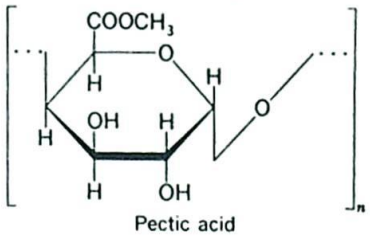
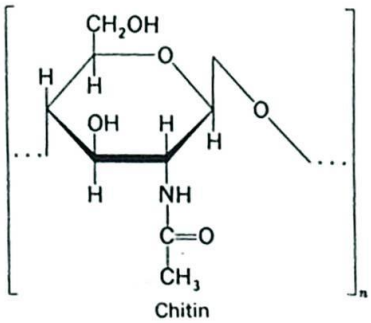
of cellulose are not hydrolyzed by the amylases found in the digestive tracts of humans or most other higher animals. Consequently, man and most animals cannot utilize the energy present in this glucose polymer. Ruminants are an important exception, however, since the bacteria that reside within the rumen secrete cellulase, a β-glucosidase, that catalyzes the hydrolysis of cellulose. These bacteria and others resident in the rumen then metabolize the glucose produced in a remarkable fermentation that is beneficial to the host animal. Snails and wood rotting fungi also secrete cellulase that can degrade cellulose. Termites can also degrade cellulose because their digestive tract contains a parasite that secretes cellulase.

Other examples of structural polysaccharides in plants are known. Plants contain pectins and hemicelluloses. The latter are not cellulose derivatives, but rather are polysaccharides enriched in D-xylose (xylans), D-mannose (mannans), and galactose (galactans) and linked by $\beta(1 \rightarrow 4)$ or $\beta(1 \rightarrow 3)$ glycosidic bonds. Pectins contain arabinose, galactose, and galacturonic acid. Pectic acid is a homopolymer of the methyl ester of D-galacturonic acid.



Pectic acid

Chitin, a homopolymer of *N*-acetyl-D-glucosamine, linked $\beta(1 \rightarrow 4)$ is the structural polysaccharide that constitutes the shell of crustaceans and the exoskeleton of insects.

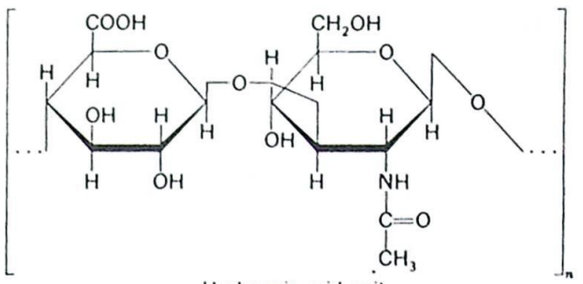


Chitin

2.8 POLYSACCHARIDES IN CELL WALLS

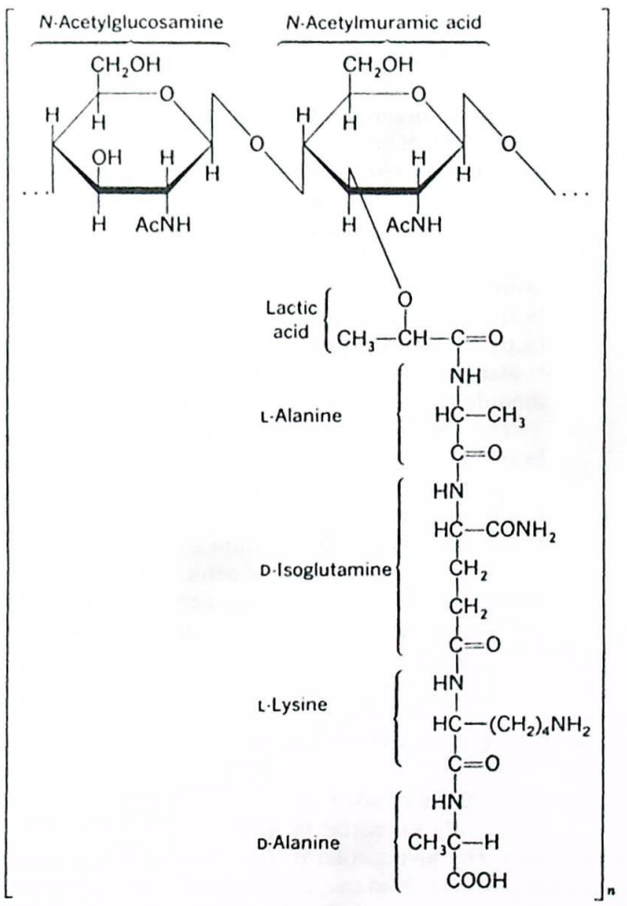
Animal cells do not possess a well-defined cell wall but have a **cell coat,** visible in the electron microscope, that plays an important role in the interaction with adjacent cells. These cell coats contain glycoproteins, glycolipids, and mucopolysaccharides. The chemical nature of the first two will be discussed later (Sections 2.9 and 7.7). The mucopolysaccharides are gelatinous substances of high molecular weights (up to 5×10^6) that both lubricate and serve as a sticky cement. One common mucopolysaccharide is hyaluronic acid, a heteropolysaccharide composed of alternating units of D-glucuronic acid and *N*-acetyl-D-glucosamine. The two different monosaccharides are linked by a $\beta(1 \rightarrow 3)$ bond to form a disaccharide that is linked $\beta(1 \rightarrow 4)$ to the next repeating unit. Hyal-

