

Carbohydrates- Chapter 8

•Introduction and definition monosaccharides

- Aldoses and Ketoses
- Cyclic glycosyl residues, Haworth Projections
- Modified monosaccharides
- Glycosidic bond
- Disaccharides
- Polysaccharides
- Peptidoglycans
- Proteoglycans
- Glycoproteins

•Individual monomeric units are called
_____ (CH₂O)_n where n≥3

- _____ (contain 2-20 monosaccharides)
_____ (two linked monosaccharides)
- _____ (> 20 monosaccharides)
- pure mono- & disaccharides are water-soluble,
colorless in solution & sweet
- _____ : aldoses & ketoses

Carbohydrates

- * _____ organic molecule on earth
- * _____ (or yield these upon hydrolysis)
- * _____ : energy storage (glycogen, starch)
metabolic intermediates (ATP, coenzymes)
part of DNA & RNA
structural elements in cell walls of bacteria,
fungi & plants
exoskeleton of arthropods
extracellular matrix of animals
cell-cell communication/signalling

_____ : carbohydrate polymer

_____ : carbohydrate derivative where
carbohydrate(s) are linked to a peptide, protein or
lipid (i.e. **proteoglycans, peptidoglycans,**
glycoproteins, glycolipids)

_____ : study of role of glycans and
glycoconjugates in living organisms

Enantiomers: compounds with the same molecular formula but different spatial arrangement of their atoms

D & L sugars differ only in steric arrangement of atoms about central C. They are non-superimposable mirror images (i.e. enantiomers)

They differ in orientation of the crystals, in directions in which solutions rotate polarized light, and in selectivity of reaction with other asymmetric molecules

Fig 8.2 Stereo view of L- and D-glyceraldehyde

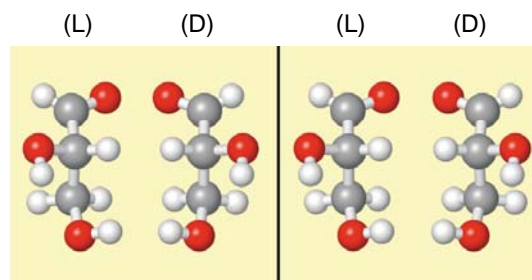
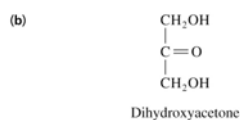
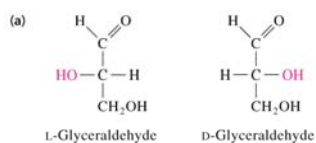


Fig 8.1 Fischer projections of: (a) L- and D-glyceraldehyde, (b) dihydroxyacetone



<u>N (# of Cs)</u>	<u>Name</u>	<u>Example</u>
3	triose	
4	tetrose	
5	pentose	
6	hexose	

For sugars with >1 asymmetric (chiral) carbon, D & L refer to chiral C furthest from aldehyde (or ketone) & correspond to D & L glyceraldehyde

of stereoisomers = 2^n where n = # of chiral C's

Diastereomers: stereoisomers that differ in configuration at only one chiral center

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Fig. 8.3 (aldoses continued)

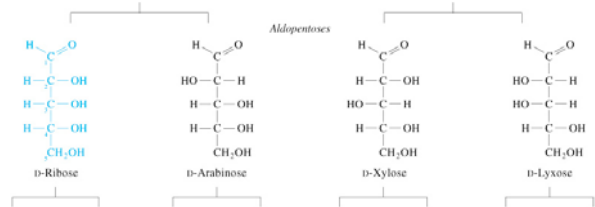


Fig. 8.3 Structure of the 3-6 carbon D-aldoses
(blue are the most common)

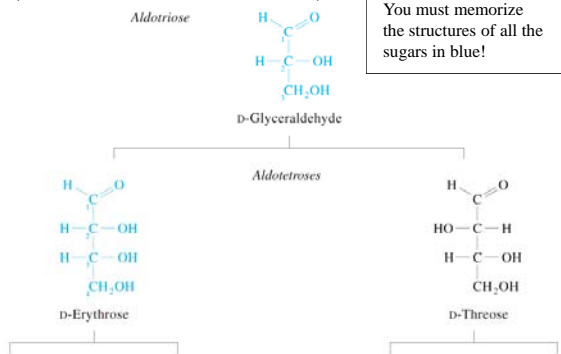


Fig 8.3 (aldoses continued)

