CARBOHYDRATES

. Aldehydes or ketone compounds with multiple hydroxyl grs.

. Multiple roles :-

- Energy stores, fuels, and metabolic intermediates
- Ribose and deoxyribose in RNA + DNA
- structural elements in the cell walls of bacteria and plants and in exoskeletons of arthropods
- linked to lipids + protein e.g. glycophorin
- Carbohydrate units on cell surface = key role in cell-cell recognition processes.... Information-rich. Cell adhesion, intercellular communication

- Monosaccharides are aldehydes or ketones with multiple hydroxyl groups (poly hydroxy aldehyde or ketone)

$(CH_2O)_n$ — Carbon hydrate X

$n = 3$ to 7.

asymmetric centers

no. of stereoisomers $= 2^n$

Dextrorotatory + levorotatory d (+) l (−)

D- + L- configuration

- Pentoses and hexoses cyclize to form furanose and Pyranose rings.

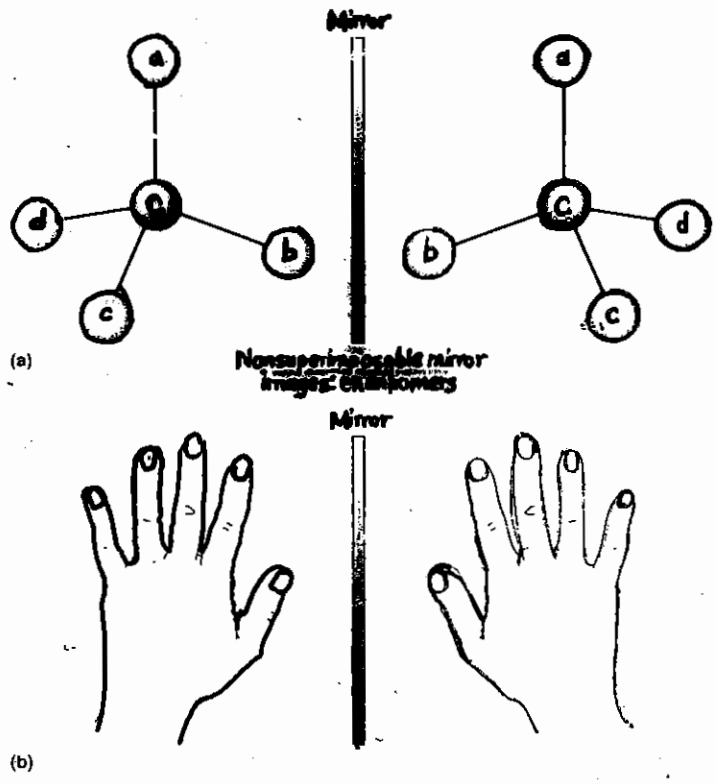


FIGURE 14.2
(a) A pair of stereoisomers for the general molecule Cabcd; (b) analogous mirror-image right and left hands.

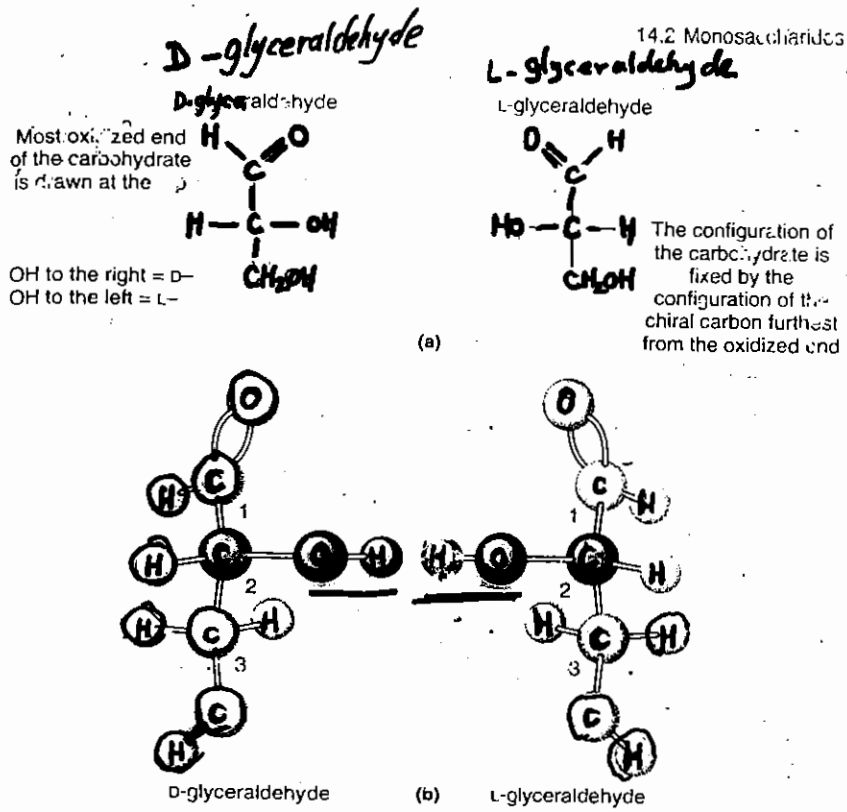
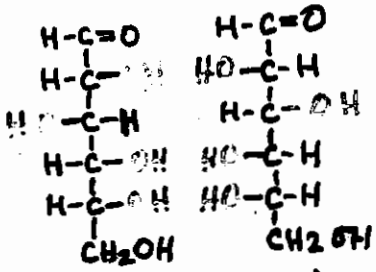


FIGURE 14.3
(a) Fischer Projection of D- and L-glyceraldehyde. (b) A three-dimensional representation of D- and L-glyceraldehyde.

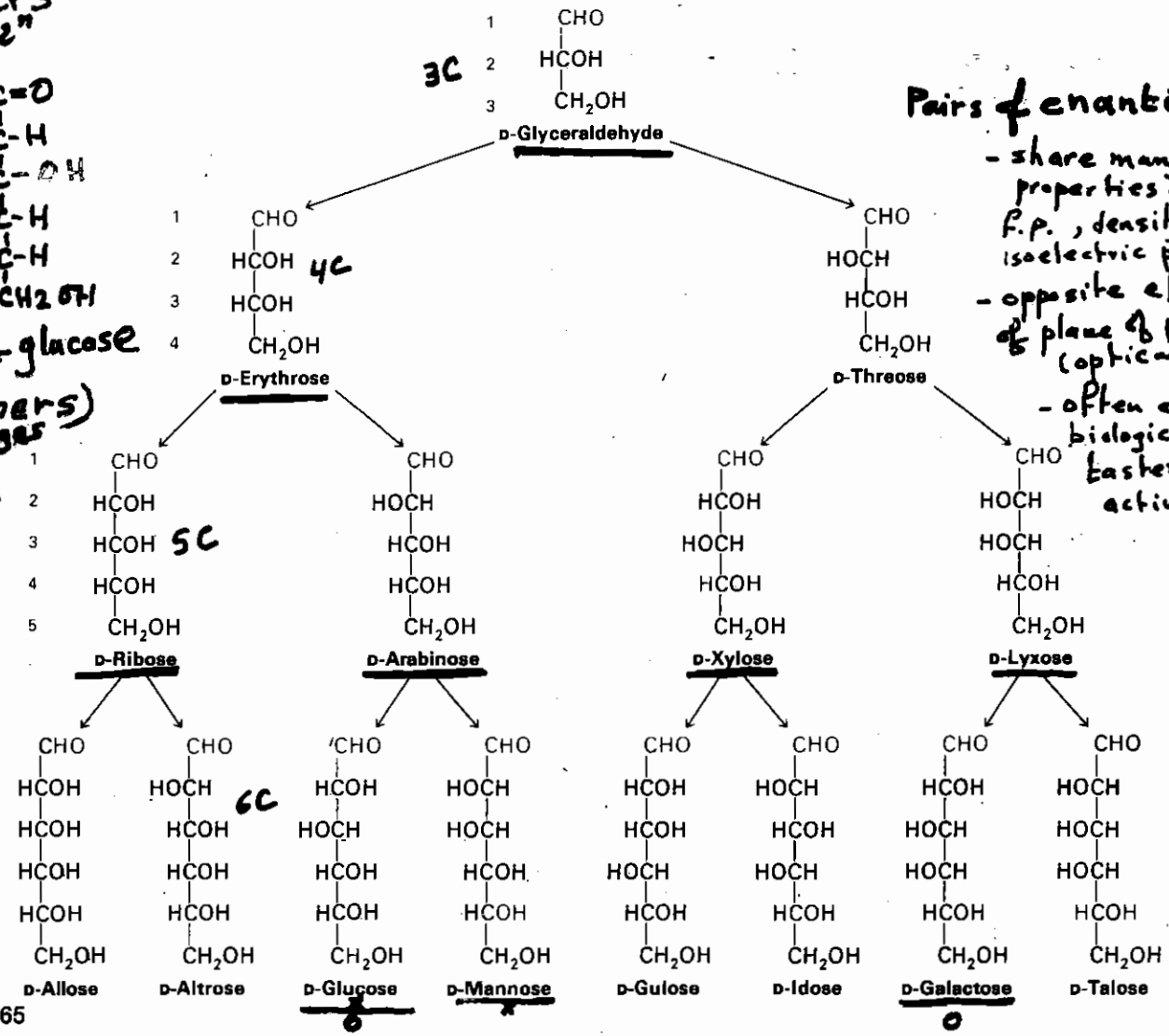
- Monosaccharides: simplest carbohydrates, are aldehydes or ketones that have 2- or more hydroxyl groups
- Steroisomers $= 2^n$



D-glucose L-glucose

(Enantiomers) mirror images

- D- + L- designation
- Diasteroisomers
- epimers
- anomers



Pairs of enantiomers

- share many physical properties e.g. m.p., f.p., density, solubility, isoelectric point ... etc
- opposite effect on rotation of plane of polarized light (optical isomers)
- often differs in biological activity, tastes, odors, or activity as drugs.

x - epimers

o - epimers

Figure 18-3, page 465

4B

- Fischer Projection

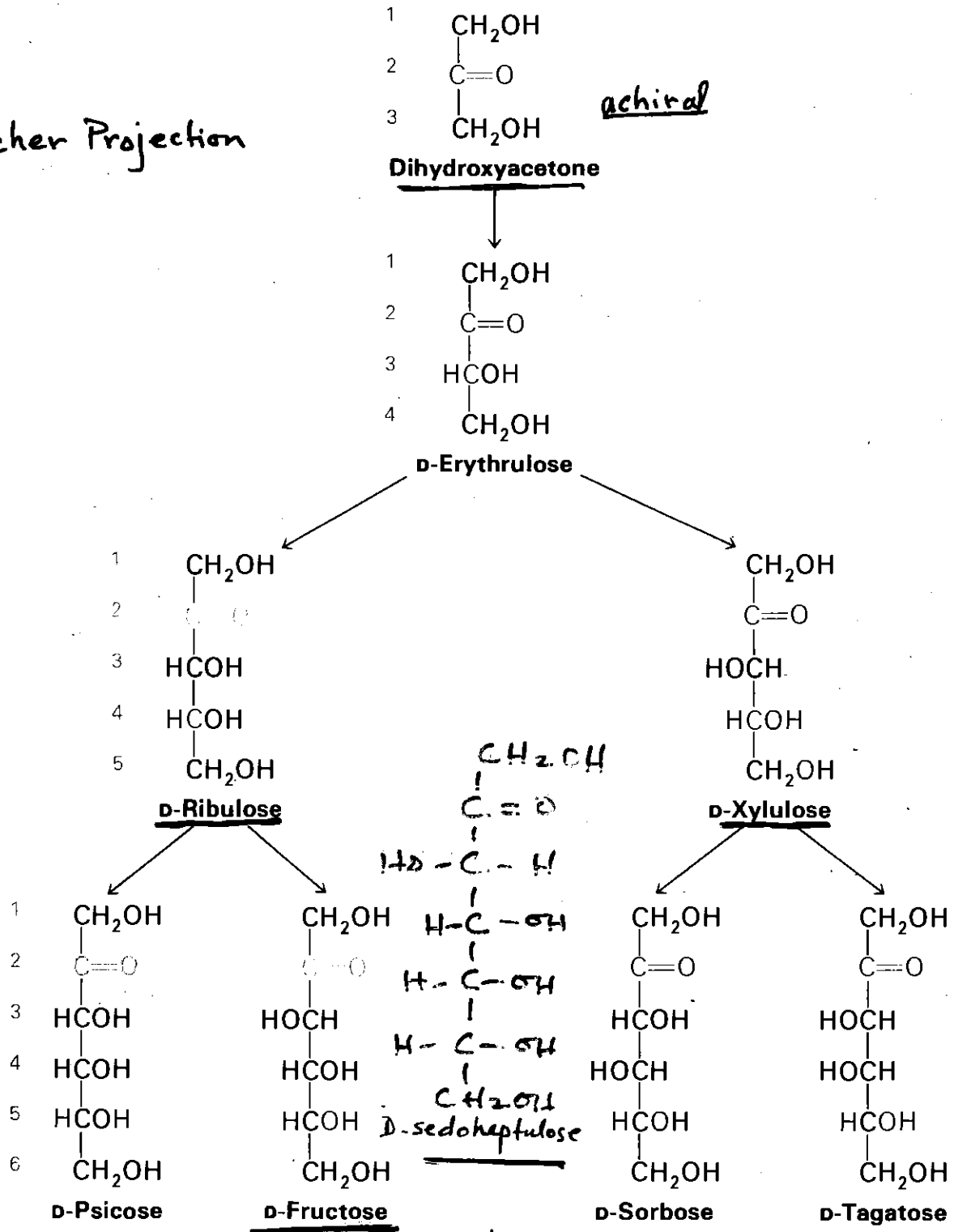
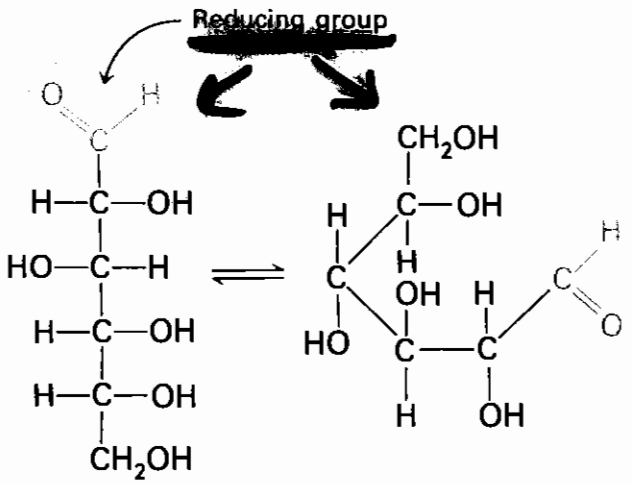
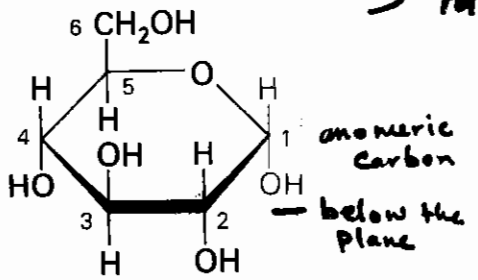