uronic acid, found in the vitreous humor of the eye and the umbilical cord, is water soluble but forms viscous solutions.



Hyaluronic acid unit

Chondroitin, similar in structure to hyaluronic acid except that the amino sugar is *N*-acetyl-D-galactosamine, is also a component of cell coats. Sulfate



Repeating unit of peptidoglycan
of *Staphylococcus aureus*

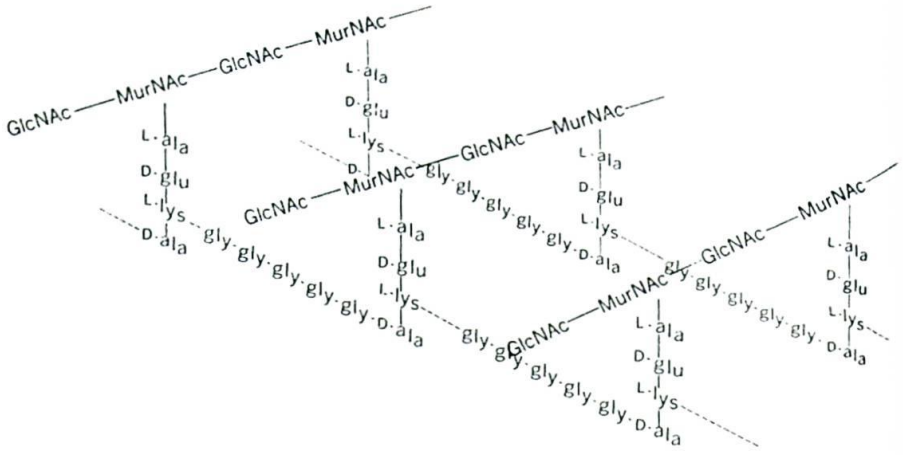


FIGURE 2.4 The linear chains of the peptidoglycan are cross-linked by glycine pentapeptides.

esters (at the C-4 or C-6 positions of the amino sugar) of chondrotin are major structural components of cartilage, tendons, and bones.

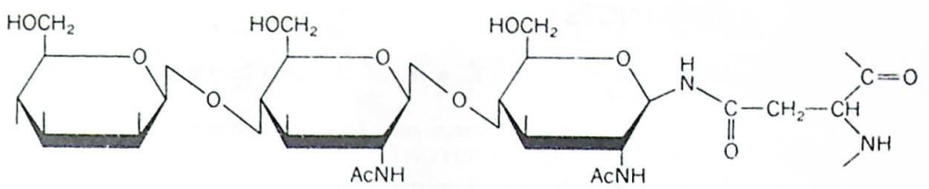
Bacterial cell walls, which determine many of the physiological characteristics of the organism they enclose, contain a heteropolysaccharide linked to a short chain of amino acids. Since the individual chains of amino acids are not as long as in proteins, such polymers have been termed peptidoglycans rather than glycoproteins. The heteropolysaccharide is an alternating chain of *N*-acetyl-D-glucosamine (GlcNAc) and *N*-acetylmuramic acid (MurNAc) joined by a $\beta(1 \rightarrow 4)$glycosidic bond. *N*-Acetylmuramic acid consists of a *N*-acetyl glucosamine unit that has its C-3 hydroxyl group joined to the α-hydroxyl group of lactic acid by an ether linkage. In the peptidoglycan, the carboxyl group of each lactic acid unit is linked, in turn, to a tetrapeptide that usually contains both D-alanine and L-alanine. Other amino acids found in the tetrapeptide may include D-glutamine, D-*iso*-glutamine, L-lysine, or diaminopimelic acid.

The linear polysaccharide chain of the peptidoglycan has a tetrapeptide branch at every second hexoseamine unit that is cross-linked to adjacent, parallel, polysaccharide chains. In the cross-linking (Figure 2.4), the carboxyl group of the terminal D-alanine moiety is attached to a pentaglycine residue that, in turn, is attached to the ε-amino group of lysine in the next adjacent glycan unit.

