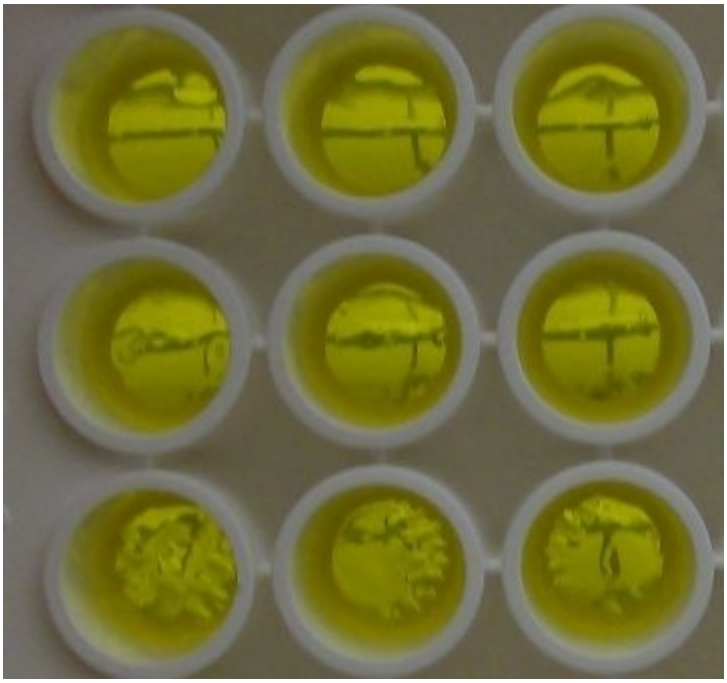
Sensor arrays are a powerful tool for chemical assays and medical diagnostics, but fabrication of sensors often requires laborious techniques and expensive equipment. As a proof of concept, we have developed a method to fabricate fluorescent hydrogel sensors directly in multi-well plates. The redox initiators sodium metabisulfite, potassium persulfate, and ferrous sulfate were used to make hydrogels of N,N'-dimethylacrylamide (DMAA) crosslinked with N,N'-methylenebisacrylamide (MBA) at low pH. The initiator concentrations were optimized to allow rapid polymerization under aerobic conditions and at ambient temperature. Effective gelation protocols included high cross-linking to minimize swelling of the gels and excess metabisulfite to prevent degradation of the fluorophore. Using this technique, functional fluorescent saccharide sensors were rapidly prepared and analyzed by a fluorescence plate reader. The sensors showed good reproducibility and precision in response to solutions of glucose in phosphate-buffered saline at physiological pH.



CARB 98

Novel strategy for neuraminidase inhibitors using mechanism-based probe

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Neuraminidase plays significant role in the infections, pathology, and homeostasis. A potent inhibitor for *Vibrio chorerae* neuraminidase were

developed using a novel two step strategies, a target amino acid validation using mechanism-based labeling reagent and potent inhibitor search using a focused library designed from the labeling information. Unrevealed target amino acid residues around active site were labeled by a suicide substrate of neuraminidase, and a pear of Arg and Asp was picked up by protease digestion followed by MALDI TOF/MSMS analysis of the labeled enzyme. Based on this information, 9-N_3-Neu5Ac2en derivative was designed and prepared a set of focused library by click reaction with alkene library to interrupt the function of the labeled residues, and novel compounds having potent inhibition properties toward *Vibrio chorerae* neuraminidase were founded from the focused library. The novel inhibitor showed selective and most potent inhibition properties among the reported inhibitor for *Vibrio chorerae* neuraminidase.

CARB 99

Neuraminidase substrate specificity studies for influenza viruses using chemoenzymatically synthesized sialosides

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Hemagglutinins (H) and neuraminidases (N) are two types of surface glycoproteins presented by influenza viruses. The viruses rely on the fine balance of the sialic acid-binding property of hemagglutinin and the sialic acid-cleavage power of neuraminidase to optimize infection and spreading in the host. Much attention has been focused on the ligand specificity of hemagglutinins and only limited information is known about the substrate specificity of neuraminidases. To better understand the relationship of ligand specificity of hemagglutinin and substrate specificity of neuraminidase of influenza viruses, a library of *para*-nitrophenol (*p*NP)-tagged sialodisaccharides containing diverse natural and non-natural sialic acid forms and different sialosidic linkages were synthesized using chemoenzymatic approaches. These compounds have been used to study the substrate specificity of neuraminidases of influenza viruses from different hosts using intact viral particles.