Figure 18-4, page 466

Carbohydrates in Cyclic structures:-

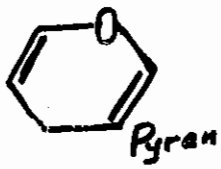


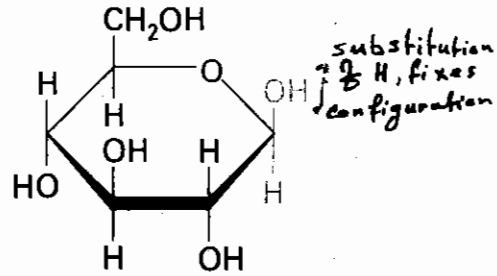
D-Glucose
(Open-chain form)



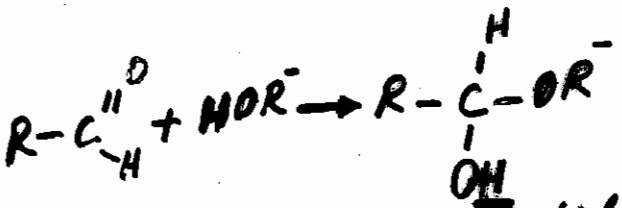
α-D-Glucopyranose

mutarotation

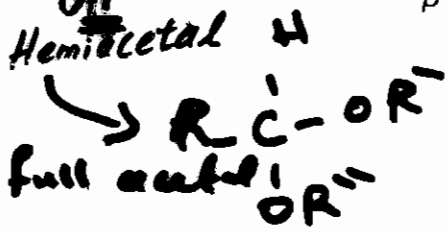




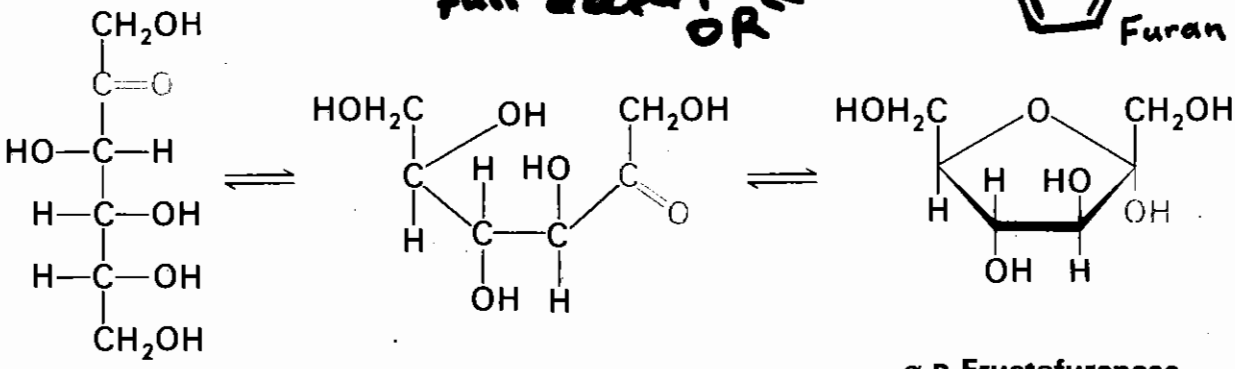
β-D-Glucopyranose



Hemiacetal

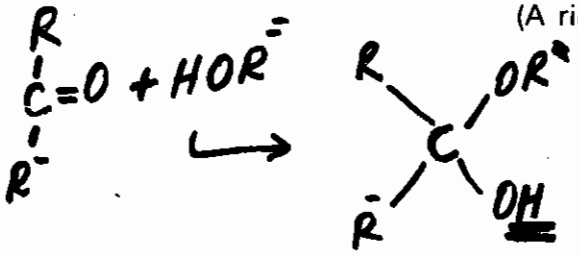


full acetal



D-Fructose

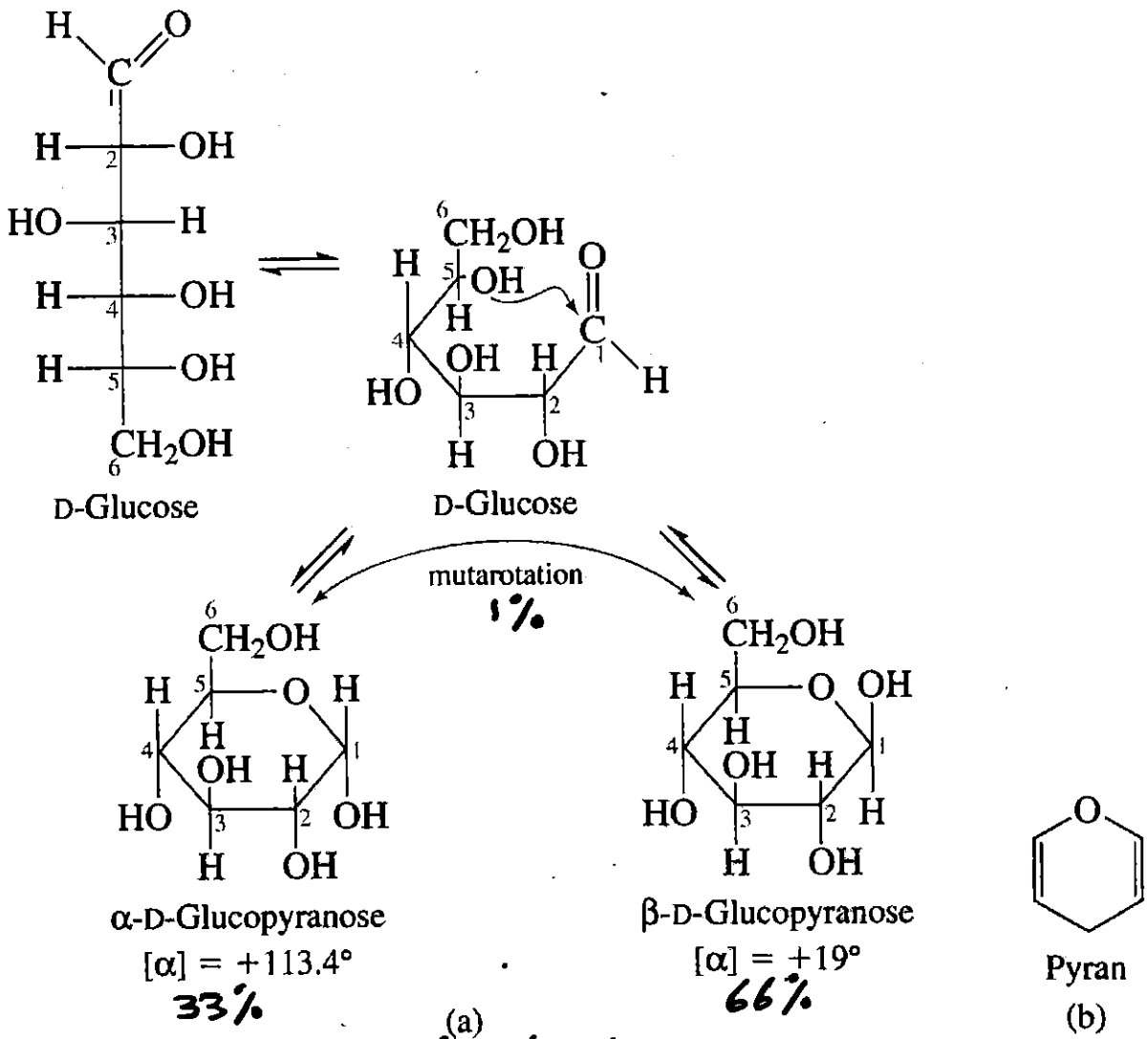
α-D-Fructofuranose
(A ring form of fructose)



Hemiketal

Page 335 (top and bottom)
Stryer: *Biochemistry*, Third Edition

Cyclization of D-glucose



final value = + 52.2

Figure 7-8 Concepts in Biochemistry, 3/e

Cyclization of D-fructose

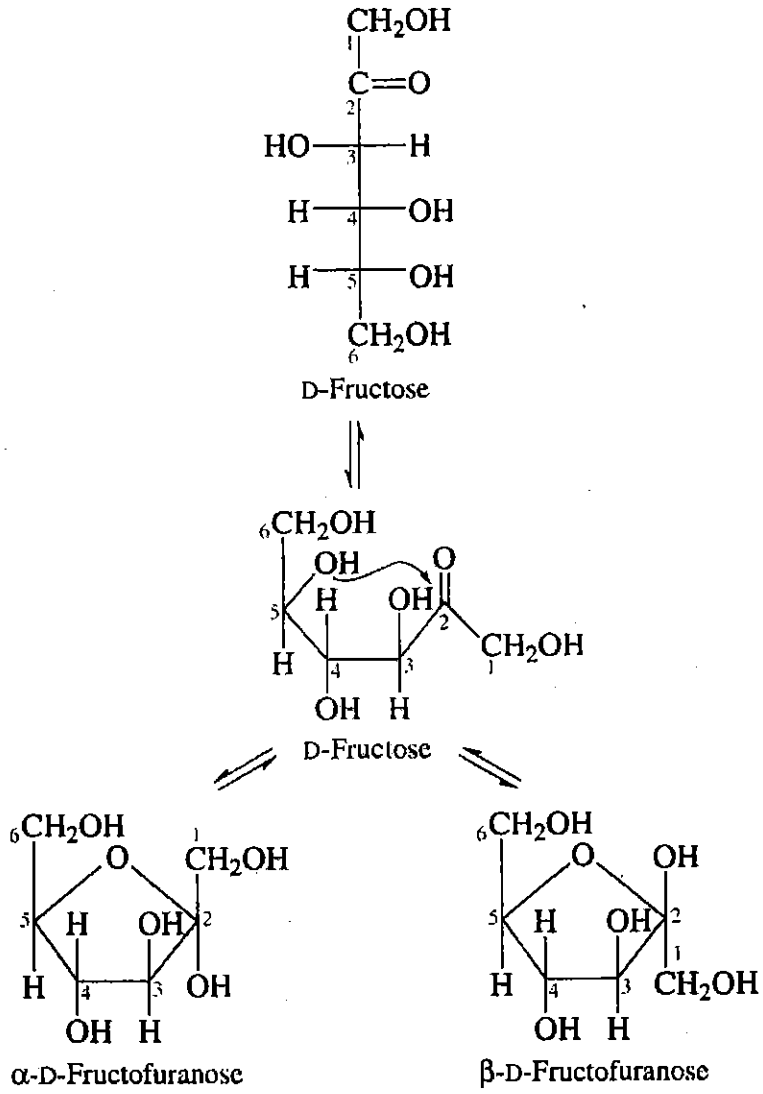
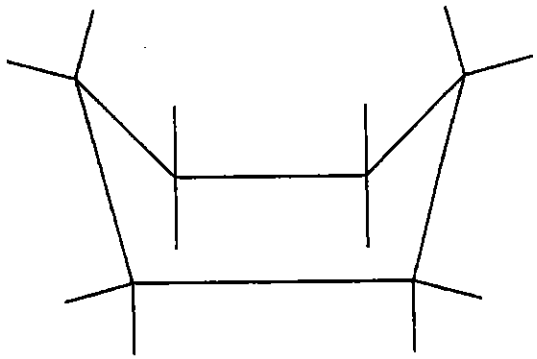


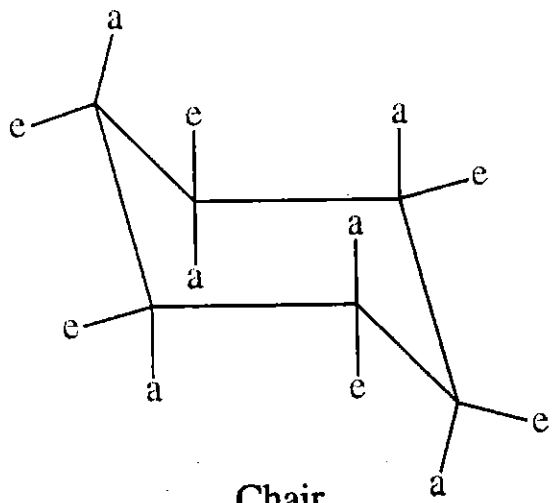
Figure 7-9 Concepts in Biochemistry, 3/e