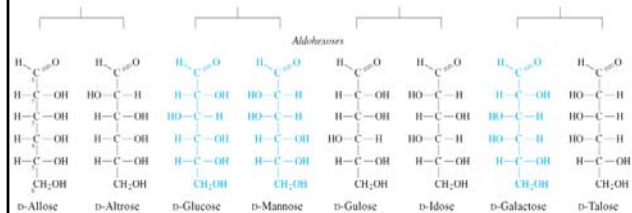


Fig 8.5 Fisher projections of the 3 to 6 carbon **D-ketoses** (blue structures are most common)

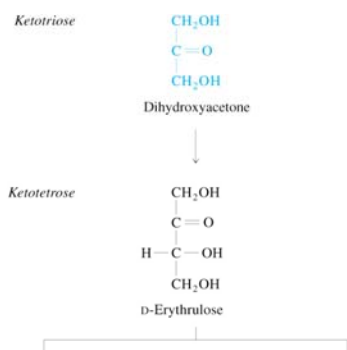


Fig 8.5 (ketoses continued)

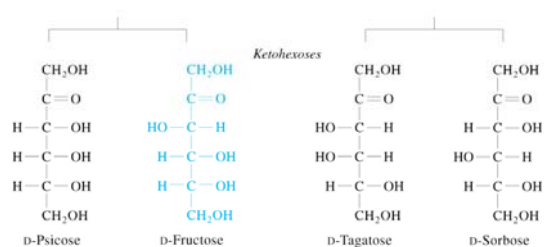
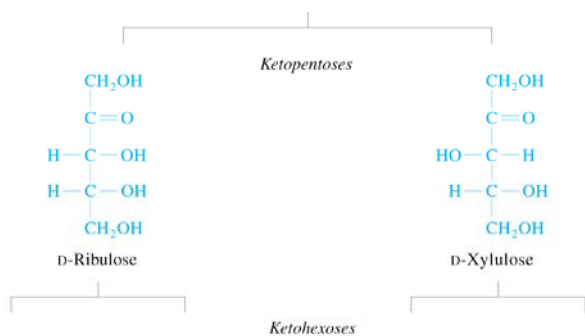


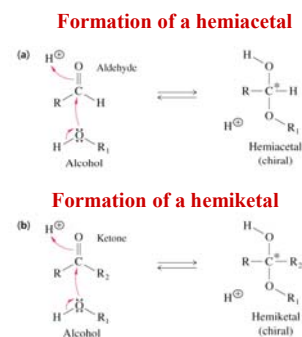
Fig. 8.5 (ketoses continued)



8.2 Cyclization of Aldoses and Ketoses

Fig. 8.6 Reaction of an alcohol with:

- (a) An aldehyde to form a hemiacetal
- (b) A ketone to form a hemiketal



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Fig 8.8 Cyclization of D-glucose to form glycopyranose

- Fischer projection (top left)
- Three-dimensional figure (top right)
- C-5 hydroxyl close to aldehyde group (lower left)

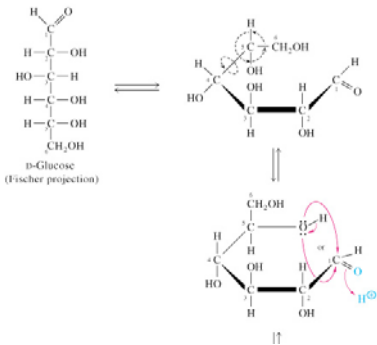
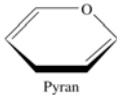


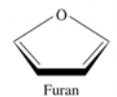
Fig 8.7 (a) Pyran and (b) Furan ring systems

(a)



(a) Six-membered sugar ring is a “_____”

(b)

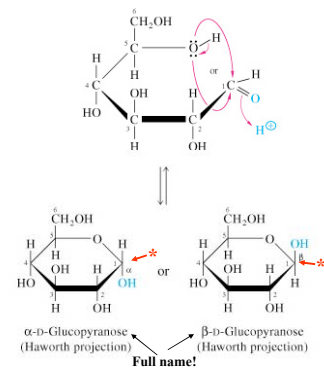


(b) Five-membered sugar ring is a “_____”

Fig. 8.8 (cyclization of D-glucose, continued) Haworth Projection

- Reaction of C-5 hydroxyl with one side of C-1 gives α , reaction with the other side gives β

