### Week 12 Pathways to Biomolecules

• Are molecules such as fats and oils, carbohydrates, proteins and nucleic acids that are found in all living things.

#### • Have an essential role in the

- supply of energy to the body,
- growth and repair of organs and tissue,
- movement of muscles,
- activity of nervous and hormonal systems,
- the elimination of waste.

• Many are polymers *e.g.* cotton, wool and silk.

#### Fats

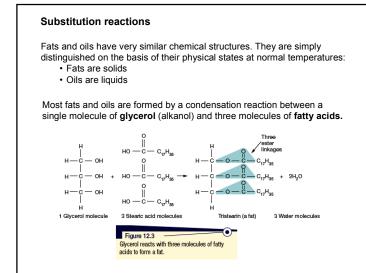
Describes a large number of organic compounds belonging to an even larger class of biological molecules called **lipids**.

Fats and **oils** are the best known types of lipids. (The oils found in foods have quite different structures and properties from the hydrocarbon oils produced by petroleum refining).

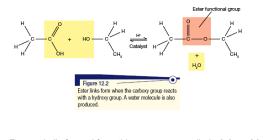
Compounds such as waxes and **steroids** (which include **cholesterol**) are also members of the lipid family.

Lipids are based mainly on carbon and hydrogen with small amounts of oxygen and, occasionally, other elements.

Most lipids are essentially non-polar and so they are insoluble in water.



- Fatty acids contain a carboxy functional group which reacts with the hydroxy groups in the glycerol.
- The -COO- groups in fat are ester functional groups or ester linkages.
- Three molecules of water are also produced in this reaction.



Fats and oils formed from this process are called **triglycerides**. Triglycerides are large, non-polar molecules and therefore insoluble in aqueous solutions.

Type	Semi-structural formula	Molecular formula	Name
Saturated	снуснуцсоон	C.H.D.	Palmiti actid
Mono-unsaturated	сңусңу,сн-сңоңу,соон	C.H.O.	Ofeic add
Polyunsaturated	сн7сн3/сн=снсн7сн=сн(сн3/соон	C.,H2202	Linolek adid

Saturated fats are made from fatty acids that contain only *single* carbon-carbon bonds.

Saturated fats are generally unreactive and occur as waxy solids at room temperature.

**Mono-unsaturated fats** are made from fatty acids that contain *one* carbon–carbon *double* bond.

**Polyunsaturated fats** are made from fatty acids that contain *more than one* carbon–carbon *double* bond. Polyunsaturated fats have lower melting points than saturated fats, and often occur as liquids (oils) at room temperature. They are more reactive than saturated fats.

Both saturated and polyunsaturated fats are present in foods that contain fat.

In general, animal fats contain higher proportions of *saturated* fats, while vegetable oils are richer in *polyunsaturated* fats.

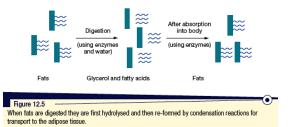
#### TABLE 12.2 Composition of fats and oils

Fat or oil	Saturated fat (%)	Polyunsaturated Tat (%)	Mono-unsaturated fat (%)
Beet	52	1077 <b>4</b>	44
Butor	65	. 4	30
Cacconut	92	2	8
Palm.	51	10	39
Peanut	18	34	48
Saybean	15	61	24
Olive	14	9	77
Com	13	62	25
Sunflower	11	69	20
Safforwer	9.	78	13

#### What happens to fat in digestion?

The pancreas and the walls of the small intestine secretions enzymes that catalyse the **hydrolysis** of fat into fatty acids and glycerol, reversing the condensation reaction from which the fat was made.

Once the fatty acids and glycerol have been absorbed into the body, they are reassembled into triglycerides via condensation reactions.





#### Condensation polymerization

The monomers used to make a polymer by a condensation polymerisation reaction have *a pair of functional groups* that are able to react together, producing a new functional group that links the monomers and also producing a small molecule such as water.

Many biologically important molecules, including proteins, DNA, cellulose and starch, are formed in this way as are synthetic polymers such as nylon and polyester.

Table 12.4 Features of monomers used to produce different types of polymers		
Type of polymer	Functional group in monoments)	
Polyester	Carbony,O30H, and hydroxy,OH	
Polyamide (polypeptide)	Carbory -COOH, and amine, -NH,	
Polysacchartide	Hydroxy,OH and hydroxy,OH	

#### Carbohydrates

The most abundant organic compound on earth is the polymer **cellulose**. Over half the world's organic carbon is bound up in plant material in the form of cellulose.

Cellulose belongs to a class of compounds called **carbohydrates**. As much as 75% of a plant's dry mass is cellulose or other carbohydrates.

Using sunlight, green plants, convert  $CO_2$  and  $H_2O$  initially into the carbohydrate glucose.