Chair and boat conformations of ring compounds:-

8



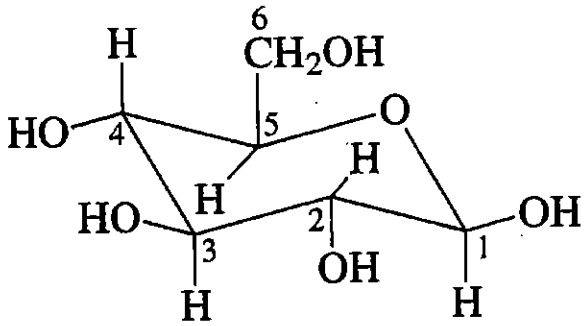
Boat



Chair

(a) Cyclohexane

- Howarth planer ring is misrepresentation



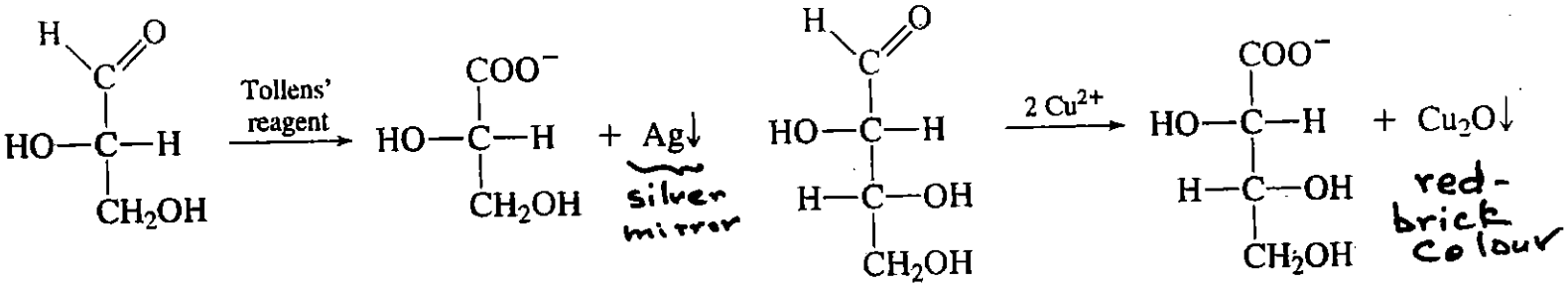
(b) Glucose in most stable chair conformation

Figure 7-10 Concepts in Biochemistry, 3/e

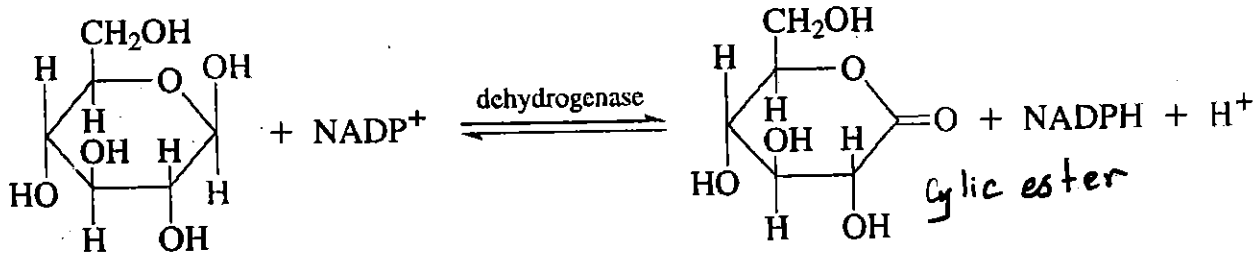
Reactions of Monosaccharides

- Oxidation - reduction

$$R-C(=O)-H \xrightarrow{[O]} R-C(=O)-OH$$



(a) (b)



(c) A lactone

- REDUCTION of Sugars:- Polyols (Alditols)

Figure 7-11 Concepts in Biochemistry, 3/e

e.g.

D-Glucose $\xrightarrow{\text{reduction}}$ D-Sorbitol

D-ribose $\xrightarrow{\text{red}^n}$ D-2-deoxyribose

Mannose $\longrightarrow$ Mannitol

Galactose $\longrightarrow$ galactitol

D-xylulose $\xrightarrow{\text{Red}^n}$ D-Xylitol

D-xylose

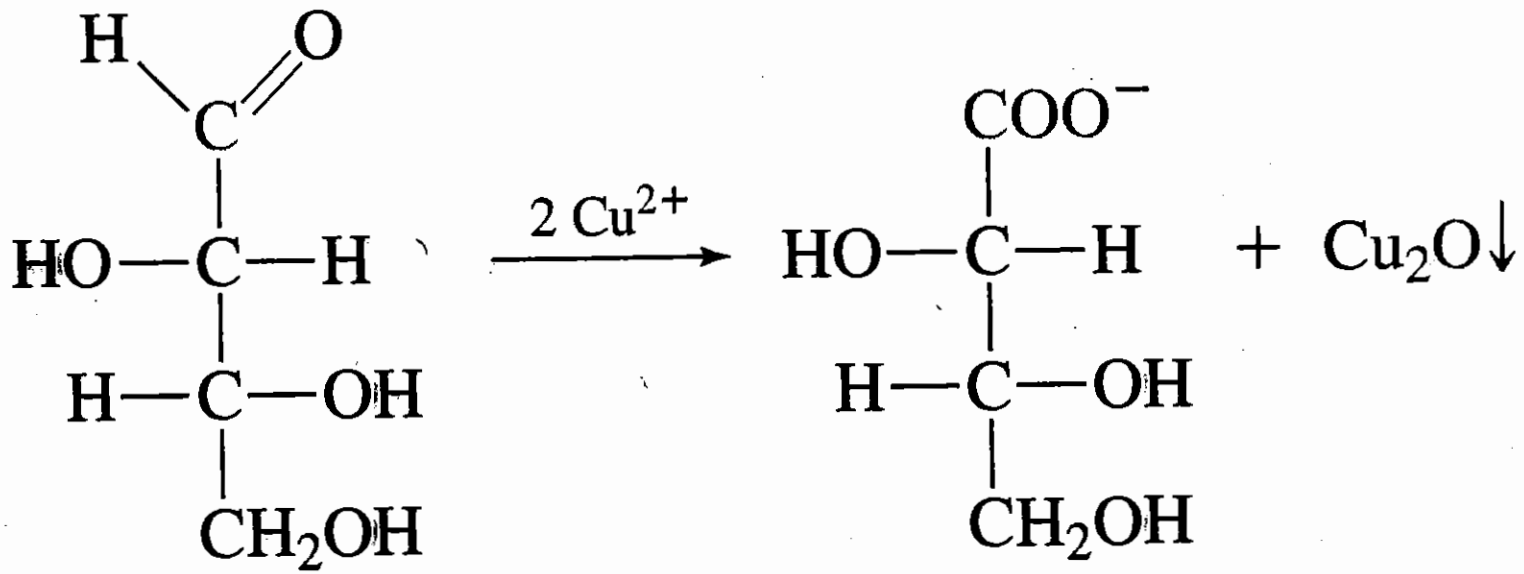
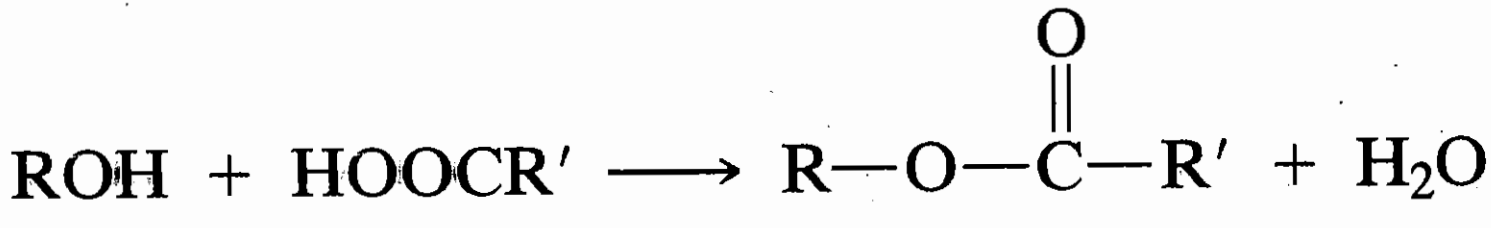
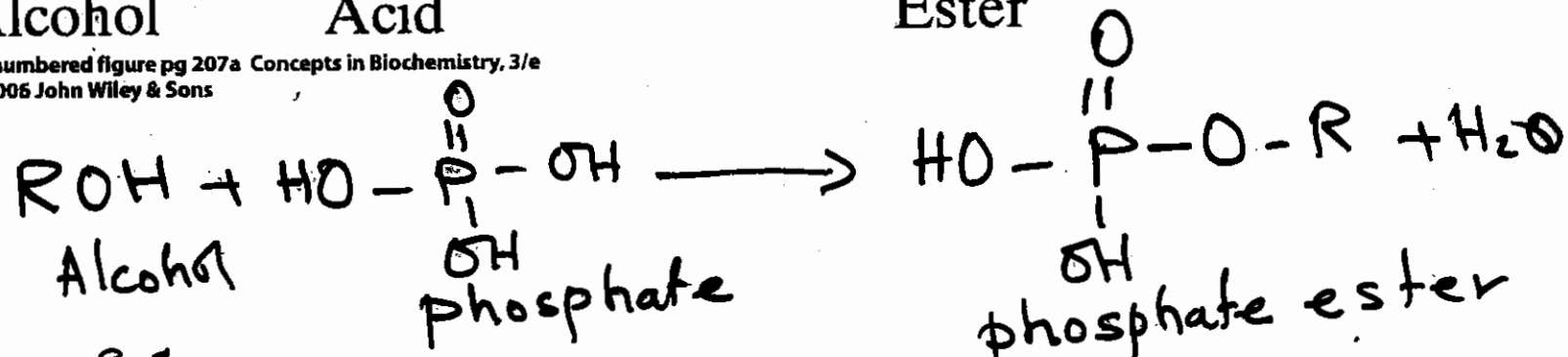


Figure 7-11b Concepts In Biochemistry, 3/e

Esterification:-

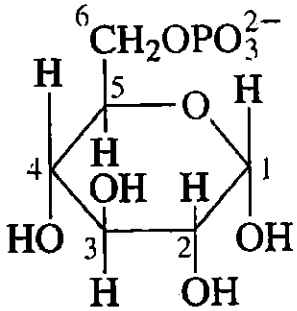




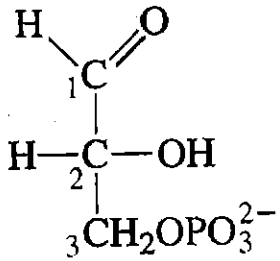
e.g.

$$\text{Glu} + \text{ATP} \xrightarrow{\text{HK}} \text{Glu-6-P} + \text{ADP}$$

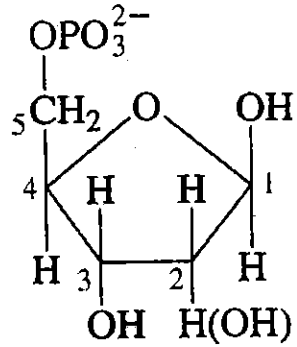
Important phosphate esters of Carbohydrate



(a) D-Glucose-6-phosphate



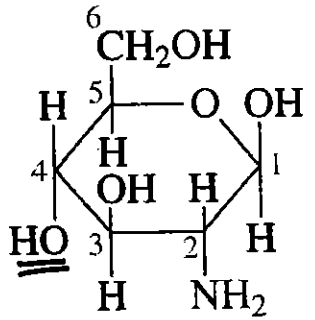
(b) D-Glyceraldehyde-3-phosphate



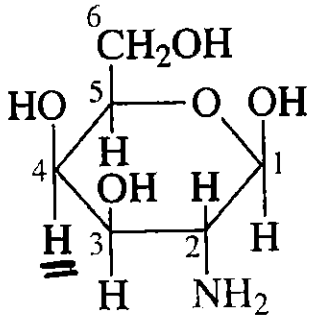
(c) D-Deoxyribose-5-phosphate
(D-Ribose-5-phosphate)

Figure 7-13 Concepts in Biochemistry, 3/e

Amino derivatives of Carbohydrates

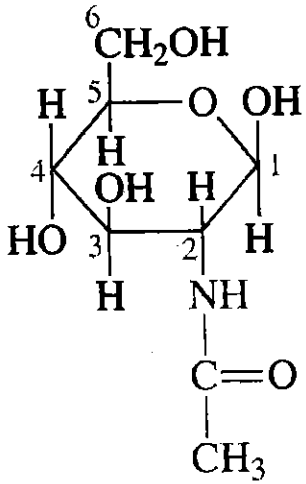


β-D-2-Aminoglucose
(glucosamine)



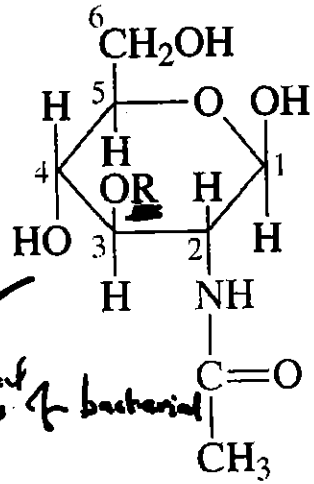
β-D-2-Aminogalactose
(galactosamine)

(a)

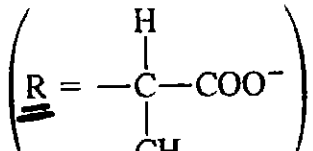


chitin polymer ← *N*-Acetylglucosamine

structural components of bacterial cell walls.