- * anomeric carbon
- * α and β refer to the anomeric configurations



8.3 Conformations of Monosaccharides

Fig. 8.10 Conformations of β -D-ribofuranose

Ten possible envelope & ten possible twist conformations

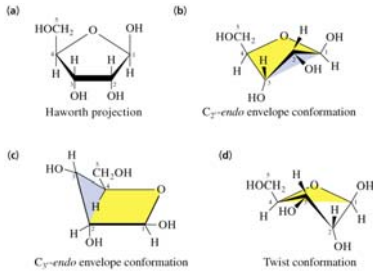


Fig 8.12 Conformations of β -D-glucopyranose

- Top conformer is more stable because it has the bulky hydroxyl substituents in equatorial positions (less steric strain)

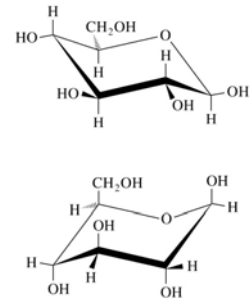
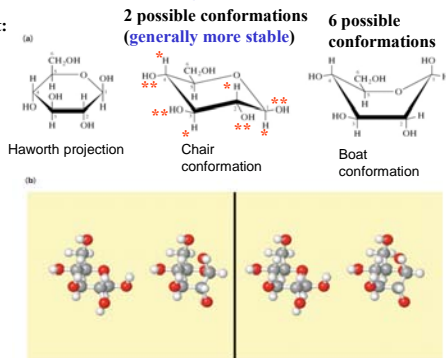


Fig 8.11 Conformations of β -D-glucopyranose

* Axial substituent: perpendicular to plane of ring

** Equatorial substituent: parallel to plane of ring

(b) Stereo view of chair (left), boat (right)



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Derivatives of Monosaccharides

- Many sugar derivatives are found in biological systems
- Some are part of monosaccharides, oligosaccharides or polysaccharides
- These include sugar phosphates, deoxy and amino sugars, sugar alcohols and acids

Fig 8.13 Some important sugar phosphates

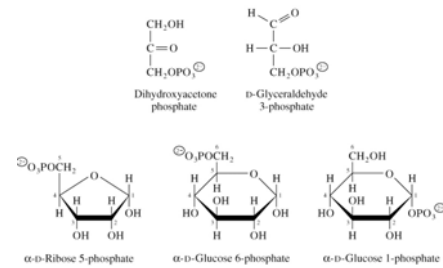


Table 8.1

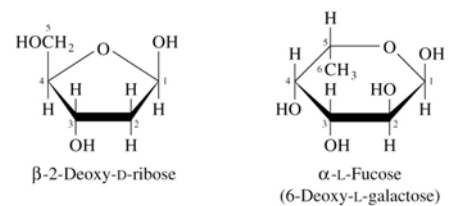
Be sure to know these abbreviations

TABLE 8.1 Abbreviations for some monosaccharides and their derivatives

Monosaccharide or derivative	Abbreviation
Pentoses	
Ribose	Rib
Xylose	Xyl
Hexoses	
Fructose	Fru
Galactose	Gal
Glucose	Glc
Mannose	Man
Deoxy sugars	
Abequose	Abe
Fucose	Fuc
Amino sugars	
Glucosamine	GlcN
Galactosamine	GalN
N-Acetylglucosamine	GlcNAc
N-Acetylgalactosamine	GalNAc
N-Acetylneuraminic acid	NeuNAc
N-Acetylmuramic acid	MurNAc
Sugar acids	
Glucuronic acid	GlcUA
Iduronic acid	IdoA

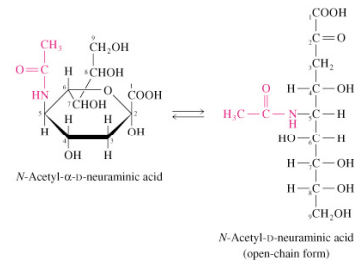
- In deoxy sugars an H replaces an OH

Fig 8.14 Deoxy sugars



- An amino group replaces a monosaccharide OH
- Amino group is sometimes acetylated
- Amino sugars of glucose and galactose occur commonly in glycoconjugates