CARB 100

Secret life of sugars: Using heteronuclear NMR to unveil molecular motion in carbohydrate TB-antigens

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Carbohydrate function is intimately related to their three-dimensional shapes or conformations; a detailed understanding of these 3D structures is essential to deciphering the underlying factors that control recognition between carbohydrates and antibodies and hence for improving vaccines. Typical carbohydrate NMR spectra show sharp lines, however, it is unknown whether these spectra are the result of a single structure or of several conformations in fast exchange. The complete description of different/several populated states is especially important in delineating the conformations of carbohydrates that can bind to various types of biomolecules; fast exchange between these states complicates effective characterization. Although motion in carbohydrates has been hard to directly detect, we show that hidden conformations can be directly detected using a combination of HMQC and HSQC. In this study, we directly detect motion in the middle portion of hexa- and pentasaccharide TB-antigens. Conformational motion of this type has not been previously reported for carbohydrates. We find this method a fast and reliable tool to investigate dynamics in these carbohydrates without the need to resort to models.

CARB 101

Synthetic proteoglycan mimetics

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Proteoglycans (PG), a special class of carbohydrate polymers, which decorate the outer surface of mammalian cells, consist of a core protein and several glycosaminoglycan (GAG) side chains. GAG chains regulate many important biological processes, including fertilization, cell-cell communication, immune defense, anti-coagulation, angiogenesis, left-right asymmetry, organogenesis, branching morphogenesis, glomerular filtration, axon guidance and growth, among other. Most PGs have multiple polysaccharide chains that play many important roles in various biological processes. We hypothesize that scaffolds containing multiple GAG chains per scaffold can mimic PGs and therefore, can be used to understand the biological roles of PGs. Toward this goal, we designed a library of cluster xylosides that can prime multiple GAG chains and mimic naturally occurring PGs. We present our findings on the synthesis of cluster xylosides and their priming of GAG fine structures.

CARB 102

Fragmentations and rearrangements in the carbohydrate moiety of esperamycins: A possible mechanism of auto-resistance to natural enediynes antibiotics through conformational control?

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The role of carbohydrate moiety in natural enediyne antibiotics of the esperamicine and calchiamicine families was investigated through the design of model enediynes equipped with the carbohydrate mimics. The acetal ring participates in a variety of fragmentations and rearrangements which are initiated by an intramolecular anomeric hydrogen transfer to the *p*-benzyne product of the Bergman cyclization. Depending on the substitution pattern, this radical follows four alternative paths – a) abstraction of an external hydrogen atom, b) O-neophyl rearrangement which transposes O- and C-atoms of the sugar, c) fragmentation of the O—C bond in the acetal ring, or d) loss of the appended acetal moiety as a whole. These processes provide insight into the mechanism of fragmentation of esperamicin A_1 upon its Bergman cycloaromatization and provide a plausible mechanism for resistance to enediyne antibiotics by the enediyne-producing microorganisms.

CARB 103

Development of SL dye displacement assays and exploration of their competitive binding properties

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Boronic acid functionalized peptide based synthetic lectins (SLs) are under trial as dependable and reproducible tools in the detection of cancer. With the ability to bind glycans and glycoproteins in a specific manner, SLs are capable of detecting cancer through abnormal glycan expression patterns, a consequence of aberrant glycosylation. SLs have great potential to be applicable provided that binding properties and other variables are properly investigated and well understood. Previous work has relied on direct labeling of the analyte which is not as advantageous in real world applications. Research to develop competition assays and understand the competitive binding properties between fluorescent dyes and unlabeled analytes will be presented. This is an integral component to developing SLs into application based sensors.

CARB 104

Bioprocess for the conversion of carbohydrates into bioisoprene™

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Metabolic pathway engineering has proven to be a powerful technology for the highly selective conversion of carbohydrates into chemicals and fuels and offers an alternative to traditional petrochemical-based processes. We describe our efforts to develop a fermentation route to BioIsoprene™ (2-methyl-1,3-butadiene), the precursor to synthetic rubber, using an engineered microorganism in an integrated bioprocess whereby the volatile product is continuously recovered from the gas-phase. A crucial aspect of this effort is the optimization of metabolic pathways that deoxygenate carbohydrate substrates, leading to the 5-carbon isoprenoid precursor 3,3-dimethylallyl pyrophosphate (DMAPP), which is then subsequently converted to BioIsoprene™ in a reaction catalyzed by the enzyme isoprene synthase. Overall, our process highlights the potential for conversion of carbohydrates to valuable chemicals using a combination of biological and process engineering.