N-Acetylmuramic acid



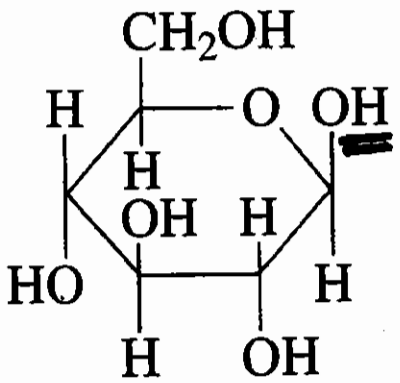
Lactic acid

(b)

Figure 7-14 Concepts in Biochemistry, 3/e

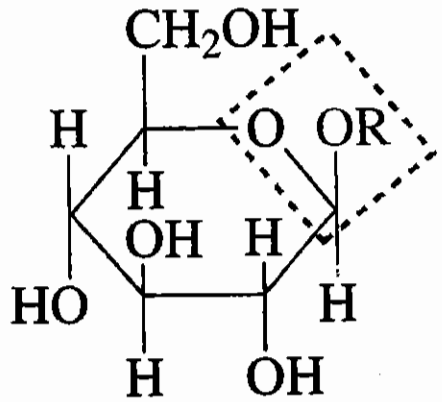
Glycosides

O-glycoside



β-D-Glucopyranose

+ ROH or another carbohydrate molecule



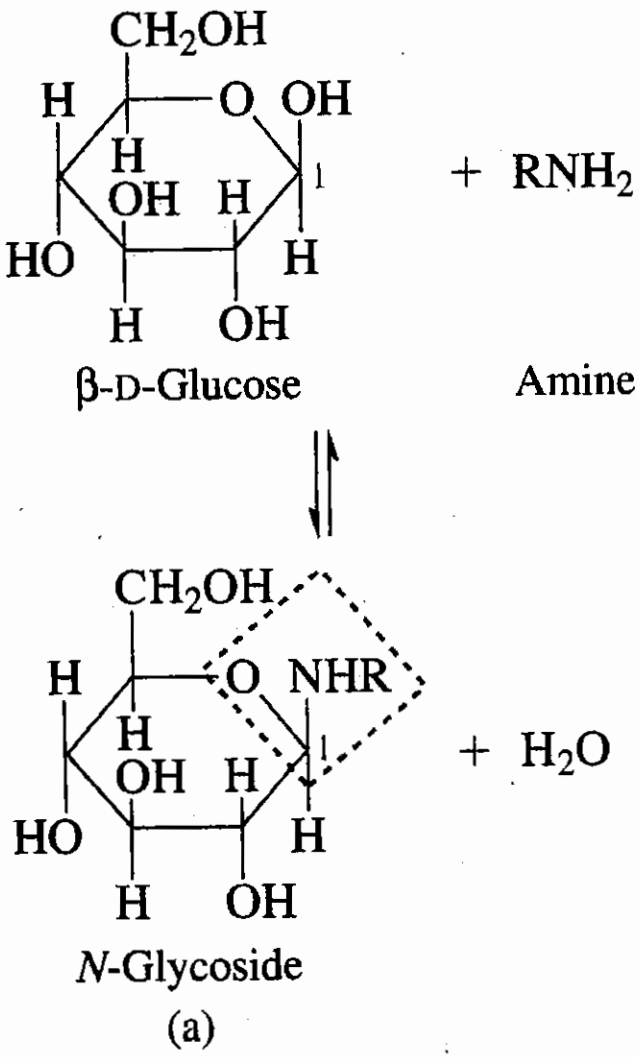
β-D-Glucopyranoside
(methyl-β-D-glucopyranoside)

+ HOH

(R = —CH_3)

Figure 7-15 Concepts in Biochemistry, 3/e

N-Glycosidic bond



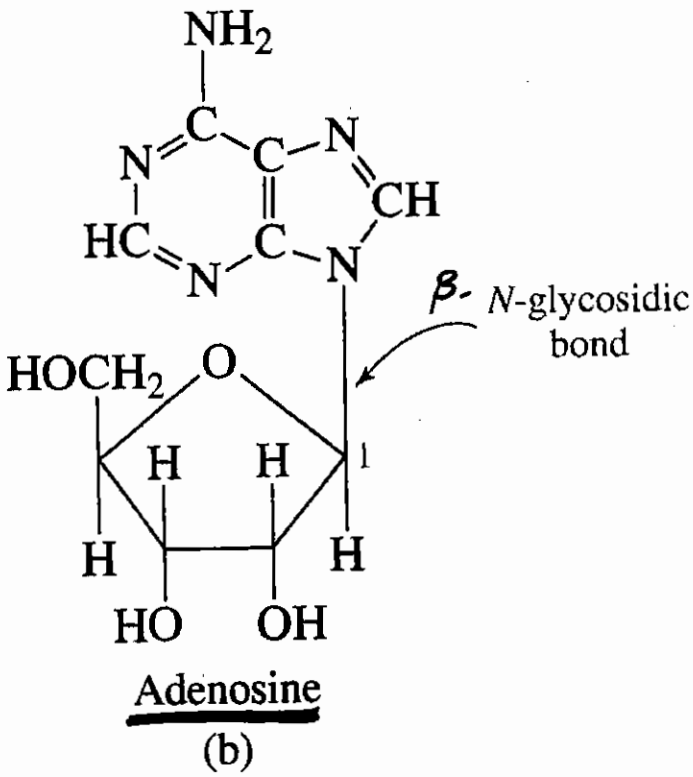
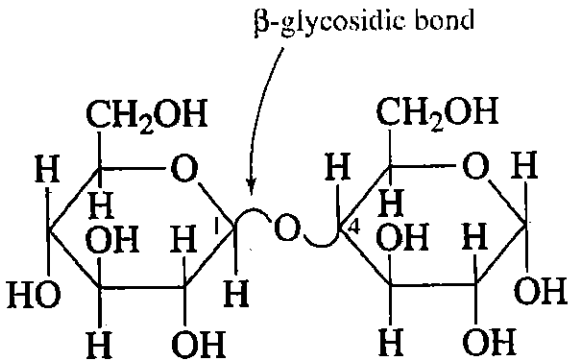


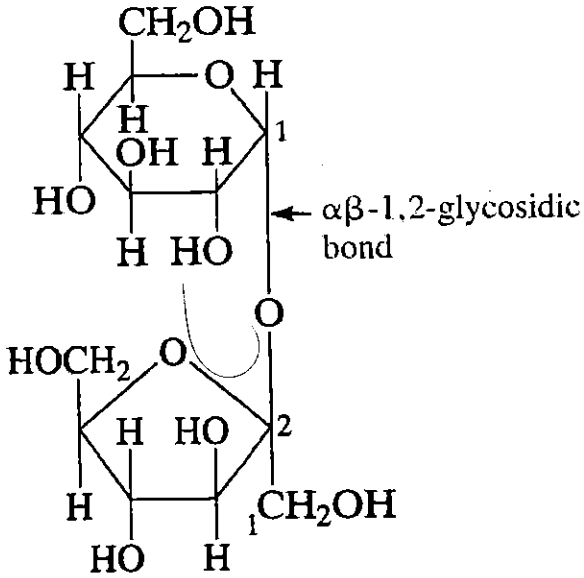
Figure 7-18 Concepts in Biochemistry, 3/e

Important disaccharides

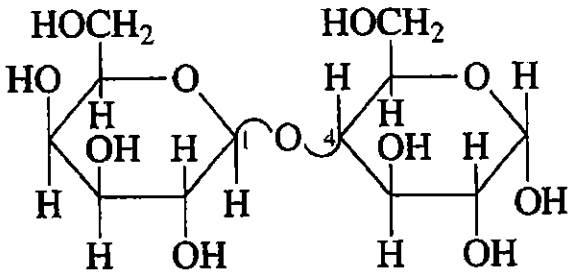
O-glycosidic bond with monosaccharide



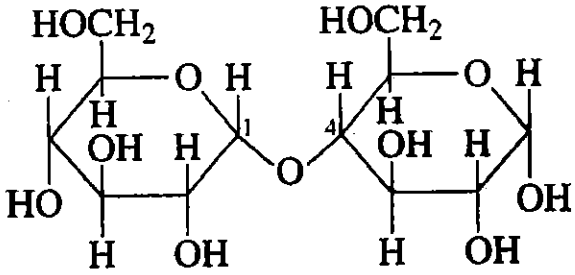
Cellobiose
[glucose-β(1 → 4)-glucose]



Sucrose [glucose-α, β (1→2)-fructose]



Lactose
[galactose-β(1 → 4)-glucose]



Maltose
[glucose-α(1 → 4)-glucose]

Figure 7-17 Concepts in Biochemistry, 3/e

Table 7.2
Common disaccharides and their structural properties

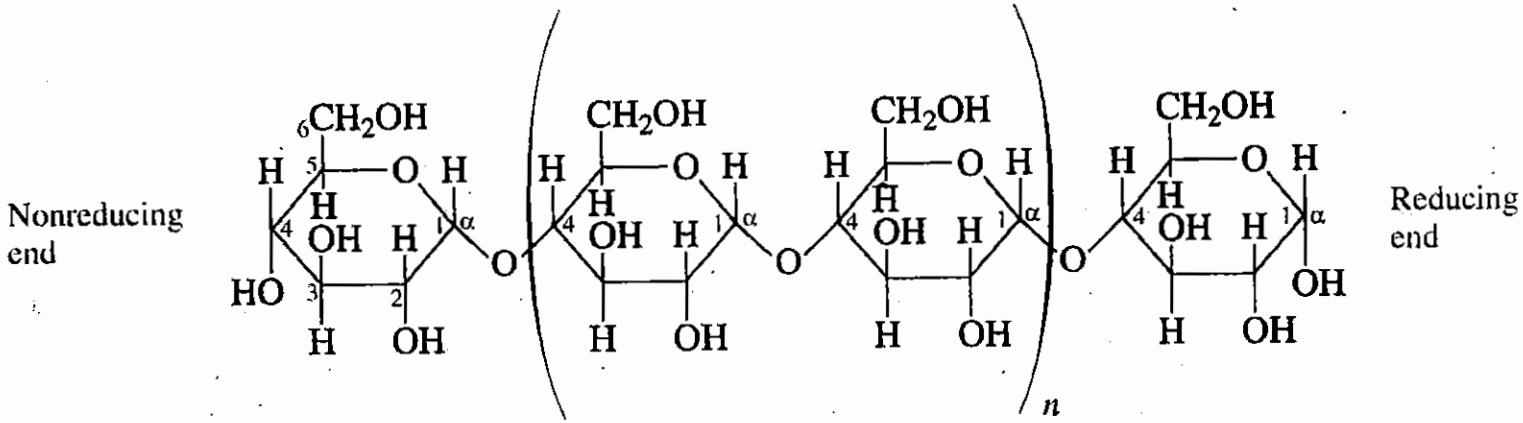
Name	Monosaccharide Components	Type of Glycosidic Linkage
Maltose	Glucose, glucose	$\alpha(1 \rightarrow 4)$
Cellobiose	Glucose, glucose	$\beta(1 \rightarrow 4)$
Lactose	Galactose, glucose	$\beta(1 \rightarrow 4)$
Sucrose	Glucose, fructose [1.7 sweeter than sucrose]	$\alpha,\beta(1 \rightarrow 2)$

Lactose $\xrightarrow{\text{lactase}}$ Gal. + Glu
H_2O

Deficiency of lactase

Polysaccharides

- Homopolysaccharides
- Heteropolysaccharides



Amylose

Figure 7-20a Concepts in Biochemistry, 3/e

Storage Polysaccharide

1 - starch

Amylose - Unbranched

Amylopectin - branched

2- Glycogen - branched

3- Dextran (yeast, bacteria)
α(1→6) glycosidic linkage.
branching at α(1→2); α(1→3) + α-(1→4)
component of dental plaque