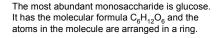
- Carbohydrates are a source of energy in our diets.
- Carbohydrates are made from the elements C, H and O, and usually have the formula  $C_x(H_2O)_y$  where x and y are whole numbers.
- Carbohydrates range in size from small molecules, with MW between 100 and 200, to very large polymers, with MW greater than one million.

#### Monosaccharides: The simple sugars

The smallest carbohydrates are the **monosaccharides**. They are white crystalline solids that are highly soluble in water. Most monosaccharides have a sweet taste. Together with another group of carbohydrates called disaccharides, are often called **sugars**.

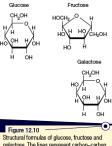
### TABLE 12.5 Important carbohydrates

Carbohydrate	Composition	Where found
Monosaccharides		
Elucose	QH_0,	Fruitjuices
Fructose	CH.O	Fruit Julces, honey
Galactose	CH_D	Not found reducally in its tree form
Disaccharides	Formed Born	
Malese	Gucose + glucose	Germinating grain
Sucrose	Glucose + fructose	Sugarcane, sugar beel
Lackse	Gucose + gametase	MR
Polysaccharides	Polymer of	
Elycogen	Guose	Energy store in animals—In the their and intuscles
Starch	Glucose	Energy store in plants-abundant in wheat, polatoes, com stc.
Celturcee	Guose	Plant fibre-in plant cell walls



Two other important monosaccharides are fructose and galactose.

All three molecules contain a number of polar OH groups, enabling them to form hydrogen bonds with water. This explains the high solubility of monosaccharides in water.



galactose. The lines represent carbon-carbon bonds; carbon atoms in the rings have been omitted for clarity. Glucose is found in all living things, especially in the juice of fruits, the sap of plants and in the blood and tissue of animals.

- functions as the key energy source in most forms of life,
- is also a major component of most of the larger carbohydrates,
- both glucose and starch are more rapidly digested food
  ⇔ the main sources of energy in most diets
  ⇒ bodies use them for energy in preference to fats and

proteins.

Fructose and galactose are not as abundant as glucose • galactose is not found in nature as a free monosaccharide (occurs frequently as a component of larger carbohydrates),

- Fructose is found in many fruit juices and honey. It is the sweetest sugar known, being 1.7 times sweeter than table sugar!
- fructose: main role in the body is as an energy source (used in much the same way as glucose).

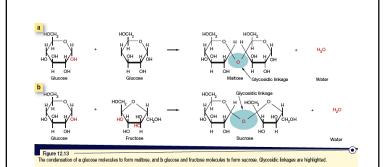
#### Disaccharides

When two monosaccharides undergo a condensation reaction, a **disaccharide** is formed.

Like monosaccharides, disaccharides also dissolve in water, taste sweet and are called sugars.

#### A disaccharide called

- **maltose** is formed when two glucose molecules react, with the elimination of a water molecule.
- **sucrose** is formed when glucose and fructose react with the elimination of a water molecule.



Note how the hydroxy functional groups react to form the disaccharide and water. The two rings are joined via an oxygen atom. This linkage is called a **glycosidic** (or ether) **linkage**.

#### Two other important disaccharides are lactose and sucrose.

Lactose is a disaccharide made by the condensation of galactose and glucose.

- It is not as sweet as glucose.
- Lactose is synthesised in the mammary glands of mammals and is the main carbohydrate present in milk.

In contrast, sucrose is widely used as a sweetener because of its intense taste.

- is formed from the condensation of fructose and glucose.
- sucrose is found in the sap of some trees and the juices of many fruits. Table sugar is produced commercially by extracting sucrose from sugarcane or sugar beet.

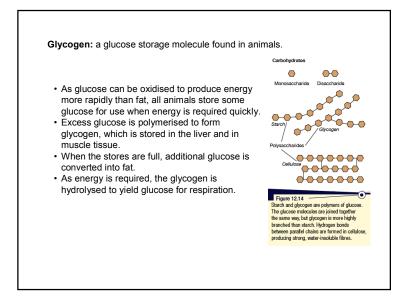
#### Polysaccharides: The complex carbohydrates

**Polysaccharides** are polymer carbohydrates made by linking the monosaccharide glucose together in different ways by condensation reactions.

Polysaccharides are generally insoluble in water and have no taste.

The three most important polysaccharides biologically are:

- glycogen
- starch
- cellulose



Starch is the glucose storage molecule in plants (the equivalent of glycogen).

Starch is stored and used at night to meet the plant's ongoing energy requirements when glucose production from photosynthesis has ceased.

During digestion of starch and glycogen the polymers must be hydrolysed to release the glucose monomers. This hydrolysis is catalysed by enzymes

Starch/glycogen ⇒ Maltose ⇒ Glucose

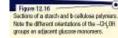
These reactions can be regarded as the reverse of the condensation reactions from which maltose and starch or glycogen are formed from glucose.