CARB 105

Stable isosteres of thio sugar templates as the new targets for galectin-3 inhibitors

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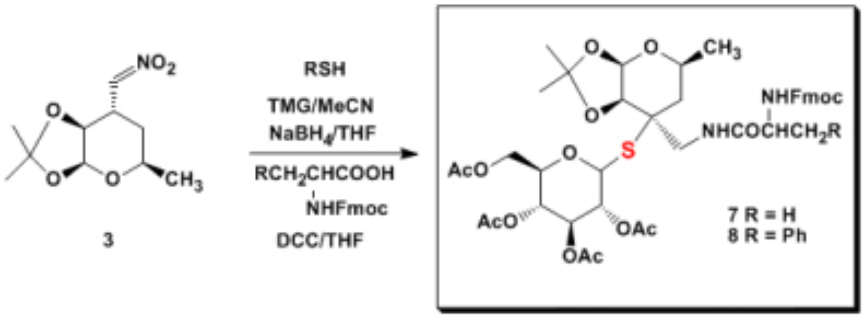
The development of new strategy for non-hydrolysable and enzymatically stable C-C- and C-S bond forming carbohydrate reactions is of fundamental importance in bioorganic chemistry and glycobiology in particular. We have developed a newest coupling reaction of functionalized new class of reactive enones, represented by enone **3** with reactive carbohydrate thiol in the presence of a catalytic amount of triethylamine, piperidine or teramethyl guanidine (TMG) in polar solvent systems MeCN, THF. The regiochemistry of the Michael addition steroselectively produced 1,4 adduct. The adduct, upon the conventional borohydride reduction, affords free amine which undergoes coupling with amino acids such as alanine and phenylalanine to produce the first representatives of a new family of non-hydrolysable glycosyl thio-carboamino peptides **7-8.**



Further examples of selected active carbohydrate thiols as substrates for Michael addition with nitroenone **3** and their application of the resulting coupling approach to produce new analogs of thio-carboaminopeptides as new tools for glycobiology specifically as new inhibitors of galectin-3 will also be discussed.

CARB 106

Preparation and physical properties of starch stearates of low to high degree of substitution

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Starch stearates of degree of substitution (DS) 0.07-2.40were prepared by heating dry starch and vinyl stearate in the ionic liquid BMIM dca at 75 ^{o}C. Starch stearates of low and high DS swelled and formed gels in water and hexane, respectively. Starch stearate films had water contact angles of 84-93^{o}, indicating very hydrophobic surfaces. X-ray diffraction and DSC of DS > 0.6 indicated some short-range crystallization of the stearate side chains. Optical birefringence was noted at moderate to high DS, suggesting liquid crystal formation. Starch stearates of DS ~;0.6 showed intense birefringence resembling starch granules in DMSO while cholesteric liquid crystalline behavior was observed in toluene (reflected blue light). Blue light reflection disappeared on heating to >60-80 ^{o}C then reformed on cooling. These results suggest that starch stearates have some interesting structural ordering and have potential applications as water absorbents, hydrocarbon/oil absorbents, water resistant coatings and liquid crystalline materials.

CARB 107

Study cellulase-cellulose interaction using FRET

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Förster resonant energy transfer (FRET) is a spectroscopic tool capable of determining the molecular distances and the presence of molecular complexes. By using a pair of appropriate fluorophores, the FRET phenomenon can be used as an analytical tool to probe molecular interactions between molecules usually between 1-10 nm. In our initial study, a water soluble cellulose derivative – carboxymethyl cellulose (CMC) was employed with cellulase as a model system for subsequent liquid/solid systems. FRET technique was for the first time applied to study the cellulase-cellulose interaction upon efficient labeling of CMC in organic solvent. After the mixing of labeled- cellulase and CMC conjugates, FRET phenomena were successfully observed in homogeneous aqueous solution via steady-state fluorescence spectroscopic method. The temperature dependence of cellulase binding to CMC was revealed by the experiment results. This developed method could be used for further investigation of cellulase-cellulose interaction in liquid phase.

