2. Structure and bonding of carbohydrates, proteins and lipids

2.1. Polymers, monomers, and bonding

Carbohydrates, proteins, and lipids are primary nutritional ingredients for humans. The breakdown of nutrients (carbohydrates, proteins and lipids) in the intestines results in small compounds (metabolites) that can pass through the wall of the intestines into the blood. Complex carbohydrates and proteins are polymers that break up into a large number of smaller similar compounds, the monomers. Lipids do not have monomer and polymer forms. *All complex compounds in an organism are produced within the organism itself and are also specific to it*.

2.1.1. Complex carbohydrates/polysaccharides

There are three main complex carbohydrates in nature. All three are polysaccharides (see also section 3.2.). *Starch* and *cellulose* are both typical plant products. They are polymeric forms of glucose, and glucose is considered the monomer of starch and cellulose. Even though they are both complexes of glucose in plants, starch and cellulose have a different shape and a different function. *Glycogen* is the glucose polymer in animals and humans. Each of the three breaks down to become a large number of D-glucose molecules.

The glucose molecules in these polysaccharides are linked together by α- or β-*glycosidic linkages*. Glycosidic bonds are special covalent bonds. The special nature of these bonds determines much of the shape of the more complex compound, largely because these linkages inhibit the rotation of specific molecules toward each other.

Starch, cellulose, and glycogen are homopolysaccharides because they contain only one type of monomer, glucose. There are heteropolysaccharides which contain more than one monomer, such as the peptidoglycans in bacterial cell walls. Mostly there are not more than two different kinds of monomer in carbohydrate polymers. We will find that carbohydrates are less differentiated in their polymer structure than proteins (section 2.1.2.).

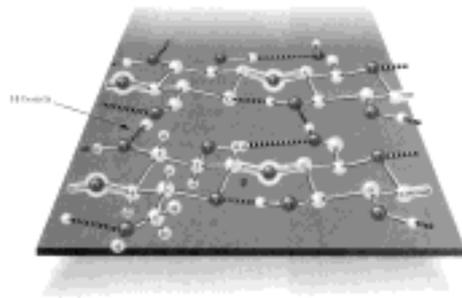Fig. 2.1 Starch (from Campbell, 1999)

Starch

Starch occurs as granules in plant cells. It breaks down to become a large number of α-D-glucose molecules. Starch has α-glycosidic bonds to link glucose molecules. The preferred conformation of amylose, the simplest form of starch, is a helix. The energy that holds together the helical shape and the glycosidic linkages comes free when it is broken down in plants or in the digestive tract of animals and humans. Its role is to be a major energy source in the living world. Enzymes in plant, animal and human organisms can easily break down the α-glycosidic linkages of the starch helix to yield glucose, and glucose can be broken down further to yield energy (section 3.3.). The α-linkage between the glucose molecules in starch also determines its function as an energy storage compound.

Fig. 2.2 Cellulose (from Campbell, 1999)

Cellulose

Cellulose is the main component of the cell wall of plants. Cellulose is formed from

β-D-glucose with β-glycosidic linkages. The β-glycosidic linkages of cellulose allow for additional hydrogen bonding between linear polysaccharide chains. This results in a strong planar shape which can neither be broken down easily in plants nor in the digestive tract of humans and many animals. The typical β-linkages of cellulose, and the possibility of hydrogen bonding which this allows, make cellulose a structural carbohydrate in plants. The cell wall around the cell membrane of plants consists mainly of cellulose, giving plants their stability. Woody plants contain more cellulose.

Further compounds with β-glycosidic linkages

Structural carbohydrates in non-plants have amino acids or contain amino acid sequences as monomers. Plant cell walls contain relatively little protein or peptide.

Carbohydrates with β-glycosidic linkages can be found in some invertebrates such as insects, shrimp, or lobster. Their exoskeleton contains chitin, which is the polymer of *N*-acetyl-β-D-glucosamine, a monosaccharide with an amine group added onto the sugar. In chitin, individual strands are held together by hydrogen bonds as in cellulose. Accordingly, chitin has a structural function. It is also found in the cell walls of yeasts, fungi and algae.

β-Glycosidic linkages also connect the two amine-group-containing monomers in bacterial cell walls: *N*-acetyl-β-D-glucosamine and *N*-acetylmuramic acid. The strands are cross-linked by amino acid residues, forming a peptidoglycan. Peptidoglycans form a strong structure that is the target of certain antibiotic agents.