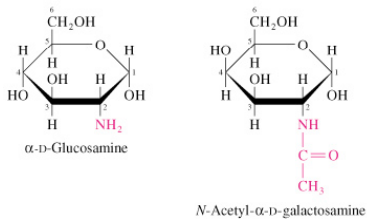
Fig. 8.15 (continued)



Sialic acids (e.g. neuraminic acid) are important in animal glycoproteins (formed from ManNAc + pyruvate)

Fig 8.15 Several _____

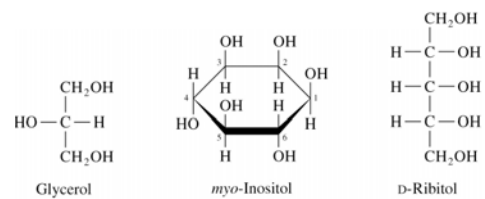
- Amino and acetylamino groups are shown in red



_____ (polyhydroxy alcohols)

- Sugar alcohols: carbonyl oxygen is reduced

Fig 8.16 Several sugar alcohols



- Sugar acids are carboxylic acids
- Produced from aldoses by:
 - (1) Oxidation of C-1 to yield an **aldonic acid**
 - (2) Oxidation of the highest-numbered carbon to an **alduronic acid**

Fig. 8.17 (continued)

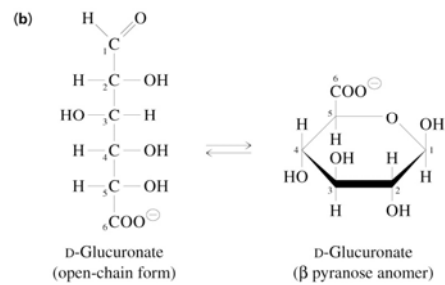
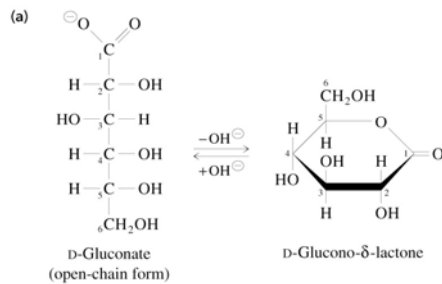


Fig 8.17 Sugar acids derived from glucose



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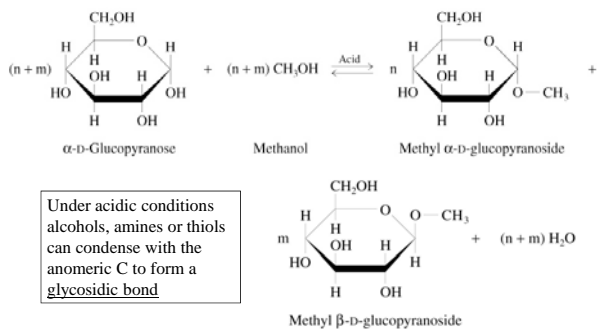
Disaccharides and Other Glycosides

- _____ - primary structural linkage in all polymers of monosaccharides
- _____ - glucose provides the anomeric carbon
- _____ – a general term meaning that a carbohydrate provides the anomeric carbon

Carbohydrates- Chapter 8

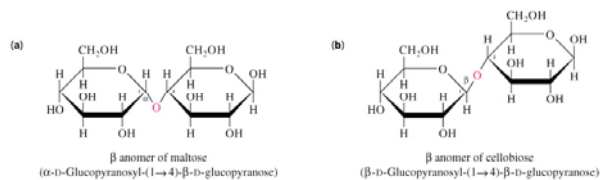
- Introduction and definition monosaccharides
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Fig 8.19 Glucopyranose + methanol yields a glycoside



Structures of Disaccharides

Fig 8.20 Structures of (a) maltose, (b) cellobiose

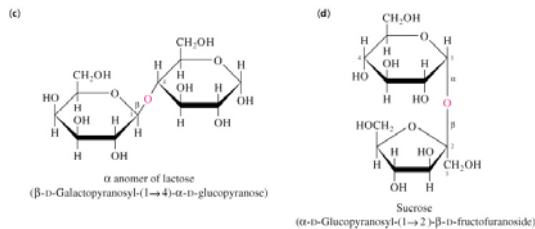


_____ is a hydrolysis product of amylose (starch)

_____ is a degradation product of cellulose

Structures of Disaccharides (continued)