4. Inulin
Polymer of D-Fru
β(2→1) linkage
found in artichokes + other veg.

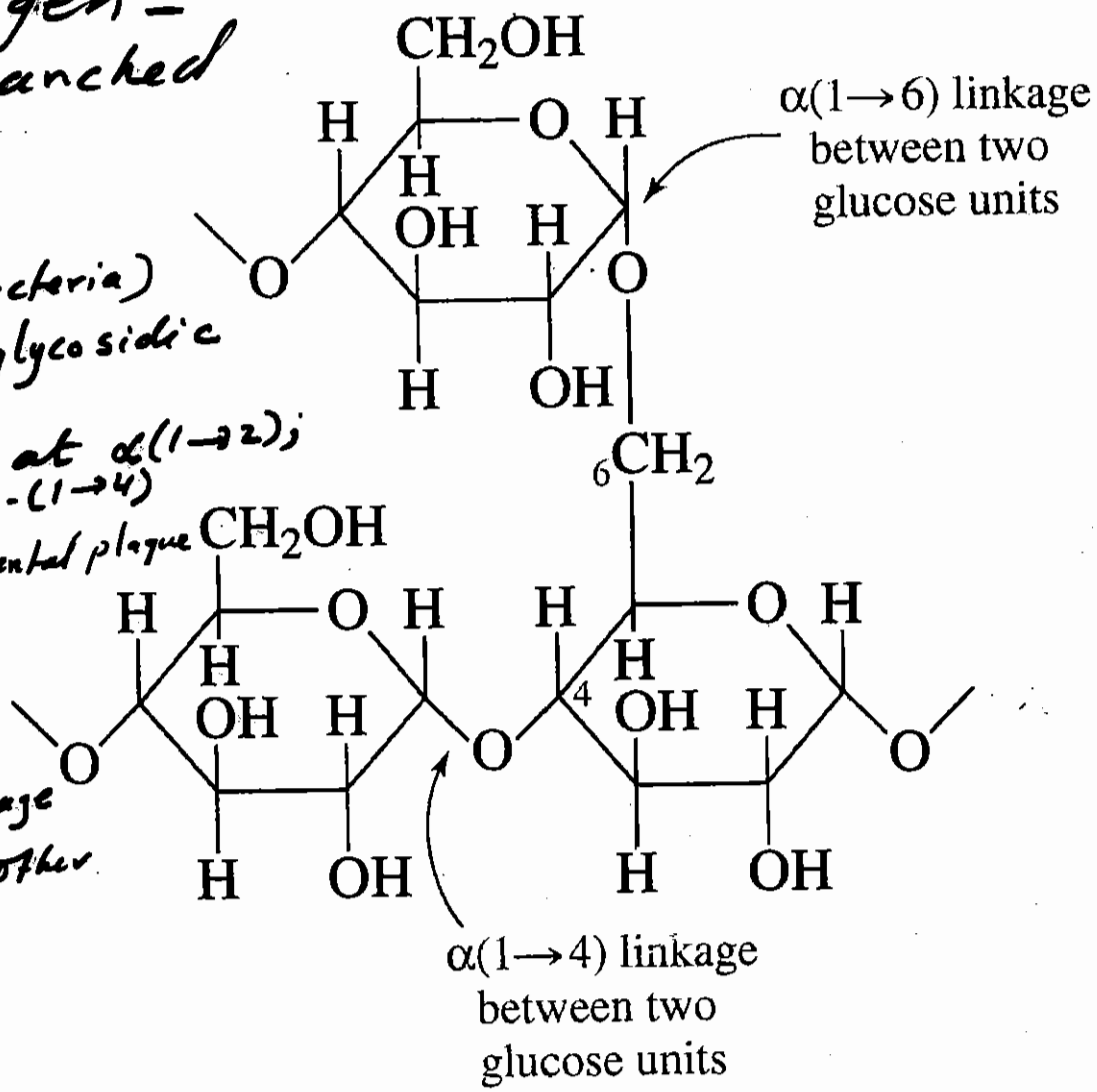
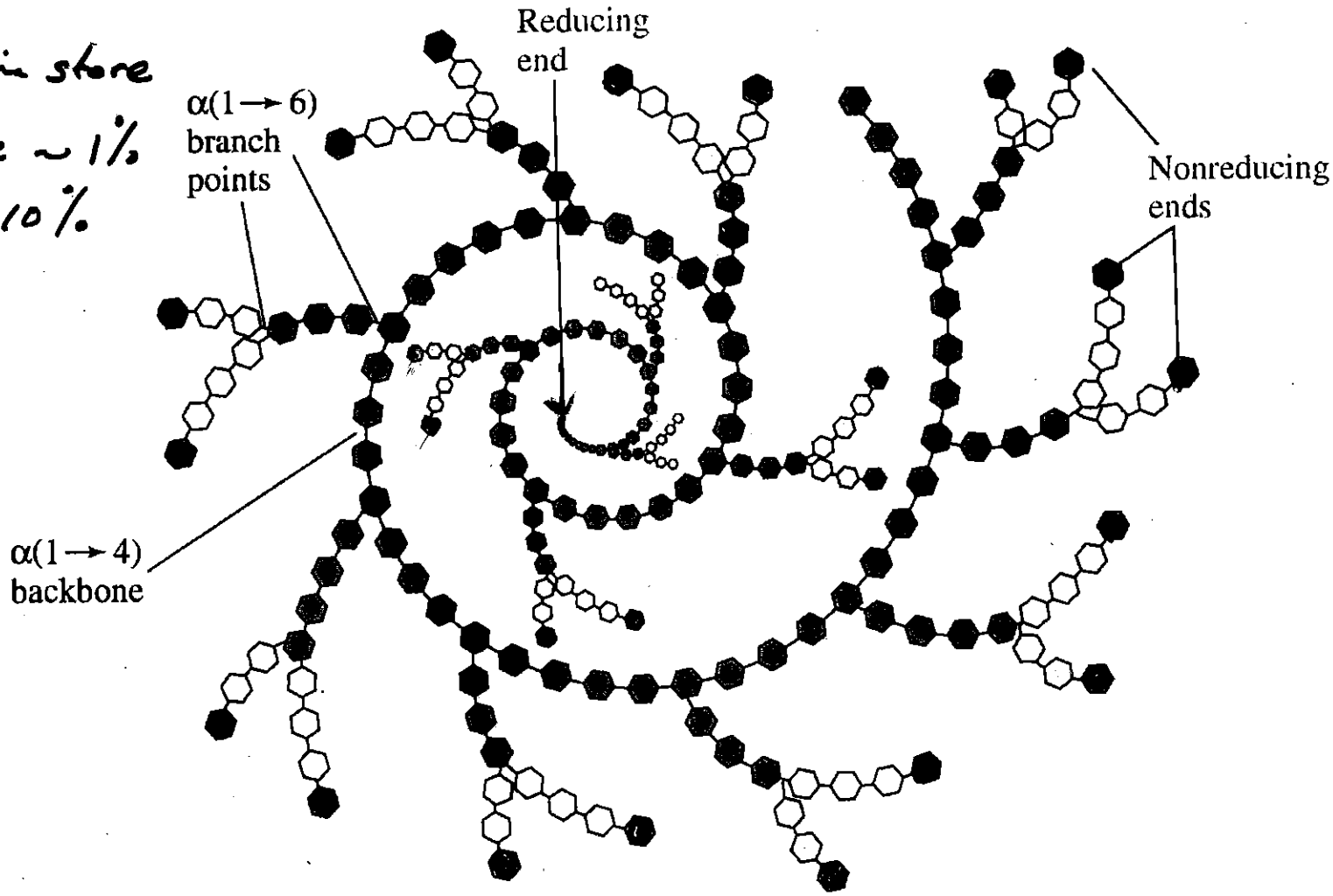


Figure 7-21 Concepts in Biochemistry, 3/e

Glycogen store
In muscle ~ 1%
Liver 10%



Amylopectin or glycogen

branching at every 25th residue α-(1→6)

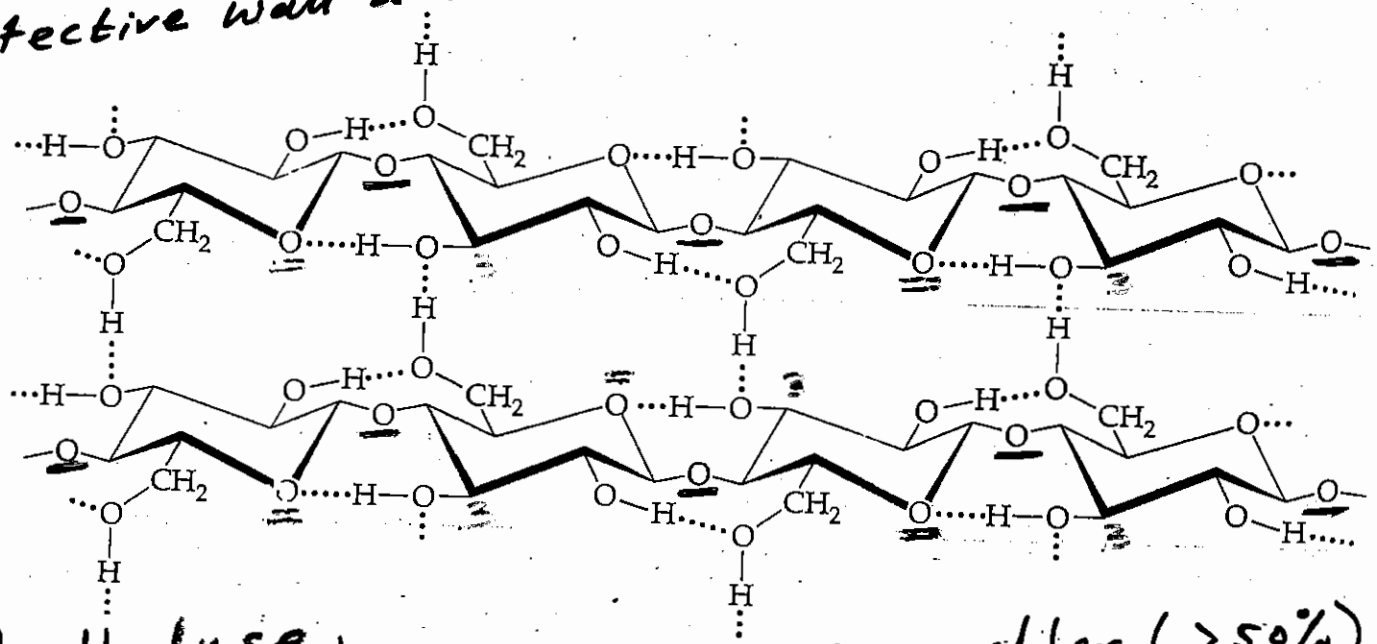
branching at every 10th residue α-(1→6)

Figure 7-20b Concepts in Biochemistry, 3/e

Structural Polysaccharides

Cellulose
Chitin
Mucopolysaccharides
synthesized inside cells but extruded to the outside → protective wall or lubricating coatings to cell

Cellulose



Cellulose :-
Most abundant organic matter (>50%)
β-(1→4) glycosidic linkage
10,000 to 15,000 glu residues per mole
extended chains connected to parallel → fibrils
inter & intra molecular H-bonds

β-(1→4) glycosidic bonds in ~~starch~~ cellulose

Rotation around β(1→4) bond brings glucose functional groups for H-bonding.

strength:- Intra and Inter H-bonds

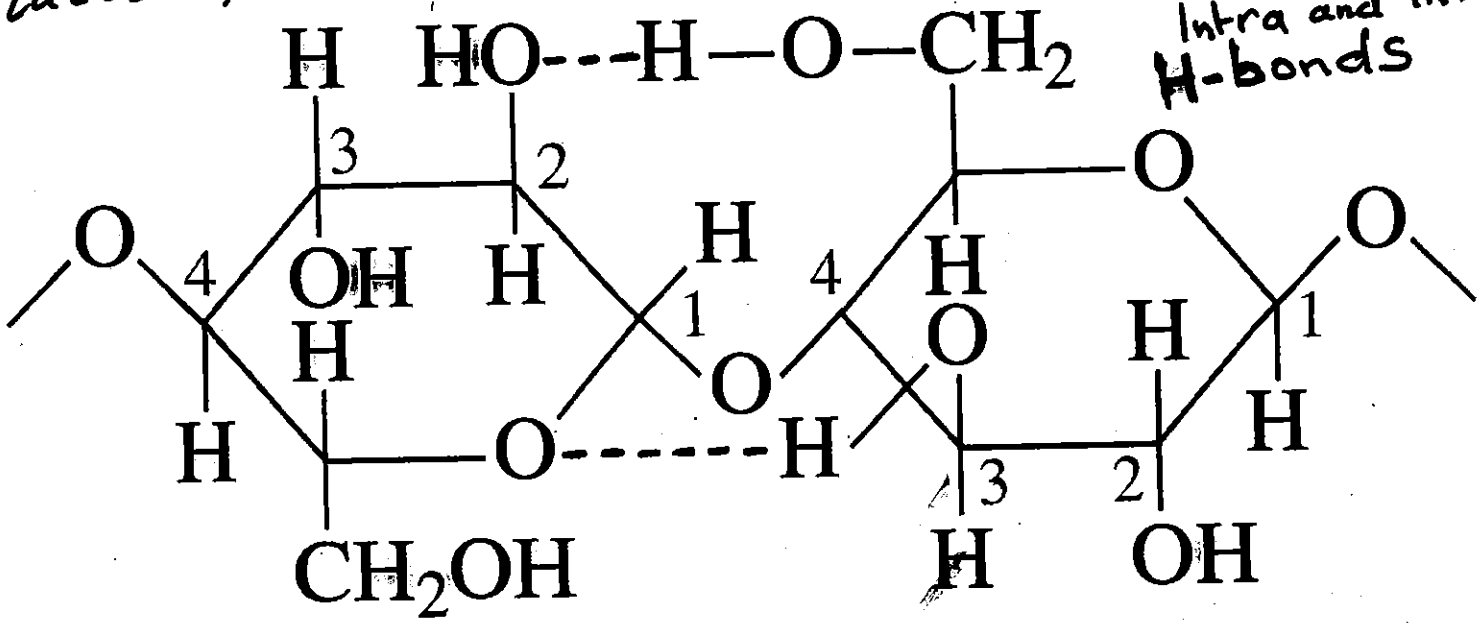


Figure 7-23a Concepts in Biochemistry, 3/e

Chitin:
structural Polymer of N-acetylglucose amine
in shells of arthropods (lobster, spider--)
β(1→4) linkage, inter + intra chain H-bonds

Pectin: plant cell wall, galacturonic acid → gelling agent in Jam + Jellies

H-bonds cross-link two Parallel cellulose chains

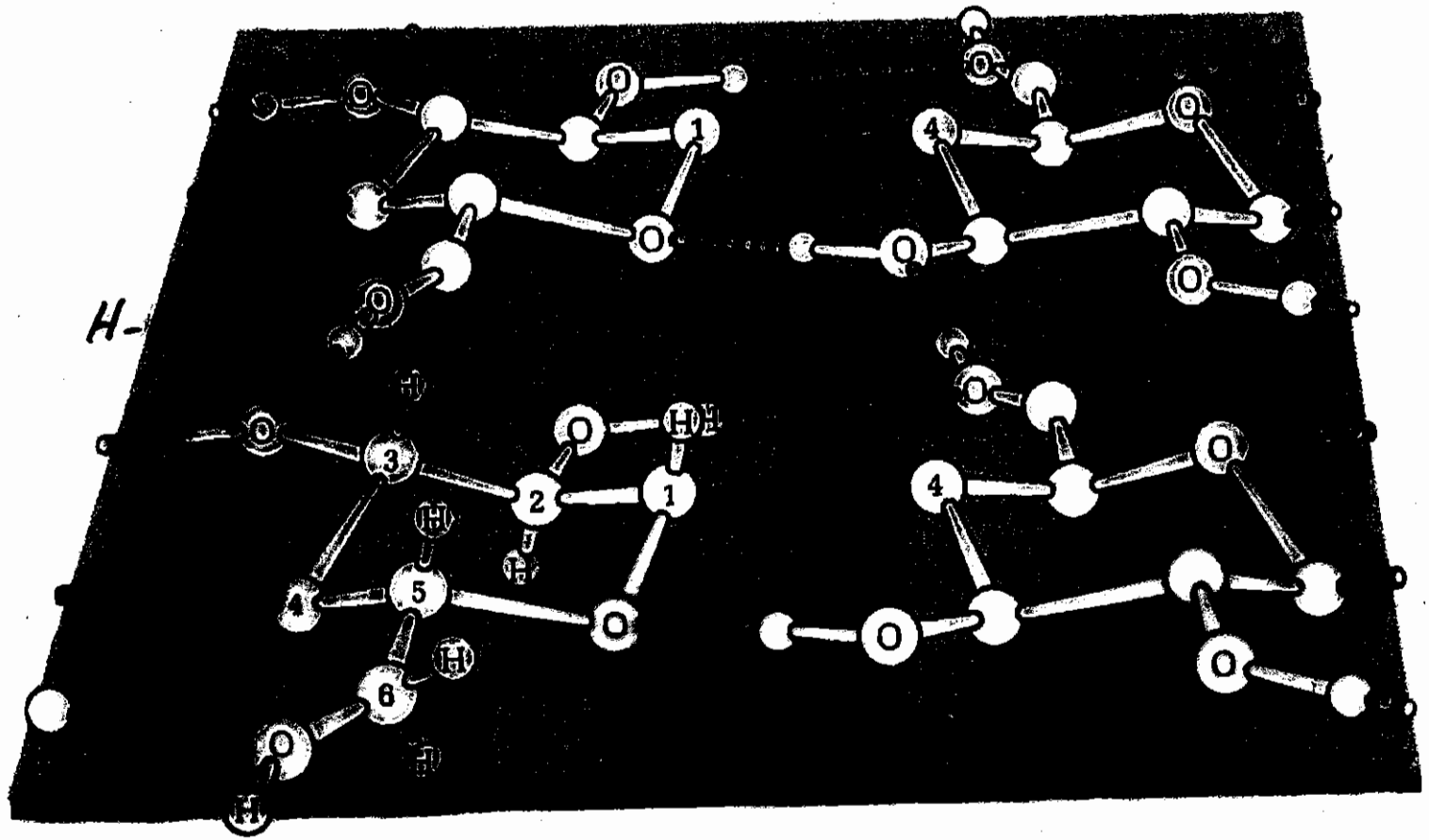
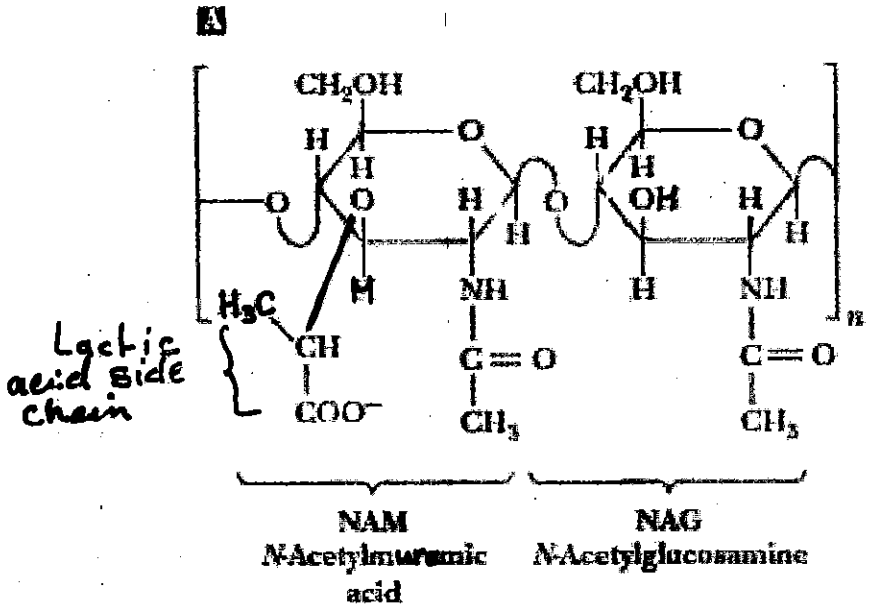


