Sugars and Polysaccharides

Monosaccharides

Polysaccharides

Glycoproteins

Monosaccharides
(simple sugars)

Classification
monosaccharides are classified according to the chemical nature of the carbonyl group and # of C atoms

aldose - aldehyde
ketose - ketone

triose - 3
tetrose - 4
pentose - 5
hexose - 6
heptose - 7

D-sugars same absolute configuration as
D-glyceraldehyde based on asymmetric center farthest removed from carbonyl group

Monosaccharides

Configuration and conformation

Hemiacetals and hemiketals - result of alcohols reacting with aldehydes and ketones

Fischer projections

Haworth projections

pyranose (pyran)

furanose (furan)

anomers - anomeric carbon

α configuration - OH group at anomeric carbon is on opposite side of sugar ring from the CH_2OH group on the chiral center

β configuration - OH group at anomeric carbon is on same side of sugar ring as the CH_2OH group on the chiral center

mutarotation - interconverts α and β forms

boat and chair - axial and equatorial group interactions determine free energy of molecule

Monosaccharides

Sugar derivatives
Chemistry of monosaccharides is largely that of their hydroxy and carbonyl groups
Anomeric hydroxyl group condenses with alcohol to form α- and β-glycosides
Polysaccharides held together by glycosidic bonds between monosaccharide units
Reducing sugars have anomeric carbons that are not involved in glycosidic bonds

Aldonic acid - oxidation of aldehyde group to carboxylic acid (i.e., gluconic acid)
Uronic acids - oxidation of primary alcohol group to carboxylic acid (i.e., glucuronic acid)
Aldaric acids - oxidation of both aldehyde and primary alcohol groups (i.e., glucaric acid)

Alditols - reduction of carbonyl group of aldose or ketose to form polyhydroxyl alcohols (i.e., glucitol)

Deoxy sugars - OH group replaced by H

Amino sugars - one or more OH groups replaced by amino group, sometimes acetylated (i.e., glucosamine)

Polysaccharides
(glycans)

homopolysaccharides - glucans
heteropolysaccharides
May form branched as well as linear chains

Carbohydrate analysis
Purification by chromatography and electrophoresis
Affinity of proteins for carbohydrates - lectins

concanavalin A binds α-D-glucose and α-D-mannose residues
agglutinin binds β-*N*-acetylmuramic acid and α-*N*-acetylneuraminic acid

Methylation analysis used to determine monosaccharide linkages - methyl esters not at the anomeric carbon are resistant to acid hydrolysis but glycosidic bonds are not

Periodic acid oxidation cleaves C-C bond between diols (forms dialdehydes, releases formate from anomeric carbon)

Exoglycosidases - specifically hydrolyze corresponding monosaccharides from nonreducing end of oligosaccharides (i.e., β-galactosidase, α-mannosidase)
Endoglycosidases - specifically hydrolyze glycosidic bonds between nonterminal sugar residues

Polysaccharides

Disaccharides

Sucrose - *O*-α-D-glucopyranosyl-(1 → 2)-β-D-fructofuranoside (nonreducing sugar)

Lactose - O-β-D-galactopyranosyl-(1 → 4)-D-glucopyranose (reducing sugar)

Maltose - *O*-α-D-glucopyranosyl-(1 → 4)-D-glucopyranose

Isomaltose - *O*-α-D-glucopyranosyl-(1 → 6)-D-glucopyranose

Cellobiose - *O*-β-D-glucopyranosyl-(1 → 4)-D-glucopyranose

Polysaccharides

Structural polysaccharides: cellulose and chitin

Cellulose - primary structural component of plant cell walls, accounts for over half of the biosphere carbon!
up to 15,000 D-glucose residues, β(1 → 4) linkage
(specific microorganisms have enzymes to cleave linkage)

Chitin - principle structural component of exoskeleton of invertebrate, also present in cell wall of fungi and algae
homopolymer of *N*-acetyl-D-glucosamine, β-(1 → 4) linkage
similar structure as cellulose

Polysaccharides

Storage polysaccharides: starch and glycogen

Starch - storage polysaccharide of plants
mixture of glucans, α-amylose and amylopectin

α-amylose - linear polymer of n X 1000 glucose residues, α(1 → 4) linkage, structure different from cellulose
amylopectin - up to 10^6 glucose residues, α(1 → 4) and branching α(1 → 6) linkages (every 24-30 residues)
specific enzymes involved in digestion of starches

Glycogen - storage polysaccharide of animals

similar to amylopectin, α(1 → 4) and branching α(1 → 6) linkages (every 8-12 residues)
specific enzymes involved in processing glycogen

Polysaccharides

Ground substance is a gel-like matrix supporting connective tissue and is composed of:

Glycosaminoglycans = mucopolysaccharides

Hyaluronic acid - D-glucuronate and *N*-acetyl-D-glucosamine, β(1 → 3) linkage

Chondroitin-4-sulfate - D-glucuronate and *N*-acetyl-D-galactosamine-4-sulfate, β(1 → 3) linkage

Chondroitin-6-sulfate - D-glucuronate and *N*-acetyl-D-galactosamine-6-sulfate, β(1 → 3) linkage

Dermatan sulfate - L-Iduronate and *N*-acetyl-D-galactosamine-4-sulfate, β(1 → 3) linkage

Keratan sulfate - D-galactose and *N*-acetyl-D-glucosamine-6-sulfate, β(1 → 4) linkage

Heparin - D-Iduronate-2-sulfate and *N*-sulfo-D-glucosamine-6-sulfate, α(1 → 4) linkage

Glycoproteins

Protein covalently attached to carbohydrate
Variable carbohydrate content

Proteoglycans

Protein plus covalently and noncovalently associated glycosaminoglycan

Basic structure - hyaluronic acid backbone noncovalently linked (stabilized by link protein) to core protein, which is covalently linked to glycosaminoglycans (often keratan sulfate and chondroitin sulfate)

Three regions to glycosaminoglycan portion:

1. N-terminal segment, relatively few chains, covalently linked to core protein Asn residues
2. Oligosaccharide rich segment, keratan sulfate chains, covalently linked to core protein Ser and Thr residues
3. C-terminal region, rich in chondroitin sulfate, covalently linked to core protein Ser residues through Gal-Gal-Xyl trisaccharides

Glycoproteins

Bacterial Cell Walls

Gram-positive - ~250 Å
Gram-negative - ~30 Å

Peptidoglycan (murein) - covalently linked polysaccharide and polypeptide chains

linear chains, alternating β(1 → 4)-linked *N*-acetylglucosamine (NAG or GlcNAc) and *N*-acetylmuramic acid (NAM or MurNAc)

NAM's lactic acid residue amide bond to D-amino acids (resistant to proteases)

Penicillin binds and inactivates cross-linking enzymes

Gram positive surfaces have teichoic acids

Gram negative have unusual polysaccharides (O-antigens)

Glycoproteins

Glycoprotein Structure and Function
Almost all secreted and membrane-associated eukaryotic proteins are glycosylated

N-linked

NAG (GlcNAc) β-linked to amide N of Asn in peptide sequence Asn-X-Ser or Asn-X-Thr, where X = any amino acid (save Pro or Asp)
Core saccharide sequence = $(Man)_3$-$(NAG \text{ or } GlcNAc)_2$

O-linked

Disaccharide core β-galactosyl-(1 → 3)-α-*N*-acetylgalactosamine α-linked to OH of Ser or Thr