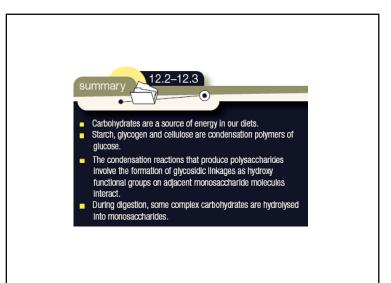


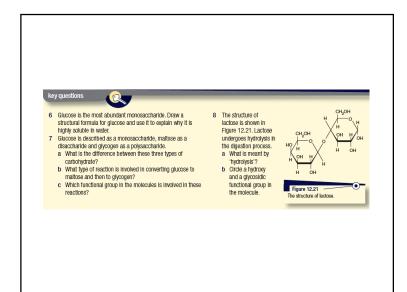
Cellulose is the main structural material in plants.

It is a linear polymer of glucose (MW varying from 50 thousand to 2.5 million). Chemical structure different from starch and glycogen due to slight differences in the linkages between the glucose monomers.

The  $CH_2OH$  groups on adjacent glucose monomers in starch are on the same side of the polymer chain, while in cellulose they are on alternating sides.









#### Proteins

There are thousands of different types of proteins, each with its own specific purpose.

Type Structural	Function Protection, support, movement	Examples Skin, bone, cartilage, ligaments, tendons, muscle, hair, teeth, feathers,
		beaks, cocoons, insect exoskeletons
Enzymes	Biological catalysts	Digestive enzymes
Hormones	Regulation of body functions	Insulin
Transport	Movement of compounds between and within cells	Haemoglobin
Protective	Defence	Antibodies
Toxins	Attack	Snake and spider venoms
Most proteins	Energy source (only in extreme circumstances)	

#### Amino acids

Proteins are polymers built up from small monomer molecules called *amino acids*.

Two of the simpler amino acids are glycine and alanine.

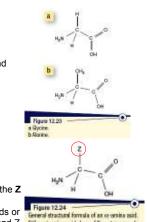
Every amino acid has an *amino group* (NH<sub>2</sub>) and a *carboxy group* (COOH).

Twenty amino acids are commonly found in proteins in the human body.

They have the general formula  $H_2N-CHZ$ COOH.

The major difference between amino acids is the **Z** group.

These amino acids are known as 2-amino acids or α-amino acids because the amino, carboxy and Z groups are all attached to the second carbon atom.

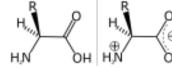


As a consequence of the polar amino and carboxy functional groups, amino acids are soluble in water.

In solution, the amino group can act as a base and the carboxy group can act as an acid.

As a result, an amino acid molecule in a solution at a particular pH will usually be in the form <code>+H3N-CHZ-COO-</code>.

Such a molecule is called a **zwitterion** or **dipolar ion**.



A proton has been lost from the acidic carboxy group and the basic amino group has gained a proton.

The pH at which an amino acid exists as a zwitterion depends on the structure of the Z group.

In acidic solutions
$^{+}H_{3}N-CHZ-COO^{-}(aq) + H_{3}O^{+}(aq) \rightarrow ^{+}H_{3}N-CHZ-COOH(aq) + H_{2}O(I)$
This form is predominant
In alkaline solutions
$^{+}H_{3}N-CHZ-COO^{-}(aq) + OH^{-}(aq) \longrightarrow H_{2}N-CHZ-COO^{-}(aq) + H_{2}O(I)$
This form is predominant
The ability of amino acids to react with both acids and bases means that they can act as <i>buffers</i> , minimising the effect that the addition of H <sup>+</sup> or OH <sup>-</sup> ions to a solution would have on acidity. Their buffering action is of great importance in cells as biochemical processes can only operate correctly if the pH is maintained within a narrow range.

#### Protein structure

When a molecule that contains a carboxy group, COOH, combines with a molecule containing an amine group,  $NH_2$ , a condensation reaction occurs to form an amide functional group, -CONH-, that links the two molecules. A water molecule,  $H_2O$ , is also formed.

# Peptides / Proteins

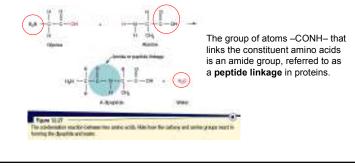
Proteins are polymers formed by *condensation reactions* between amino acids

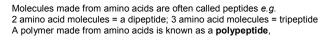
During these reactions the amino acids join and form long unbranched chains.

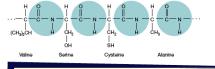
The amine group of one amino acid

reacts with the carboxy group of an adjacent amino acid.

A covalent bond is formed and a molecule of water is eliminated.







## Figure 12.28 A section of a polypeptide chain, showing peptide linkages.

and polypeptides built up from more than 50 amino acids are usually called proteins. There can be more than 500 amino acid units in a large protein.