CARB 108

Indicators of Maillard polymer formation in commercial moist snuff products

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Maillard polymers formed from the reactions of ammonia and its compounds with endogenous and/or added sugars in cigarette tobaccos are well known as important flavor precursors that yield flavorful nitrogen heterocyclic compounds on pyrolysis. However, a similar situation would not be expected to occur in moist snuff products. We have now found marker compounds for such polymers in commercial product. Possible mechanisms and importance of these polymers to toabcco regulatory efforts will be discussed.

CARB 109

Interaction of cellulase enzymes with amorphous and crystalline cellulose

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We are studying the binding and activity of cellulase enzymes on amorphous and crystalline cellulose, with an emphasis on cellulose that has been treated with

ionic liquids. The experimental methods include fluorescence imaging in confocal and total internal reflection geometries, quartz crystal microbalance, and neutron reflectivity. These methods are being used to study the interaction of cellulose binding domains (CBDs) with amorphous and crystalline cellulose, and also to test proposed mechanisms of synergy between endoglucanases and exoglucanases. A particular point of emphasis, motivated by the use of ionic liquids for biomass pretreatment at the Joint Bioenergy Institute, is to examine the effects of residual ionic liquid on the abovementioned phenomena.

CARB 110

Enzymatic modification and characterization of pectin nanostructure

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To be Emailed on Friday

CARB 111

Sugar, salt and sugar, salt-water complexes: Structure and dynamics

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Molecular Dynamics (MD) simulations are carried out for complex of glucose with KNO_3 and complexes of glucose – KNO_3 - $(H_2O)n$ (n <= 11). Structure and dynamic properties of the systems are explored with DLPOLY / OPLS force field, and minimum energy structures of some of the systems are compared with ab initio MP2 calculations. Main findings include: (1) Complexation with KNO_3 leads to “inverse anomeric effect”: β-glucose complex more stable than α-glucose by ~; 1.74 Kcal/mol. (2) For n>=3 water molecules added to the system, charge separation into ions takes place. (3) For n=11 water molecules, glucose adopts surface position at the water cluster. (4) DLPOLY structure predictions compare well with those from ab-initio MP2, but fail in energy-ranking of conformers. Implications of effects of salts on saccharides are discussed.

Aknowledgment: This work was supported by a grant from the U.S. DOE, Office of Science Program, contract DE-FG02-09ER64762.

CARB 112

Viscous dietary fibers as part of a healthy diet for the prevention and control of coronary heart disease and diabetes

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Viscous fiber has been shown to decrease the glycemic index of the diet and to have cholesterol-lowering effects. We have conducted a large study evaluating the effectiveness of dietary advice to follow a low glycemic index (GI)-high viscous fiber diet in diabetes. The high fiber-low GI diet significantly improved glycemic control and decreased cornoary heart disease (CHD) risk factors. These data indicate that a high fiber-low GI diet can have a clinically significant effect on diabetes control. The National Cholesterol Education Program (NCEP) ATP Panel III recommends viscous fibers (10-25g) and the FDA permits health claims for CHD risk reduction for foods contining viscous fibers, soy protein, nuts and plant sterols. We have found that a combination of cholesterol-lowering foods (dietary portfolio) could acheive 30% reductions in LDL-C, similar to that obtained with a statin. Under 'real world' conditions, approximatley one third of individuals maintained LDL-C reductions of 20%.

CARB 113

Towards the identification of ionic liquids that stabilize cellulases for sachharification of cellulosic biomass

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The highly crystalline structure of cellulose is a barrier to enzymatic hydrolysis in the fermentation of biomass to sugars. To increase enzyme accessibility, we are exploring the use of ionic liquids (IL), in the pretreatment of cellulosic biomass. Significant decreases in cellulase activity in the presence of trace amounts of IL's have been reported in the literature, necessitating extensive processing to remove IL's. Thus it is necessary to develop cellulases that are stable and active in the presence of IL's. Towards that goal, we are investigating the stability of extremophilic enzymes, for use with the IL, 1-Ethyl-3-methylimidazolium acetate and its variants. Herein, we show a comparison of the enzymatic efficiency between the commercially available *T. viride* cellulase from Sigma and the endoglucanase from the hyperthermophilic bacterium *Thermatoga maritima* (*Tma*

cellulase) and the differences related to biochemical properties of the enzymes and the identities of the cation and anion in IL's.