Figure 7-23b Concepts in Biochemistry, 3/e

Polysaccharides in Cell Walls
(bacteria and plants)

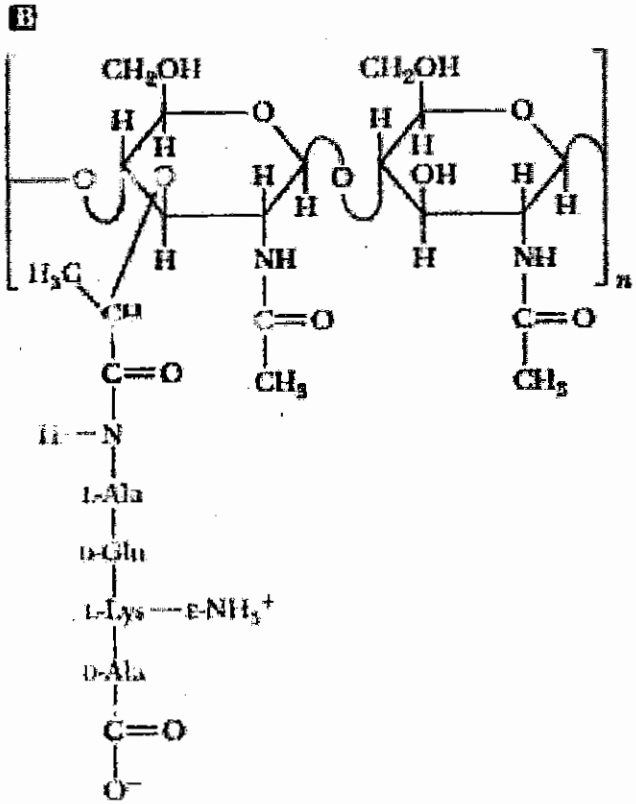


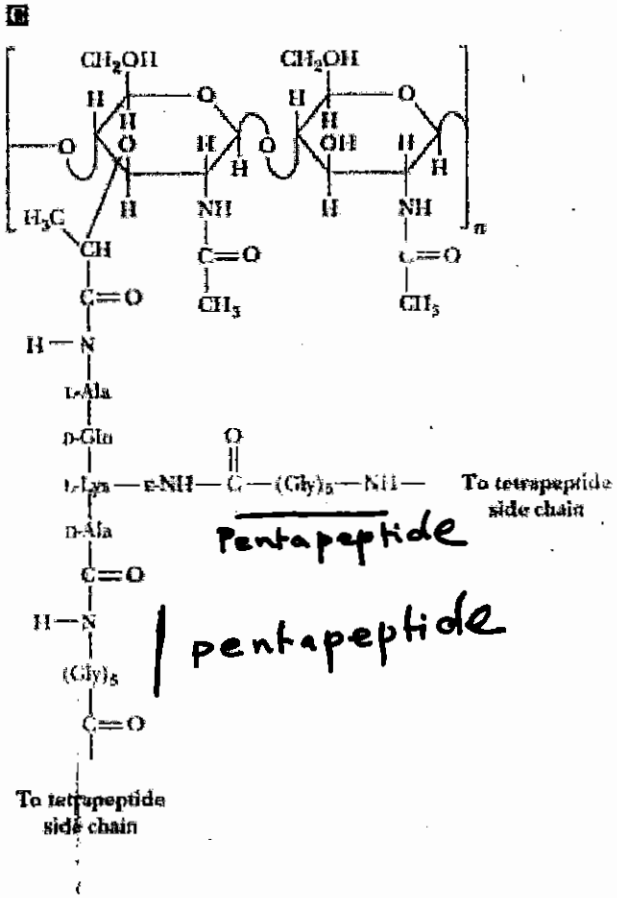
Bacteria:

- Heteropolysaccharides, crossed linked by peptides
- N-acetylmuramic acid is found only in prokaryotic cell walls, it does not occur in eukaryotic cell walls
- Cross links in bacterial cell walls consist of small peptides that contain D-amino acids
- plant cell walls contain little peptide or protein but <u>no</u> D-amino acids
- Plant cell walls
  - largely cellulose
  - also Pectin (galacturinic acid)
  - non-polysaccharide component lignin (polymer of coniferyl alcohol)

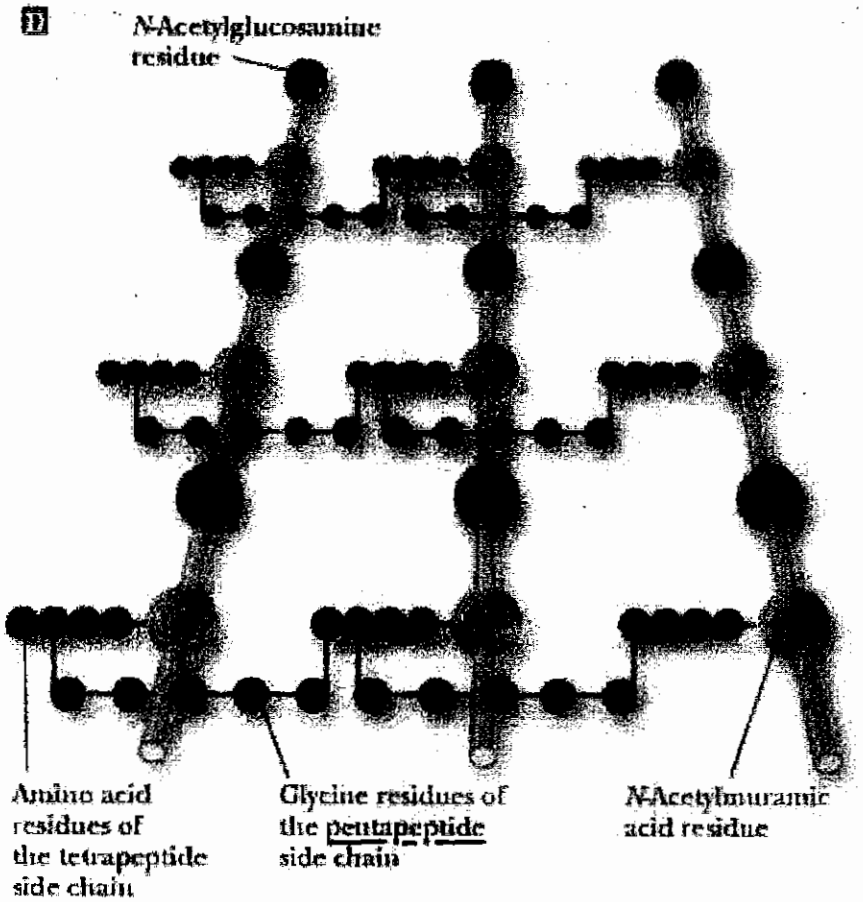
Peptidoglycan in bacterial cell wall

- D-amino acids





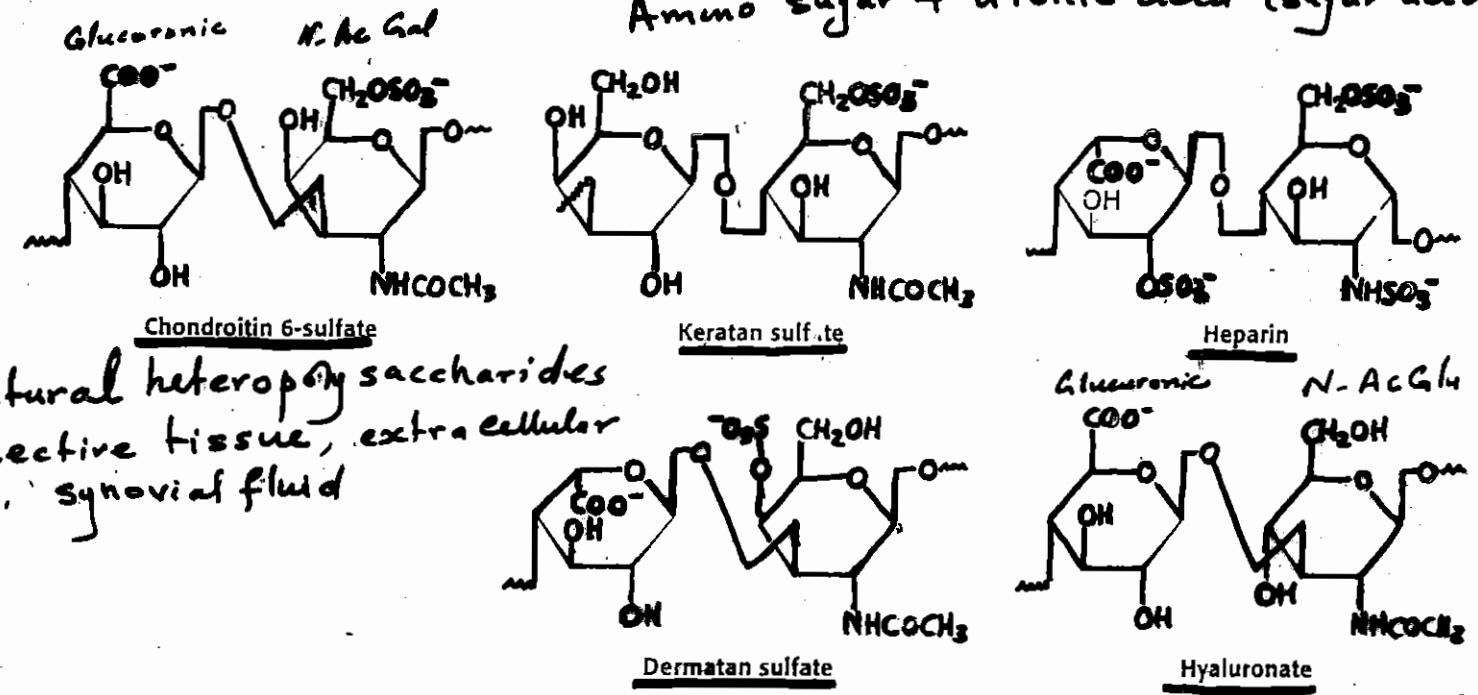
PEPTIDOGLYCAN of CELL WALL



Glycose aminoglycans (GAG) :-
(Mucopolysaccharides)

Anionic Polysaccharides chains made of repeating disaccharide units

Amino sugar + Uronic acid (sugar acid)



structural heteropolysaccharides in connective tissue, extracellular matrix, synovial fluid

Lubricant in synovial fluid

FIGURE 11.15 Repeating units in glycosaminoglycans. Structural formulas for five repeating units of important glycosaminoglycans illustrate the variety of modifications and linkages that are possible. Amino groups are shown in blue and negatively charged groups in red. Hydrogens have been omitted for clarity. The right-hand structure is glucosamine in each case.