Fig. 8.20 Structures of (c) lactose, (d) sucrose



_____ is an abundant disaccharide in milk

_____ : table sugar, most abundant disaccharide in nature, synthesized only in plants

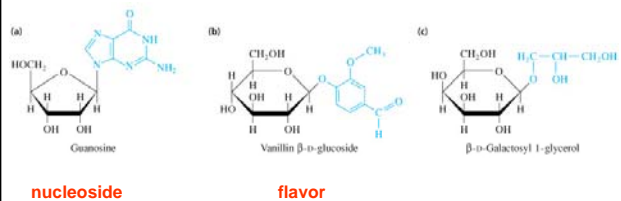
Nucleosides and Other Glycosides

- Anomeric carbons of sugars can form glycosidic linkages with alcohols, amines and thiols
- _____ : nonsugar molecule attached to the anomeric sugar carbon
- _____ : compound containing glycosidic bonds
- _____ + _____ = _____

Reducing and Nonreducing Sugars

- Carbohydrates with a reactive carbonyl (i.e. aldoses with free C1) are called _____ because they can reduce metal ions (e.g. Cu^{2+} , Ag^+)
- Carbohydrates with no free anomeric Carbon are called _____ (e.g. sucrose)

Fig 8.21 Structures of three glycosides



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Starch and Glycogen

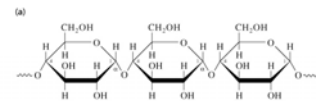
- D-Glucose is stored intracellularly in polymeric forms
- Plants and fungi - starch
- Animals - glycogen
- Starch is a mixture of amylose (unbranched) and amylopectin (branched)

Polysaccharides

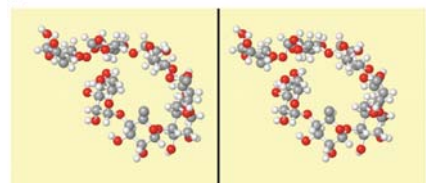
- _____ - homopolysaccharides containing only one type of monosaccharide
- _____ - heteropolysaccharides containing residues of more than one type of monosaccharide
- Lengths and compositions of a polysaccharide may vary within a population of these molecules

Fig 8.22 Structure of amylose

- (a) Amylose is a linear polymer of D-glucose in an α -1,4-linkage; DP of 100-1000

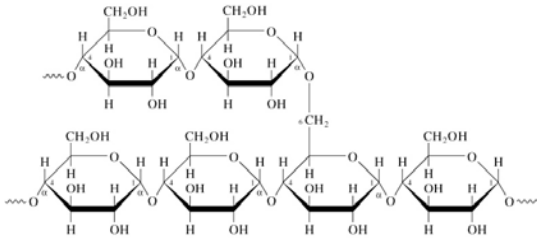


- (b) Assumes a left-handed helical conformation in water



DP: degree of polymerization

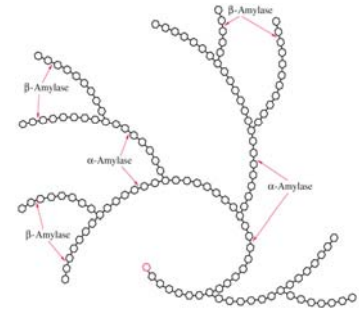
Fig 8.23 Structure of amylopectin



Amylopectin is amylose strands connected by an α -1,6-linkage; DP of 300-6000

Fig 8.24 Action of α - and β -amylase on amylopectin (both cleave α -1,4-glucan)

- α -amylase cleaves random internal α -(1-4) glucosidic bonds (endoglycanase)
- β -amylase acts on nonreducing ends, exoglycosidase, releases dimers



Comparison of between amylopectin and glycogen

- Both are energy storage forms of glucose
- Both are strands of α -1,4-linked glucose connected by α -1,6-linkages
- **Amylopectin:** found in plants; DP 300-6000, crystallin, α -1,6-linkages branches occur 1/25 residues
- **Glycogen:** found in animals; DP \leq 50,000, NOT crystallin, α -1,6-linkages branches occur 1/8 to 1/12 residues

Cellulose: most abundant organic molecule on earth, DP 300 - $>$ 15,000, synthesized by plants & some bacteria, cell wall polysaccharide

Fig 8.25 Structure of cellulose (β -1,4-linked glucose homopolymer)