CARB 114

Study on the chiral separation of some flavonoids with rhizobial oligosaccharides

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Bacteria within the *Rhizobiaceae* family can produce various cyclooligosaccharides and non-cyclioooligosaccharides. Among them, cyclic β-1,3-1,6-glucans, produced by *Bradyrhizobium*, are branched cyclic glucans and consist of 10 to 13 glucose residues linked by both β-1,3 and β-1,6 glycosidic linkage. *Sinorhizobium meliloti* produces low-molecular-weight (LMW) succinoglycan, composed of monomers, dimers, and trimers of the succinoglycan octasaccharide. More-detailed analyses of the LMW fraction of succinoglycan showed that there is a considerable heterogeneity according to the succinate moiety among noncabohydate substituents such as acetyl, pyruvate, and succinate. These cyclo- or noncyclooligosaccharides were purified from rhizobial species to investigate the chiral separation of some flavonoids. Cyclic β-1,3-1,6-glucans, produced by *B. japonicum* USDA 110 and linear succinoglycan octsaccharides, produced by *S. meliloti*, were effectively used for the chiral separation of various flavonoids such as eriodictyol, homoeriodictyol, hesperetin, naringenin, catechin and isosakuranetin in capillary electrophoresis (CE) or nuclear magnetic resonance (NMR) spectroscopic analysis. Particularly, sinorhizobial linear octsaccharides were firstly used for the successful chiral separation where succinylation of sinorhizobial octsaccharides is a decisive factor for the effective chiral separation. This study indicates that rhizobial noncyclooligosaccharides as well as cyclic ones can be successfully used as an effective chiral selector for the chiral separation of some flavonoids, suggesting the significance of the molecular interactions between flavonoids and rhizobial oligosaccharides as well as biotechnological applications for chirotechnology.

CARB 115

Effort towards the development of synthetic carbohydrate-based vaccine

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Development of fully synthetic carbohydrate-based vaccines becomes a promising and exciting new research focus. Recently, considerable efforts have been directed toward design, synthesis and clinical evaluation of carbohydrate-based vaccines against microbial pathogens and cancers. Organic synthesis has

clearly emerged as a key force in providing sufficient, pure, and structurally well-defined natural/unnatural carbohydrates for research and biomedical applications. Herein, we demonstrate our efforts in developing a simple, facile, and cost-effective glycosylation method for rapid access to biologically important carbohydrate antigens. We will also demonstrate the application of this new glycosylation method in the synthesis of the saponin immune adjuvant, another important component of our multi-component fully synthetic carbohydrate-based vaccine design.

CARB 116

Glycosylation using alkynyl donors

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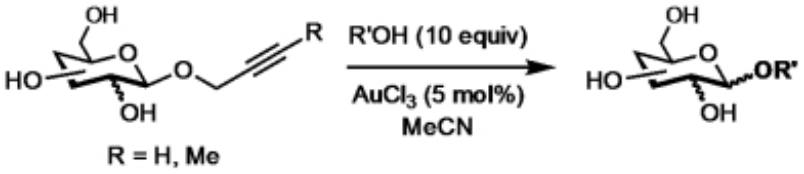
Gold (III) activation of unprotected propargyl glycosyl donors has been shown to be effective for the synthesis of saccharides. When heated in the presence of 5% $AuCl_3$, terminal propargyl glycosides of glucose, galactose, and mannose reacted cleanly with various primary alcohol acceptors, the latter used in 10-fold molar excess relative to donor. Donors containing the 2-butynyl group were more reactive, giving good yields of glycoside products at lower temperatures. Secondary alcohols could also be used but with diminished efficiency. The propargylic family of donors is especially convenient because they can be easily prepared on large scale by Fischer glycosylation and stored indefinitely before chemoselective activation by the catalyst.