Table 7.3
Structures and properties of common polysaccharides

	Name	Type	Components and Linkage	Biological Function
	Starch			
	Amylose	Homopolymeric	Glucose, α(1 → 4)	Nutrient storage (plants)
storage	Amylopectin	Homopolymeric	Glucose, α(1 → 4) with α(1 → 6) branches	Nutrient storage (plants)
	Glycogen	Homopolymeric	Glucose, α(1 → 4) with α(1 → 6) branches	Nutrient storage (animals)
	Dextran	Homopolymeric	Glucose, α(1 → 6) with α(1 → 2), α(1 → 3), and α(1 → 4) branches	Nutrient storage (yeast and bacteria)
	Inulin	Homopolymeric	Fructose, β(2 → 1)	Nutrient storage (plants)
	Cellulose	Homopolymeric	Glucose, β(1 → 4)	Structural function in plants
	Pectin	Homopolymeric	Galacturonic acid	Structural rigidity in plants
	Chitin	Homopolymeric	*N*-Acetylglucosamine, β(1 → 4)	Structural function in exoskeletons
structural	Hyaluronic acid	Heteropolymeric	*N*-Acetylglucosamine; glucuronic acid; β(1 → 4) and β(1 → 3)	Lubricant in synovial fluid, extracellular matrix
	Chondroitin sulfate	Heteropolymeric	*N*-Acetylgalactosamine sulfate; glucuronic acid; β(1 → 3) and β(1 → 4)	Lubricant in synovial fluid, extracellular matrix
	Peptidoglycans	Heteropolymeric, with peptide cross-links	*N*-Acetylglucosamine; *N*-acetylmuramic acid; β(1 → 4)	Structural function in bacterial cell walls

Table 7-3 Concepts in Biochemistry, 3/e

Glycoproteins

- 1% – 30% w/w are carbohydrate
- Many biological functions
  - Immunological
  - cell recognition
  - blood clotting
  - signal transduction
  - Host-Pathogen inter.
- Most common monosaccharides →
- branched
- Information-rich
- O-glycosidic link
  N-glycosidic link

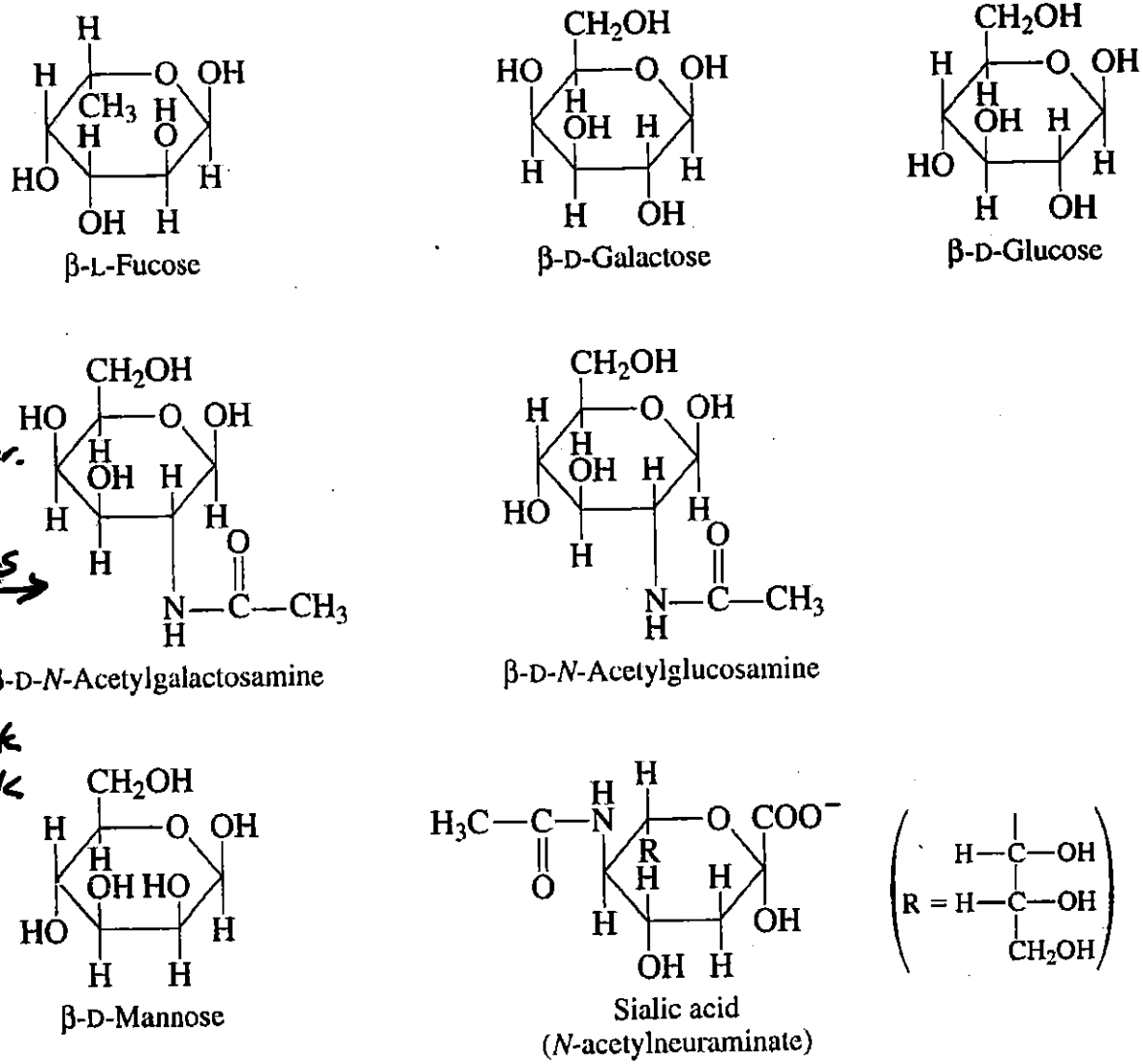
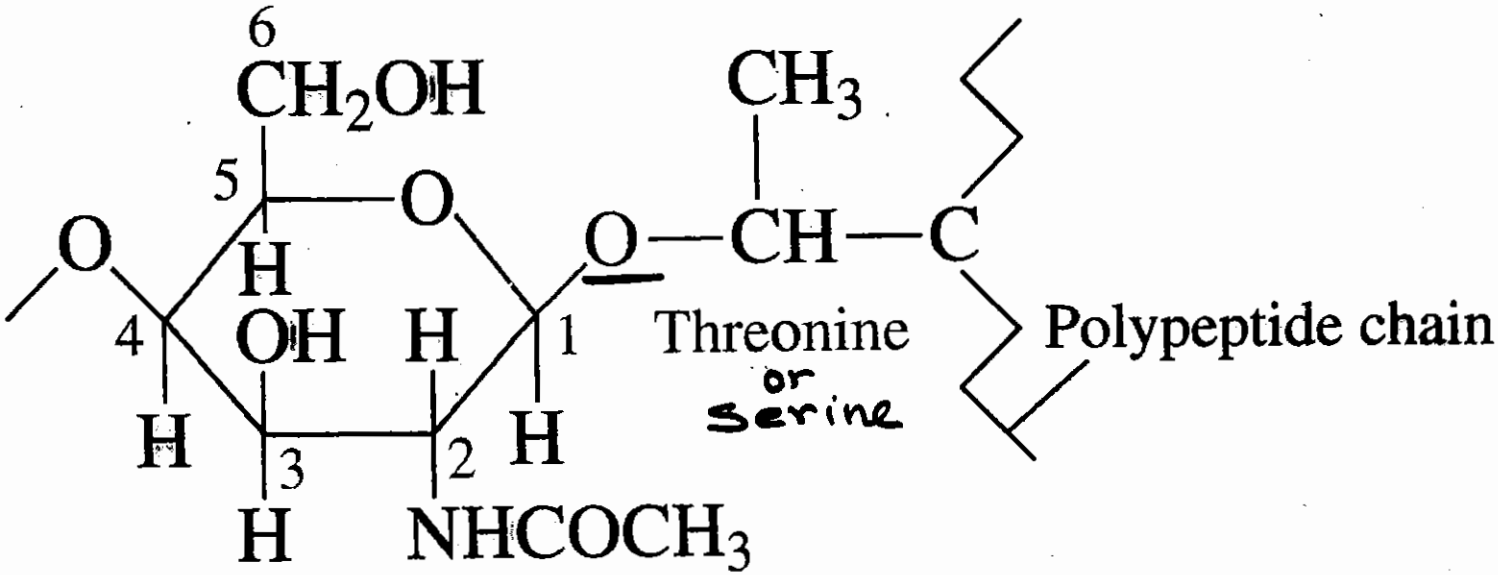


Figure 7-29 Concepts in Biochemistry, 3/e

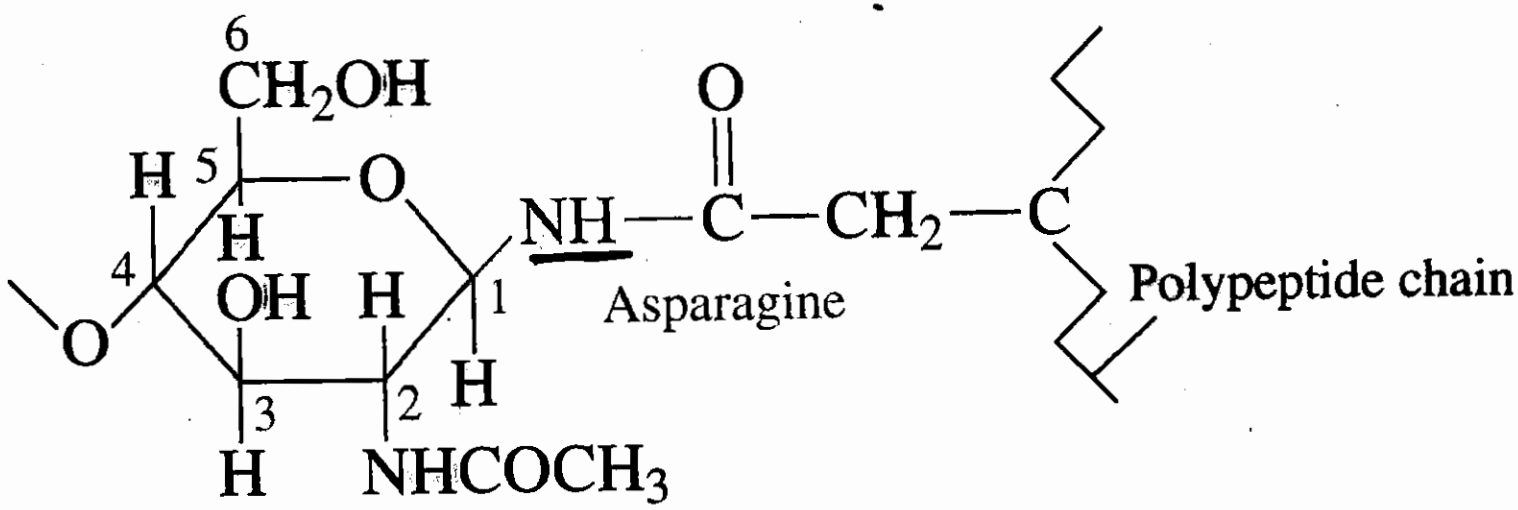
Glycoprotein: O-glycosidic bond



N-Acetylgalactosamine

Figure 7-30a Concepts in Biochemistry, 3/e

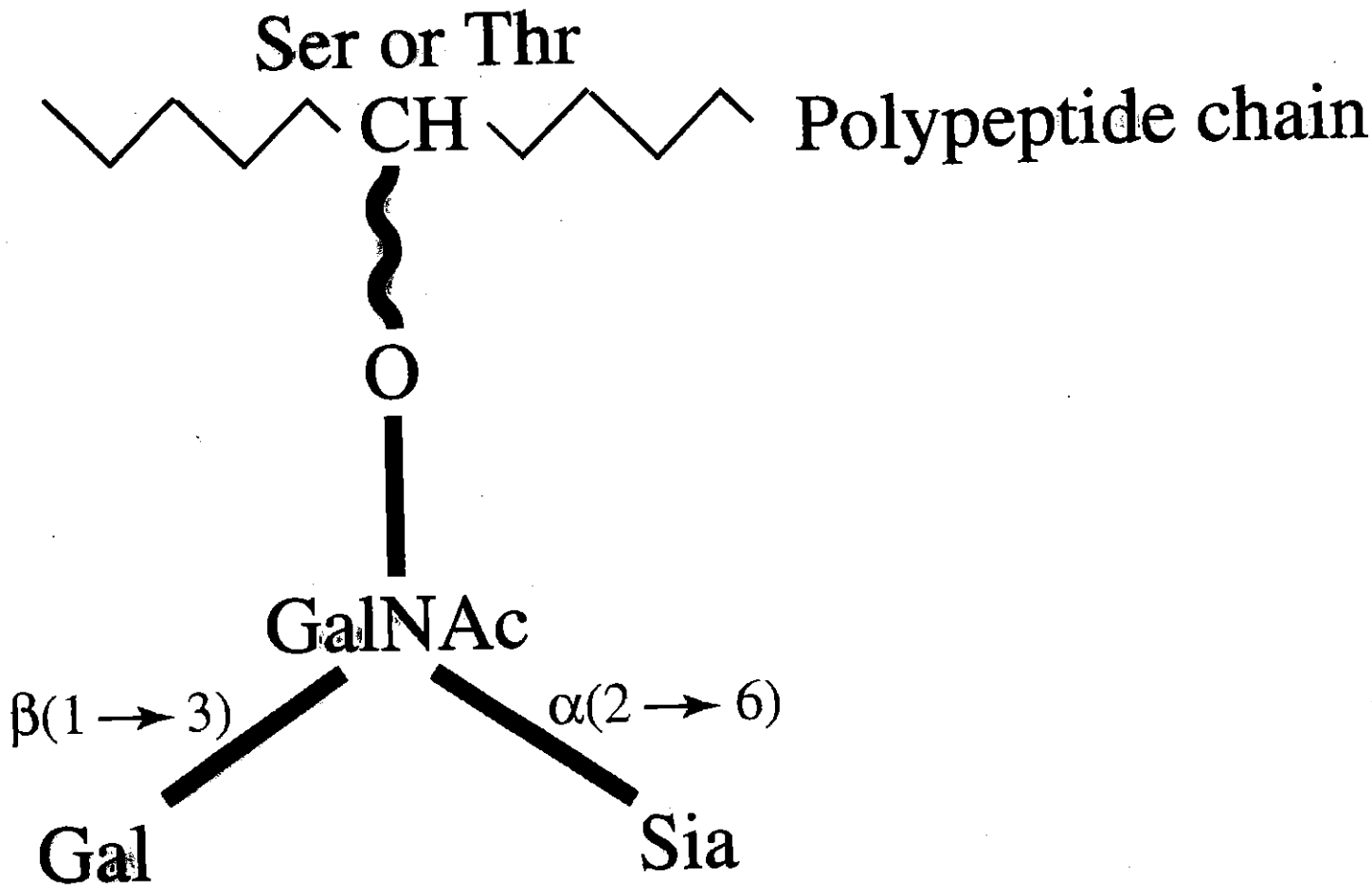
Glycoprotein with N-Glycosidic bond



N-Acetylglucosamine

Figure 7-30b Concepts in Biochemistry, 3/e

Oligosaccharide units in Glycoprotein



O-Glycosidic bonds

Figure 7-31a Concepts in Biochemistry, 3/e

Oligosaccharide Unit in Glycoprotein

- Mannose-rich

Function of Glycoprotein

- Blood type determination A, B, AB, O
- Ab action
- Cancer initiation
- turn-over of aged proteins
- Viral Growth
- antifreeze proteins