Glycogen

Glycogen is found in granules in certain types of cells in animals and humans, like liver and muscle cells, but not normally in heart and brain cells in the human organism. α-Glycosidic linkages connect the glucose molecules in glycogen. As in starch, the α-glycosidic linkages allow for glycogen's function in energy storage because glucose can readily be cleaved off.

2.1.2. Proteins
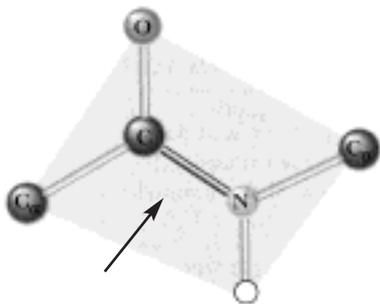
Fig. 2.3 **The peptide bond (from Campbell, 1999)**

When proteins are hydrolyzed this results in a large number of amino acids. Unlike the monomers of polysaccharides, the amino acids in proteins are of many different forms. Twenty different amino acids are found in human protein in varying quantities and combinations. They are linked together by peptide bonds to form the *primary structure* of proteins. Peptide bonds in proteins are also specialized covalent bonds, like the glycosidic bonds in carbohydrates. And, like glycosidic linkages, peptide bonds inhibit rotation of specific molecules in the amino acids around each other and therefore play a role in the final shape of proteins.

However, the final shape of proteins is not exclusively determined by the sequence of amino acids and the peptide bonds linking them together (the protein's primary structure of covalent bonds). The conformation of proteins is also subject to intricate folding processes connected to different types of bonds such as hydrogen bonds and disulfide bonds. The primary structure of proteins, though, determines their ability to form a secondary and tertiary structure, which is required for proteins to be biologically active in the organism.

The *secondary structure* of proteins is based on the hydrogen-bonded arrangement of the protein's amino acid backbone. It is responsible for α-helix and β-pleated sheet sections in the protein chain. Hydrogen bonds are important in the final structure of collagen, a structural protein (see section 4.2.2.).

The *tertiary structure* of proteins adds to their actual three-dimensional structure with the help of covalent disulfide bonds between sulfide-containing amino acid side chains, hydrogen bonding between amino acid side chains, electrostatic forces of attraction and hydrophobic interactions. Proteins can exhibit a rod-like fibrous or a compact globular conformation, depending not only on the bonding forces mentioned above but also on the conditions under which the protein is formed (sections 4.2.2. and 4.2.3.).

Proteins can also have a *quaternary structure*, which involves several different polypeptide chains. The bonds involved to hold this protein structure together are noncovalent.

The conformation of a protein is specific to it and determines its function and its functional ability.

2.1.3. Lipids

Acetyl-CoA can be considered an important common component of lipids. In the group of lipids, fatty acids and cholesterol are both ultimately synthesized from acetyl-CoA. The open chain lipids contain one or more of the fatty acids, and the fused ring lipids, the steroids, are conversions of cholesterol. Fatty acids are also oxidized to acetyl-CoA. Cholesterol derivatives are not broken down in the human body but are excreted (section 5.4.1.).

Lipids have the tendency to form clusters in the watery milieu of the body because they have long nonpolar tails which are hydrophobic. The hydrophobic fatty acid tails are "hidden" inside the cluster, sequestered from water, and at the periphery of the cluster the water-soluble hydrophilic side, connected to the head group, is exposed (see fig. 2.4.). Hydrophobic interactions occur spontaneously in aqueous surroundings. In terms of thermodynamics, this type of interaction does not require added energy when hydrophobic side chains or tails are present in the watery milieu of the body. This is in contrast to the types of bonding described earlier, which do require extra energy to occur (see section 1.1.).

Lipid clusters can take on either micelle or membrane-like forms to allow sequestering of their hydrophobic portions from watery surroundings. The *micelle form* occurs, for instance, when lipids are taken up into and transported in the body. Micelles have a single layer of lipids in their structure. They get a high degree of complexity in low-density lipoprotein (LDL) particles, for instance, in which a mosaic of cholesterol and phospholipids bound to a protein (apoprotein B-100) forms the outer structure around many molecules of cholesteryl esters. LDL particles play an important role in the transport of cholesterol in the blood stream.

The triacylglycerols (triglycerides) are the energy storage form of lipids and accumulate as *fat globules* in the cells of adipose tissue (see section 5.2.1.).

All lipids except for triglycerides can be found as components of *membranes*.