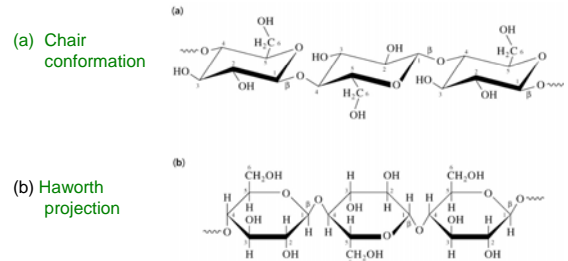
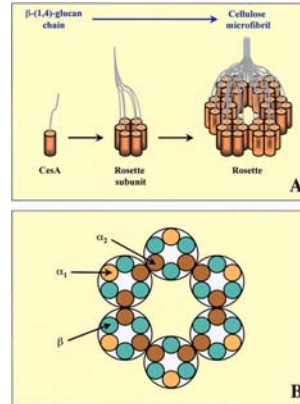
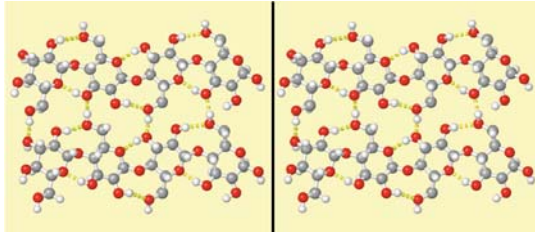


Fig 8.26 Stereo view of cellulose fibrils
Individual cellulose chains interact to give cellulose microfibrils and bundles

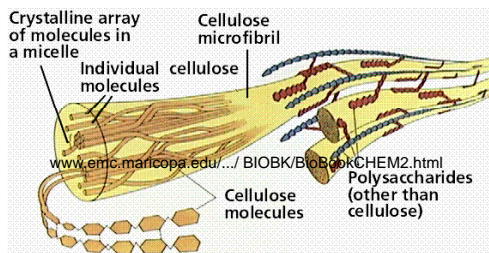
- Intra- and interchain H-bonding gives strength



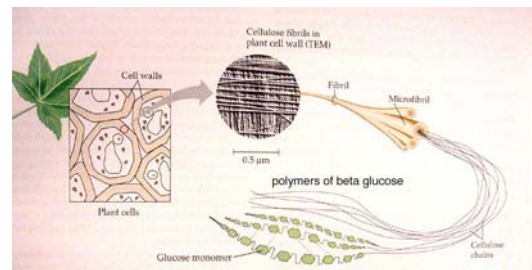
In plants a cellulose synthase rosette complex of 6 X 6 cellulose synthase subunits synthesizes a cellulose microfibril of 36 individual cellulose molecules bound together by H-bonds.

Doblin et al., 2002, Plant Cell Physiol. 43:1407

Cellulose chains interact via H-bonds to form microfibrils and fibers.



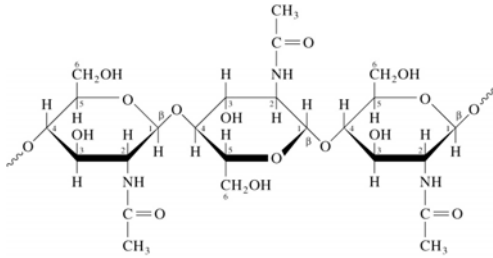
www.emc.maricopa.edu/.../BIOBK/BioBookCHEM2.html



academic.brooklyn.cuny.edu/biology/bio4fv/pag...

Fig 8.27 Structure of chitin: exoskeleton of spiders & crustaceans, & in cell wall of some fungi & algae

- Repeating units of β -(1-4)GlcNAc residues



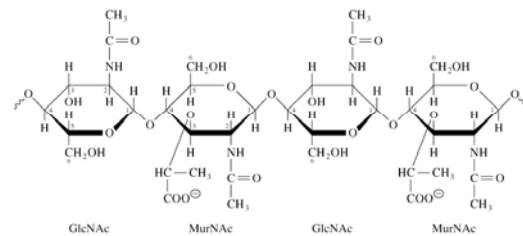
Peptidoglycans

- **Peptidoglycans** - heteroglycan chains linked to peptides
- Major component of bacterial cell walls
- Heteroglycan composed of alternating GlcNAc and N-acetylmuramic acid (MurNAc)
- β -(1 \rightarrow 4) linkages connect the units

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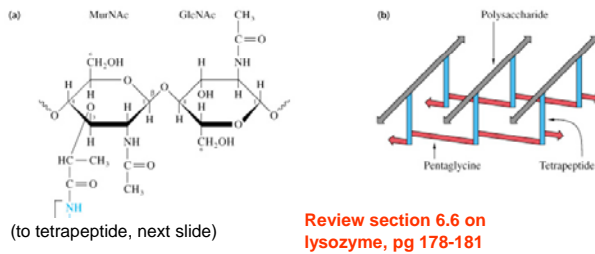
Fig 8.30 Glycan moiety of peptidoglycan



MurNAc found only in bacteria and consists of GlcNAc connected at C-3 by an ether linkage to lactate.