- Cancer cells lack glycosyl transferase → contact inhibition ↓
- Many viruses uses glycoproteins for attachment to host

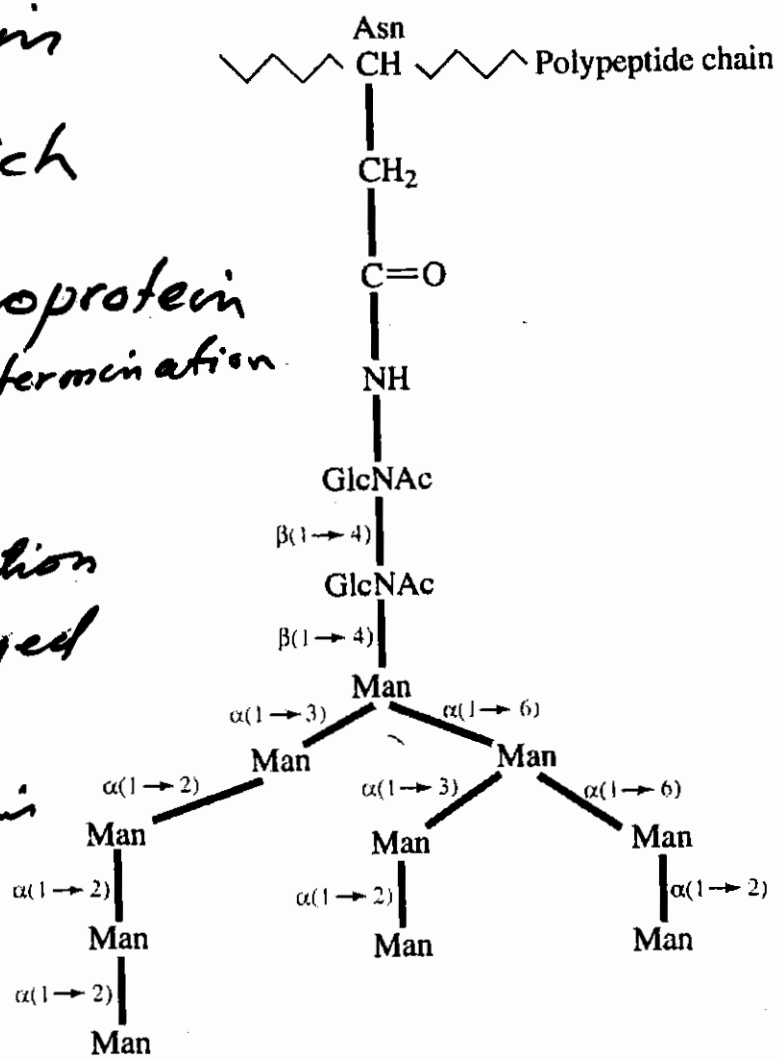


Figure 7-31b Concepts in Biochemistry, 3/e

Protein turnover

Removal of carbohydrate residues e.g. sialic acid initiate

Protein turnover.

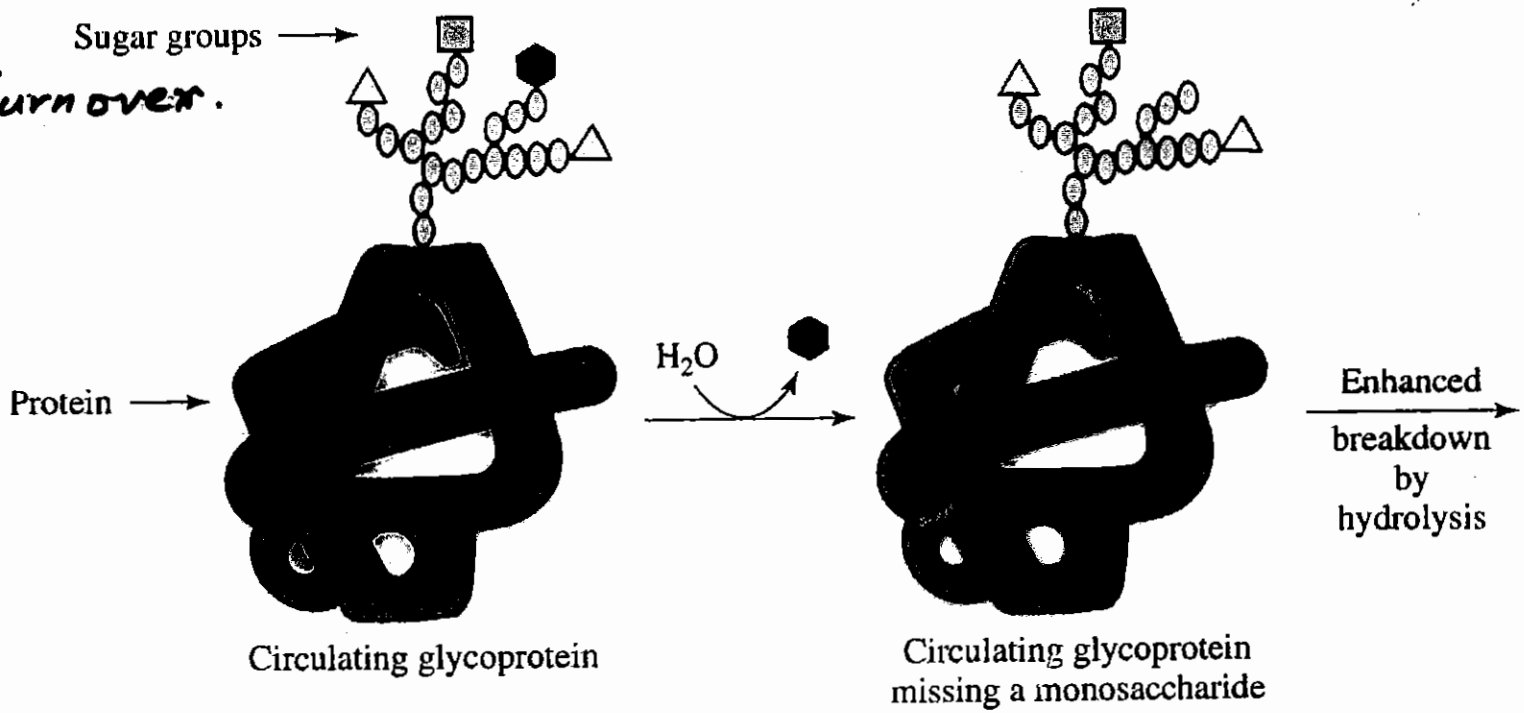
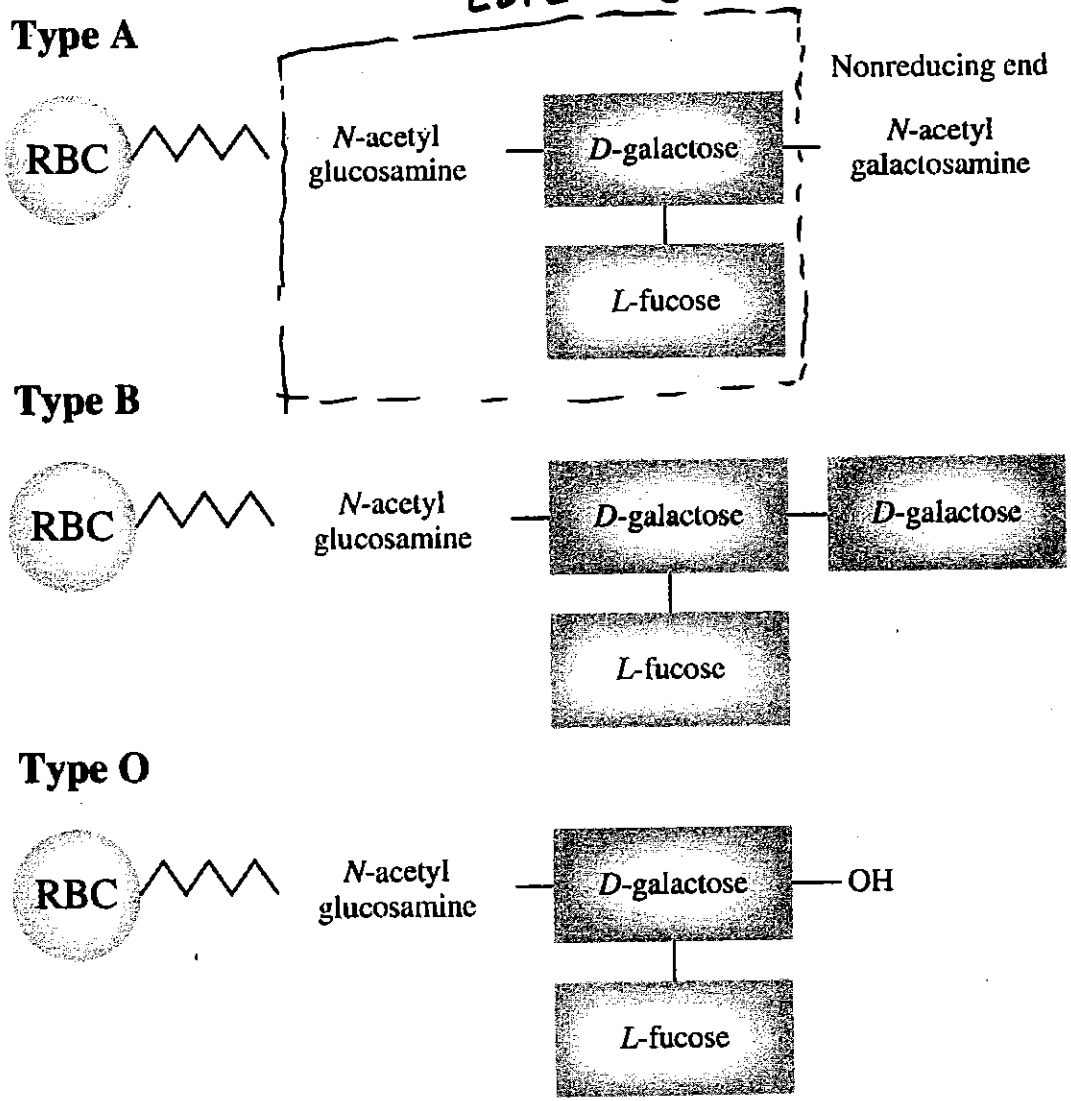


Figure 7-32 Concepts in Biochemistry, 3/e

The ABO blood group



Unnumbered figure pg 225 Concepts in Biochemistry, 3/e

Lectins — proteins that recognize
Carbohydrates
Concanavalin A
agglutinin
selectins

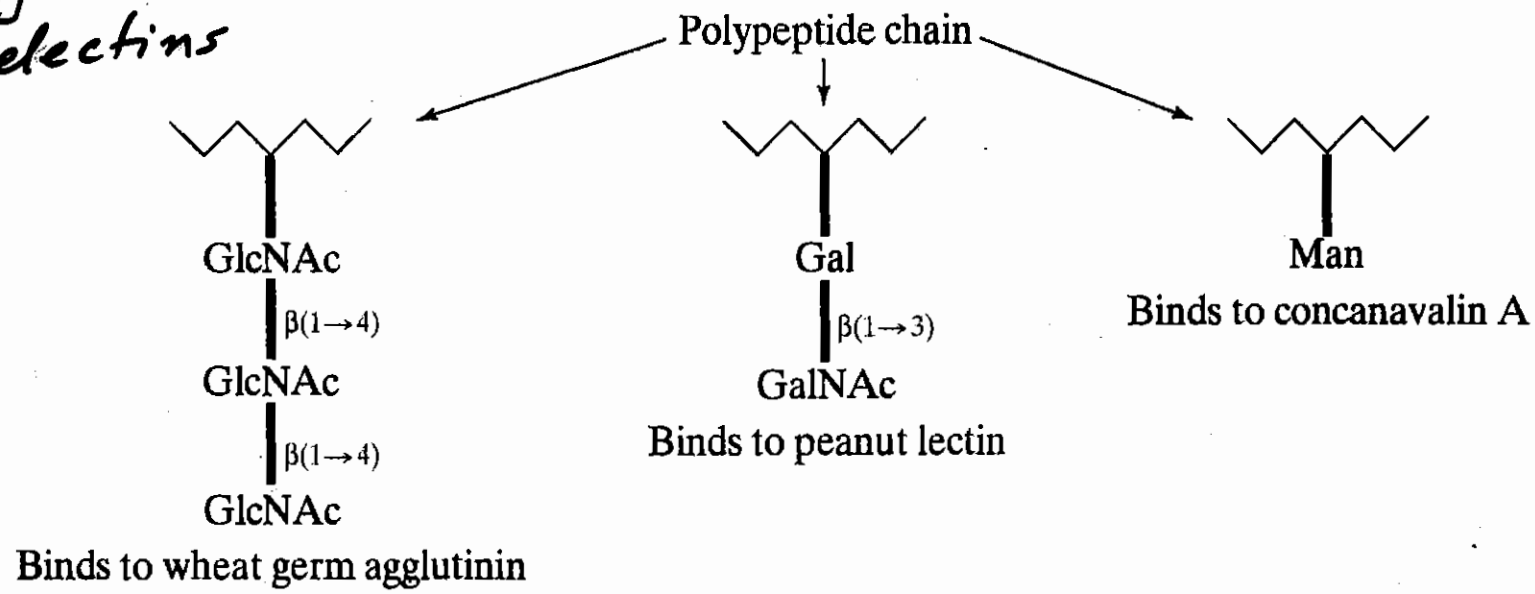


Figure 7-33 Concepts in Biochemistry, 3/e