Membranes: Lipids are necessary for the formation of membranes because of their hydrophobic property, and the consequent clustering that occurs. Membranes are bilayers
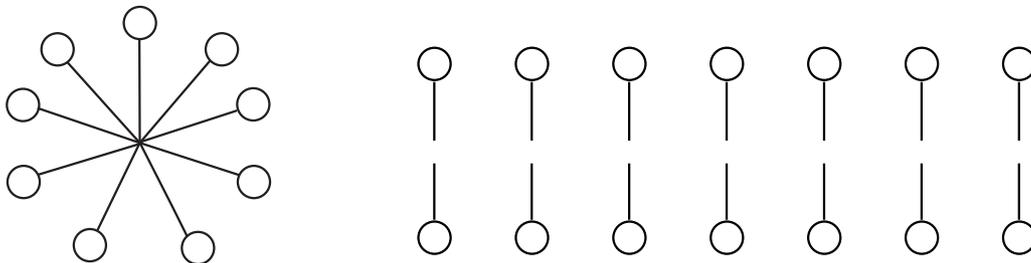
The micelle form   The membrame form

Fig. 2.4 The micelle and membrane forms of lipids. (◯ indicates the hydrophilic backbone of the lipid, | indicates the hydrophobic tail of the lipid). The micelle can be large and have an inner space that is sequestered from water in which lipids can be transported, as in LDL particles. Membranes are actually also round structures and enclose an inner space, the interior of cells or cell compartments.

of lipids. They divide water into compartments, which is essential for the functioning of all organisms. In single-cell organisms it makes the formation of organelles possible and separates the organism from its (mostly aqueous) environment.

Membranes are semi-permeable mainly as a result of the presence of proteins, which function as channels in between the lipids. This allows for the transportation of compounds across the membrane and ensures the connection between the watery milieu inside the membrane with that outside the membrane. Semi-permeable membranes allow for the possibility of a different intracellular milieu from the environment. This makes the single cell into an organism. In multi-cell organisms, membranes make differentiated functioning possible. Cells can have different functions and yet have the same extracellular environment. Metabolism mainly occurs in the intracellular milieu. The extra-cellular milieu has an important role in transportation of metabolic substances and connecting the cells in the organism to form a whole. In vertebrates, the separation of intracellular and extra-cellular milieu makes functions such as the contraction of muscles and conduction of electrical impulses in the nervous system possible.

The presence of the fused-ring lipid, cholesterol, which is rather rigid in its structure, and of unsaturated fatty acids, which have kinks in their tail portion, influences the fluidity of membranes in opposite ways. The membranes of prokaryotes (such as bacteria) are the most supple of all since they hardly contain steroids. Plant membranes contain phytosterols (a steroid similar to cholesterol) and have less fluidity. The many unsaturated fatty acids in plant membranes make them more fluid than membranes in animals and humans, which contain cholesterol.

Lipids (possibly except for the triacylglycerols) occur in specific structured forms in organisms. Lipid structures such as micelles and membranes could perhaps be seen as the polymer form of lipids. The defining interaction in these structures is the spontaneously occurring hydrophobic interaction, supported by weak and changeable van der Waals bonds. Hydrophobic interactions induce the relative immobility of the lipid components toward each other.

However, all components of membranes are in flux, as the seemingly constant shape of organisms is always in movement.

2.2.   Summary and conclusion

Carbohydrates and proteins can occur as polymers, which can be broken down to monomers. Lipids do not have polymer forms but form clusters in the watery milieu of the organism.

Compound structures

In *carbohydrates* the polymer forms have mostly not more than two different monomers in their structure. Glucose is the only monomer in the most common polysaccharides - starch, cellulose and glycogen. The difference in functions among polysaccharides results from the different types of glycosidic bond. Starch and glycogen have α-glycosidic linkages, and they function as a source of energy of plants or animals and humans respectively. Cellulose, chitin, and peptidoglycans have β-glycosidic linkages, and they serve as a structural element in plants and lower animals.

Proteins are more differentiated polymers. In the human organism they may contain as many as 20 different amino acids. The three-dimensional conformation of proteins takes on specific forms that achieve the protein's ability to function.

Lipids have no monomer or polymer forms as such; they all have the energized form of acetate as acetyl-CoA at the beginning of their anabolic pathway. They have the possibility to form secondary structures in the form of membranes or micelles.

Characterization
Carbohydrate, protein, and lipid structures can vary in complexity of form, from storage forms, such as granules or globules in cells, to functionally important helix or planar forms in carbohydrates and proteins, fibrous or globular conformations of proteins, or micelle and membrane lipid structures. In multi-cellular higher organisms, storage forms will occur