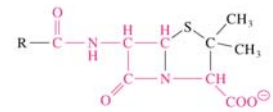
Fig 8.31 Structure of the peptidoglycan of *S. aureus* (gram positive bacteria cell wall peptidoglycan)

(a) Repeating disaccharide unit, (b) Cross-linking of the peptidoglycan macromolecule



Penicillin inhibits a transpeptidase involved in bacterial cell wall formation

• **Fig 8.32** Structures of penicillin and -D-Ala-D-Ala



• Penicillin structure resembling -D-Ala-D-Ala is shown in red

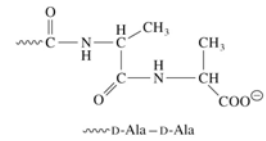
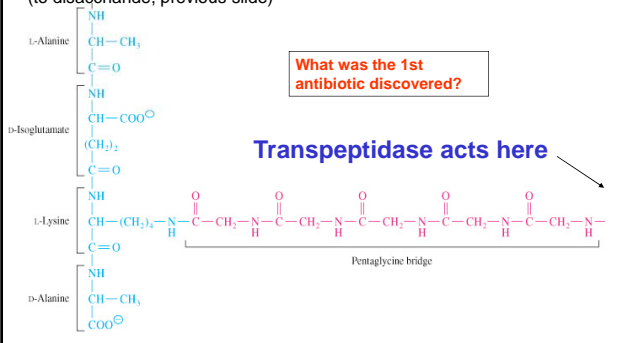


Fig. 8.31 (continued)

(to disaccharide, previous slide)



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- Lipo-oligosaccharides
- Glycoproteins

Proteoglycans

- _____ – glycosaminoglycan (~95%)- carbohydrate-protein conjugates. Often found in ECM. Function as lubricants, cell-cell adhesion, messengers, & give tensile strength & elasticity to soft tissues
- _____ (GAGs)- unbranched heteroglycans of repeating disaccharides (many sulfated hydroxyl and amino groups)
- Disaccharide components include: (1) amino sugar (D-galactosamine or D-glucosamine), (2) an alduronic acid

Types of GAGs

1. Not covalently attached to protein
 - *Hyaluronic acid
2. Covalently attached to proteins (i.e. present in proteoglycans)
 - *Heparin (and heparan sulfate)
 - *Keratan sulfate
 - *Chondroitin sulfate
 - * Dermatan sulfate

Fig 8.28 Repeating disaccharide of hyaluronic acid

- GlcUA = D-glucuronate
- GlcNAc= N-acetylglucosamine

hyaluronic acid is GAG not attached to protein

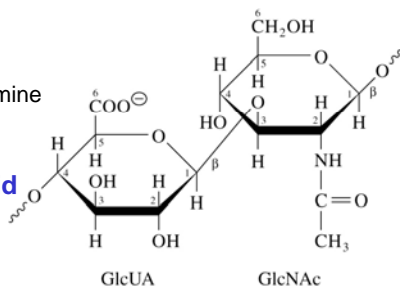
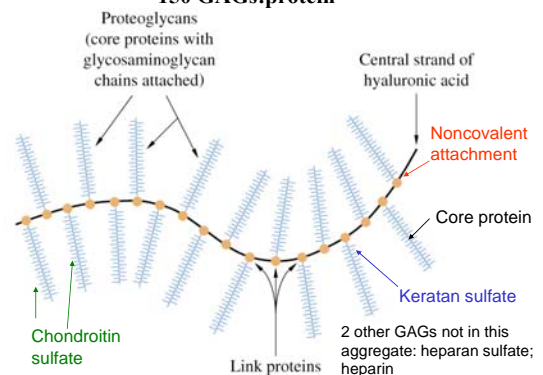
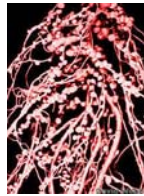
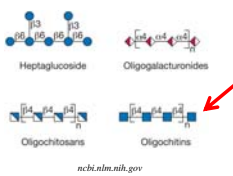


Fig 8.29 Proteoglycan aggregate in cartilage ~150 GAGs:protein



Lipo-oligosaccharides and oligosaccharides can serve as signal molecules

Specific lipo-oligosaccharides are produced by nitrogen-fixing bacteria that interact specifically with certain plants (i.e. legumes) to form root nodules (Box 8.1). These lipo-oligosaccharides resemble chitin oligomers with specific modifications.