The antibiotic activity of penicillin is due to its ability to inhibit the last step in the biosynthesis of bacterial peptidoglycans. With the synthesis of this essential component of the cell wall inhibited, the bacteria are unable to grow or replicate.

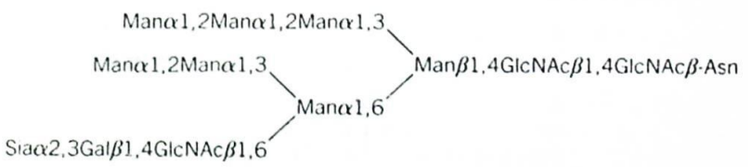
2.9 GLYCOPROTEINS

Most of the oligo- and polysaccharides in the animal and plant cell are linked covalently to protein or lipid molecules known as glycoproteins or glycolipids. In many glycoproteins, the amide group of asparagine is linked through an *N*-glycosyl bond to a core trisaccharide consisting of one molecule of mannose (Man) and two molecules of *N*-acetyl glucosamine (GlcNAc).

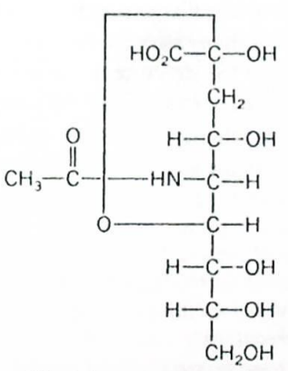


Manβ1,4GlcNAcβ1,4GlcNacβ-Asn

The mannose moiety of the core polysaccharide constitutes a branch point where two more mannose molecules are linked in $\alpha(1 \rightarrow 3)$ and $\alpha(1 \rightarrow 6)$ linkages. Either or both of the two mannose units may then serve as additional branch points for further enlargement of the polysaccharide component. In a highly branched example, galactose, sialic acid, and *N*-acetyl glucose are additional components of the branched polysaccharide.



A sialic acid is a ketose containing nine carbon atoms (ketononose) that may be acylated with acetic or glycolic acid. *N*-acetyl-D-neuraminic acid is a specific example of a sialic acid.



N-Acetyl-D-neuraminic acid

The core polysaccharide can also be linked to the protein component through an *O*-glycosyl bond to the hydroxyl group of serine instead of the asparagine amide group. Hydroxylysine can substitute for serine, and other sugars such as xylose and galactose can substitute for the GlcNAc. The latter are found in such glycoproteins as collagen and proteoglycan. It is apparent that glycoproteins, which are widely distributed in all living matter, can show considerable diversity.

Much remains to be learned of the structure of cell walls before we can completely understand such important phenomena as the immune response and cellular growth and differentiation.

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REVIEW PROBLEMS

1. If heptoses (7-carbon sugars) are synthesized by Kiliani synthesis from a given 4-carbon sugar, how many isomers would be obtained?

2. An equilibrium mixture of α- and β-D-galactose has an $[\alpha]_D^{25^\circ}$ of $+80.2^\circ$. The specific rotation of pure α-D-galactose is $+150.7^\circ$. The specific rotation of pure β-D-galactose is $+52.8^\circ$. Calculate the proportions of α- and β-D-galactose in the equilibrium mixture.

3. Draw the structure of any β-D-aldoheptose in the pyranose ring form, using the Fischer projection or the Haworth ring structure, and answer the following questions:

(a) How many asymmetric carbon atoms does the above sugar have?

(b) How many stereoisomers of the above sugars are theoretically possible?

(c) Draw the structure of the *anomer* of the above β-D-aldoheptose.

(d) Draw the structure of the *enantiomer* of the above β-D-aldoheptose.

(e) Draw the structure of an *epimer* (other than the anomer) of the above sugar.

(f) Draw the structure of a *diastereoisomer* of the above β-aldoheptose.

(g) Draw the structure of a *structural isomer* of the above β-aldoheptose.

(h) Draw the structures of the two different sugars that you would obtain if you used the aldoheptose drawn initially as the starting material for a Kiliani synthesis (involving HCN addition, etc.).

(i) Why does the Kiliani synthesis yield two different sugars starting from a single precursor?

(j) Draw the structures of two different sugars that would yield the same osazone as the β-D-aldoheptose drawn initially.

(k) Draw the structure of the same β-D-aldoheptose drawn initially in the furanose ring form.

4. An unknown disaccharide was purified from bacteria. Equal amounts of D-glucose and D-galactose were obtained after acid hydrolysis of the disaccharide and the two sugars were found to be linked by an α-glycosidic linkage. Exhaustive methylation of the disaccharide produced equal amounts of 2,3,4,6-tetramethylgalactose and 2,4,6-trimethylglucose. Using the Haworth formula, draw the structure of the disaccharide suggested by the above information and show clearly the linkage between the sugars.