

## ST-Carbohydrate Chemistry

Chemistry 459

Section: D100

Term: 2001 Fall

Instructor: Dr. B. M. Pinto. Office SSB-8140.

Discussion Topics: General Course Description:

A detailed treatment of the structure and reactions of monosaccharides, the use of carbohydrates as chiral templates in organic synthesis, advances in glycoside synthesis, the occurrence, chemistry, and conformational analysis of complex carbohydrates and their roles in biological systems.

3 one hour lectures per week. In addition, graduate students will present seminars at night.

Topics:

### 1. Introduction

#### 1.1 Biological Recognition Events Mediated by Carbohydrates

#### 1.2 Glycobiology and Glycochemistry

### 2. Structures, Conformations, and Solution Behaviour of Monosaccharides

#### 2.1 The Structure of Glucose

#### 2.2 Interrelationships of the Monosaccharides

#### 2.3 Molecular Shapes of Sugars and Related Compounds

#### 2.4 Equilibria of Sugars in Aqueous Solution

### 3. Reactions and Products of Reactions at the Anomeric Centre

#### 3.1 Reactions with Alcohols-Glycosides

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3.2 Reactions with Sulfur Nucleophiles-Thioacetals and Thioglycosides

3.3 Reactions with Nitrogen Nucleophiles-Glycosylamines, Oximes, Hydrazones and Osazones

3.4 Reactions with Carbon Nucleophiles

3.5 Reductions to Alditols

3.6 Oxidations to Aldonic and Aldaric Acids

3.7 Reactions with Bases

3.8 Reactions with Acids

3.9 Reactions with Glycosyl Esters, Orthoesters, and Glycosyl Trichloroacetimidates

3.10 Properties and Reactions of O-Protected Glycosyl Halides

4. Reactions and Products of Reactions at Non-anomeric Carbon Atoms

4.1 Nucleophilic Displacement of Leaving Groups

4.2 Opening of Epoxide Rings

4.3 Deoxy Sugars

4.4 Amino Sugars

4.5 Thio Sugars

4.6 Deoxyhalogeno Sugars

4.7 Anhydro Sugars

4.8 Other Intramolecular Displacements

4.9 Branched-chain Sugars

4.10 Dicarbonyl Compounds-Ascorbic Acid, KDO, N-Acetylneuraminic Acid

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### 4.11 Unsaturated Sugars-Glycal Synthesis and Reactions

## 5. Reactions and Products of Reactions of the Hydroxyl Groups

### 5.1 Relative Reactivities of the Hydroxyl Groups

### 5.2 Ethers

### 5.3 Esters

### 5.4 Acetals

### 5.5 Oxidative Cleavage

## 6. Chemical and Enzymatic Synthesis of Oligosaccharides

### 6.1 General Features: Glycosyl Acceptors and Donors; Promoters and Catalysts

### 6.2 New Advances in Chemical Synthesis

### 6.3 Control of Reactivity with Protecting Groups-The Armed/Disarmed Approach

### 6.4 Control of Reactivity with Promoters

### 6.5 Control of Reactivity with Different Donors-Selective Activation Strategies

### 6.6 Enzymatic Synthesis with Glycosyl Transferases and Glycosidases

### 6.7 Solid-Phase Chemical and Enzymatic Synthesis

## 7. Synthesis of Enantiomerically Pure Non-carbohydrate Compounds from Monosaccharides

### 7.1 Carbohydrates as Chiral Auxiliaries

### 7.2 Conversions of Carbohydrates into Non-carbohydrates

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### 8. Conformational Analysis of Oligosaccharides

8.1 Conformational Effects: Anomeric and Exo-Anomeric Effects, Gauche Effects, and Perlin Effects

8.2 Computational Methods—Molecular Mechanics, Molecular Dynamics, and Monte Carlo Calculations

8.3 Experimental Methods—NMR Spectroscopy, X-ray Crystallography

8.4 Combined Experimental/Theoretical Protocols

8.5 Conformations of Oligosaccharides Bound to Protein Receptors -- Transferred NOE NMR Spectroscopy and X-ray Crystallography

### 9. Natural Products Related to and Containing Monosaccharides

9.1 Oligosaccharides

9.2 Blood Group Substances

9.3 Oligosaccharines—Plant Growth Regulators and Defense Agents

9.4 Polysaccharides

9.5 Glycoproteins, Proteoglycans, Glycolipids, Lipopolysaccharides

9.6 Other O-Glycosides

9.7 N-Glycosides—Nucleosides, Nucleotides, Nucleic Acids

9.8 S-Glycosides

9.9 C-Glycosides

9.10 Cyclitols

9.11 Aminoglycoside and Amilocyclitol Antibiotics

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10. Biosynthesis of Glycoproteins, Glycolipids, Lipopolysaccharides, Cellulose, Hemicellulose, Lignin, Tannins, Glycosaminoglycans, Deoxysugars

Note: Some of the above topics will be covered by graduate student seminars.

Grading: 40% Midterm Exam

60% Final Exam

Required Texts: P. M. Collins & R. J. Ferrier, "Monosaccharides; Their Chemistry and Their Roles in Natural Products". 1st Ed. 1995. John Wiley & Sons.

Recommended Texts: None

Materials/Supplies: None

Prerequisite/Corequisite: Chem 380(357), or permission of the Instructor.

Notes: None

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