<http://www.botany.hawaii.edu/faculty/webb/Bot410/Roots/RootSymbiosis.htm>

Glycoproteins

- Proteins that contain covalently-bound oligosaccharides
- O-Glycosidic and N-glycosidic linkages
- Oligosaccharide chains exhibit great variability in sugar sequence and composition
- _____ - proteins with identical amino acid sequences but different oligosaccharide chain composition

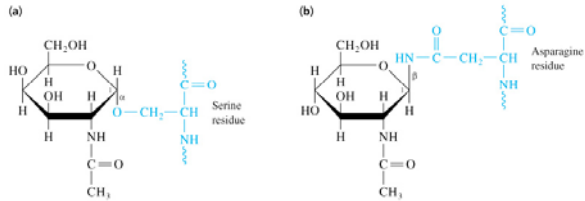
Carbohydrates- Chapter 8

- Introduction and definition monosaccharides
- Aldoses and Ketoses
- Cyclic glycosyl residues, Haworth Projections
- Modified monosaccharides
- Glycosidic bond
- Disaccharides
- Polysaccharides
- Peptidoglycans
- Proteoglycans
- Glycoproteins

Four subclasses of _____ linkages

- (1) GalNAc-Ser/Thr (most common)
- (2) 5-Hydroxylysine (Hyl) to D-galactose (unique to collagen)
- (3) Gal-Gal-Xyl-Ser-core protein (in proteoglycans)
- (4) GlcNAc to a single serine or threonine

Fig. 8.33 O-Glycosidic and N-glycosidic linkages



Consensus sequence for N-glycosylation: Asn-X-Ser/Thr

Fig 8.35 Structures of N-linked oligosaccharides

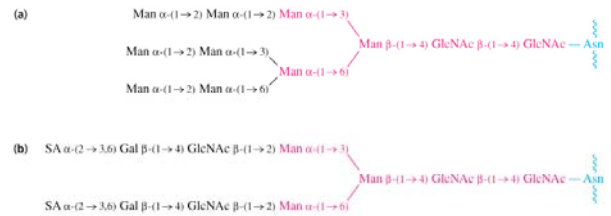


Fig 8.34 Four subclasses of O-glycosidic linkages

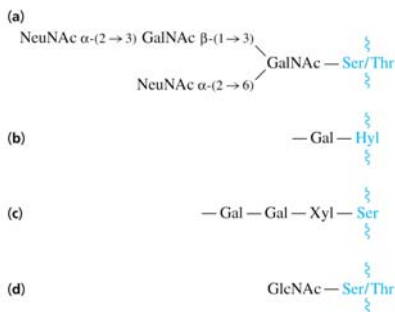
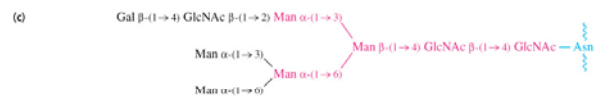


Fig. 8.35 (continued)



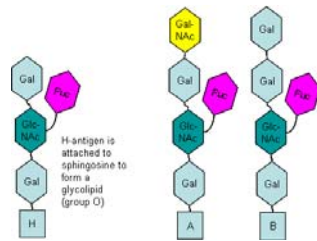
The oligosaccharides attached to proteins may alter physical properties such as size, shape, solubility, or stability, may effect folding, and/or may have biological roles

Why do blood transfusions sometimes cause death?

Reason discovered by Karl Landsteiner at University of Vienna in 1901.

See Box 8.2

All humans and many primates have **A, B, AB or O types** of oligosaccharides on the *N*-linked and *O*-linked oligosaccharides on the surface of their red blood cells (includes glycoproteins and glycolipids).



http://www.steve.gb.com/images/science/abo_glycolipids.png