CARB 117

Synthesis and characterization of polyesters derived from linear sugar alcohols and citric acid

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The thermal polycondensation of polyols and polyacids (functionality ≥ 2) has become a popular method for synthesizing polyesters for biomedical applications. Compared to other synthetic methods, thermal polycondensation is straightforward and inexpensive. Additionally, this technique, which needs no catalysts or co-reagents, allows for the use of naturally occurring metabolites as monomers. One particular class of potential monomers, sugar alcohols, is

attractive due to their high concentration of hydroxyl groups per molecule. By polymerizing linear sugar alcohols with citric acid, a series of polyester thermosets have been developed that exhibit a wide range of mechanical and physical properties. However, unlike some other similarly developed polyesters, the number of hydroxyl groups per sugar alcohol molecule allow for these materials to achieve large Young's modulus and ultimate tensile stress values. Due to the strength of the poly(sugar alcohol citrate) series, we believe that they may suitable for biomedical applications requiring hard, rigid materials.

CARB 118

Synthesis and metal-catalyzed decomposition of furanose-derived diazoesters

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Treatment of phenylacetyl esters of various furanoses with arylsulfonyl azides and base results in either diazo transfer or azidation depending upon the site of acetylation. Subsequent metal-catalyzed decomposition of the diazoesters results in the products of intramolecular insertion, dimeric ether formation, or intramolecular trapping by an azide group. The azidation process has been studied in detail and now offers a useful alternative to azidodeoxysugar synthesis without having to use a metallic azide such as NaN_3.

CARB 119

Nucleosides with 1,4-dioxane as sugar moiety

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A wide variety of six-membered nucleosides and nucleotides have been reported over the years. We here report the synthesis of nucleosides with 1,4-dioxane as sugar moiety. Synthesis of the corresponding H-phosphonates allowed incorporation into oligonucleotides and evaluation of their effect on duplex stability and geometry.

CARB 120

Synthesis of a "clickable" GPI anchor

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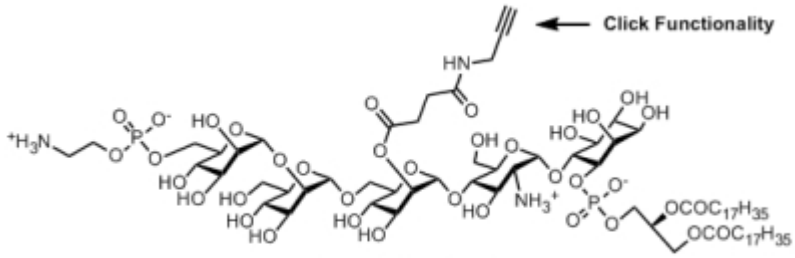
Although much progress has been made in the field of glycosylphosphatidylinositol (GPI) synthesis, the current standard for global

hydroxyl protection, the benzyl ether, prevents the incorporation of functional groups that are intolerant to catalytic hydrogenation, such as alkenes, alkynes, thiols, sulfides, etc. To overcome this limitation, we have developed a synthetic strategy that employs th *para*-methoxybenzyl (PMB) ether as the global protecting group. As a representative example of the utility of this method, the synthesis of an alkyne-functionalized GPI anchor is discussed.



Clickable GPI Anchor (**1**)

CARB 121

Synthesis of carbohydrate-porphyrins conjugates via palladium-catalyzed cross-coupling approach

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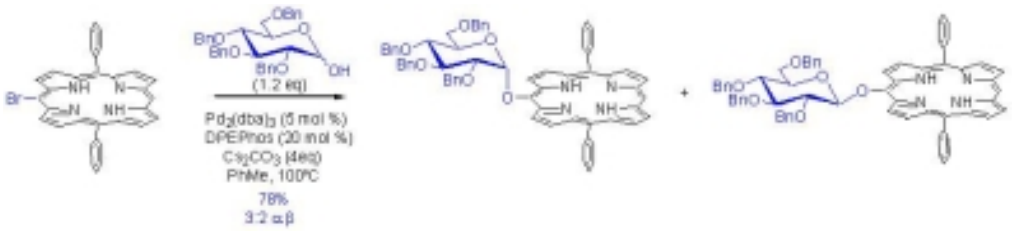
The recent development of palladium-catalyzed cross-coupling reactions between mono-, di-, and tetrasubstituted bromo-porphyrins and amides, amines, alcohols, and thiols has allowed for the preparation of a number of chiral porphyrin analogs. Metalated derivatives of these chiral porphyrins have been used to catalyze a number of key functional group transformations with good diastereo- and enantioselectivity. Despite the progress that has been made in the development of these catalysts, two key problems still exist. First, the hydrophobic nature of the porphyrin ring makes these systems insoluble in most polar solvents, limiting substrate scope. In addition, the aromatic nature of the porphyrin ring facilitates pi stacking with some existing porphyrin catalysts, resulting in aggregation and decreased turnover. In an effort to address these problems, we have started synthesizing novel porphyrins bearing carbohydrate residues using a palladium-catalyzed cross-coupling approach. Here we present the preliminary results of our research.



CARB 122

Carbohydrate *C*-glycoside ketones: Introducing ketone chemistry into locked-ring aldose sugars

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Chemical modification of aldose sugars at the anomeric position typically results in ring opening, and therefore the loss of structural integrity of the parent sugar molecule. This produces modified carbohydrates that differ markedly from the parent molecule. The research presented here focuses on development of new carbohydrate “locked-ring” *C*-glycosides and the subsequent formation of functionalized ketohydrazones and oximes. This chemistry is accomplished using an aqueous-based, one-pot strategy that involves first converting the sugar to a *C*-glycoside ketone, followed by conversion to hydrazones or oximes. Activation of the anomeric center and protecting group manipulations are not required and the chemistry is mild enough for a wide range of carbohydrates, producing a variety of functionalized *C*-glycosides that retain the closed ring conformation of the parent sugars. Using standard hydrazide/oxime chemistry the *C*-glycoside ketones can be tagged with fluorescence, colored, cationic, alkyl, or biotin-labeled groups, or immobilized onto hydrazine-functionalized beads.

CARB 123

Kinetic study of oxidation of Glucose by N-bromophthalimide in the presence of ruthenium(III)chloride

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Carbohydrates are important biological substances whose microbiological and physiological activities depend largely on their redox behavior . The study of carbohydrates is one of the most exciting fields of organic chemistry. Vast literature is available on the kinetics of oxidation of carbohydrates by various organic and inorganic oxidants.D-Glu is a monosaccharide with wide synthetic

applications and plays an active role in biological system. Oxidation of D-Glu is of great importance both from chemical and biological point of view. Considering its importance for life on earth, the reaction involving carbohydrates are of considerable interest . Kinetics of oxidation of D-glucose (D-Glu) by N-bromopthalimide (NBP) in presence of chloro complex of Ru(III) as a homogenous catalyst in perchloric acid medium has been investigated. The kinetic results indicate that the reaction was first order on [NBP] and zero order on [D-Glu]. The reaction followed first-order kinetics with respect to Ru(III) chloride in its lower concentration range and tends to zero-order at its higher concentration. Negative effect of [H^+] and [Cl^-] ion on the rate of oxidation were observed whereas change of ionic strength (μ) of the medium had no affect on the oxidation velocity. The values of rate constants observed at five different temperatures were utilized to calculate the activation parameters. Formic acid and Arabinonic acid have been identified as the main oxidation products of the reaction. A plausible mechanism from the results of kinetic studies, reaction stoichiometry, and product analysis has been proposed.

CARB 124

Study of Hantzsch synthesis reaction in the preparation of a novel dihydropyridine C-glycosylated compound

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1, 4 Dihydropyridines (1, 4-DHPs) have received much attention because of their wide range of pharmaceutical and biological properties such as antiviral, antibacterial, and antitumor effects.[1] The original Hantzsch synthesis has been widely used for the preparation of the 1,4 dihydropyridines and the components bearing different pharmacophoric groups have been used in Hantzsch cyclocondensation. The synthesis of glycosylated heterocycles by using carbohydrate-based reagents as components in cyclocondensations would allow the assembly of the heterocyclic core nucleus and its functionalization with sugar moieties simultaneously in the cyclocondensation step[2] .The use of a designed sugar components in some of the possible combinations in Hantzsch synthesis would lead to a collection of artificial C-nucleosides.[3] In this work we firstly planned to place the aldehyde functional group at the anomeric position of the sugar in order to display the carbohydrate moiety. As a result 6-methoxy-2, 2-dimethyltetrahydrofuro [3, 4-d] [1, 3] dioxole-4-carbaldehyde was synthesized. Then we examined the first step of three-component reaction by using the synthesized sugar aldehyde and ethyl acetoacetate to give the enone product which in turn reacted with enamine. The structural assignments of the synthesized compounds were based on elemental analysis, IR, ^{1}H NMR, ^{13}C NMR spectroscopy.