Proteins differ from one another in the number, type, and sequence of their constituent amino acids.

Each protein has a precise chemical composition, amino acid

sequence, and three-dimensional shape.

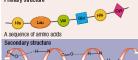
Determining the structure of these complex materials has provided challenging problems for chemists.

### Protein shape and function

The role that any protein fulfils in an organism depends on its shape: primary, secondary and tertiary structures.

forces.

#### Primary structure



Hydrogen bonds between sections of the keratin chains in hair

and wool give these proteins a helical structure

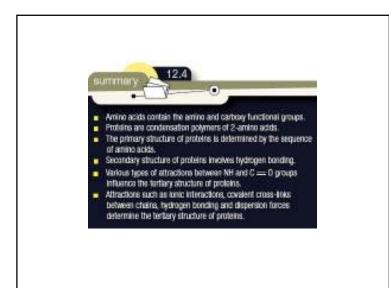
Folding and twisting of the chain, held in place by H bonds between the CO and NH groups in adjacent parts of the chain. Some proteins form a 3-dimensional helical shape

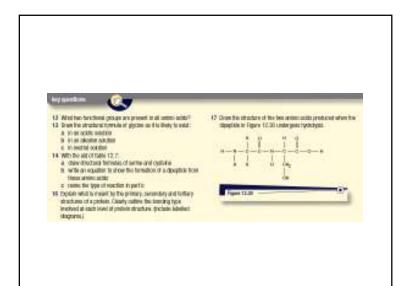
The order in which the amino acids making up the protein are joined together



Overall 3-dimensional structure of the protein, which is formed by the presence of different functional groups in the Z-part of the amino acid, creating shapes that are held in place by disulfide (S-S) covalent bonds, ionic bonds between NH3\* and

COO<sup>-</sup> groups, H bonds and dispersion





#### **Enzymes: Biological catalysts**

Biological catalysts are called **enzymes**. Enzymes *control* the manufacture of complex substances as well as the breaking down of chemicals to provide energy. Enzymes make life possible.

Compared to inorganic catalysts:

- Enzymes produce much faster reaction rates. They can increase the rate of a chemical reaction by as much as 1010 times.
- Enzymes operate under much milder conditions. Even with a catalyst, the conditions for the Haber process for ammonia are 500°C and 250 atm. Enzymes found in bacteria in the roots of leguminous plants perform a similar reaction at normal temperatures and pressures.
- *Enzymes are more sensitive.* The catalytic activity of many enzymes is destroyed when they are heated strongly because their delicate structure breaks down (described as being denatured).
- Enzymes are very selective. For example, platinum metal catalyses many reactions. On the other hand, the enzymes catalyse only particular reaction.

#### Enzymatic catalysis

The catalytic activity of an enzyme depends on its tertiary structure (its three-dimensional shape, a change in which can render an enzyme inoperative).

Some enzymes have small, non-protein parts called **cofactors**, such as vitamins or metal atoms, associated with the active site. These cofactors are necessary for the catalytic effect.

The **active site** of an enzyme is usually a flexible hollow or cavity within the molecule.

A reactant molecule, known as the **substrate**, is manoeuvred into this site and it is there at the *surface* of the enzyme that reaction takes place.



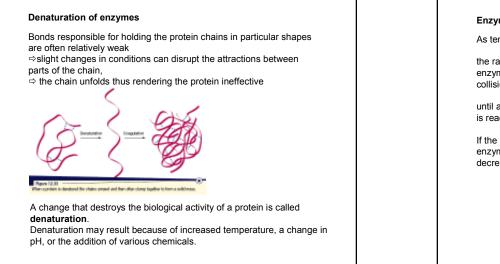
- Bonds formed between the enzyme and substrate weaken bonds within the substrate, lowering the reaction's activation energy.
- The substrate breaks or rearranges into new products and these products are released.

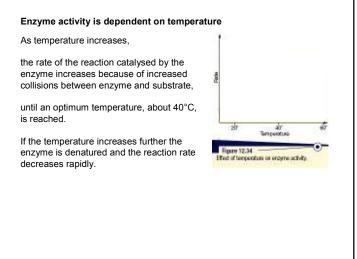
Figure 12.31 \_\_\_\_\_\_ a-c Steps in the action of an enzyme. The *selectivity* of enzymes is one of their most important features.

Although thousands of different reactions are possible in a cell, the presence of enzymes ensures that particular reactions occur rapidly and that others proceed at insignificant rates. In this way, order is maintained in living cells.

This selectivity is due to the shape and functional groups in the active site of the enzyme which allows it to bind only with certain substrates.

The enzyme and substrate are often described as fitting together 'like a lock and key'.



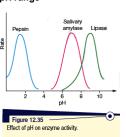


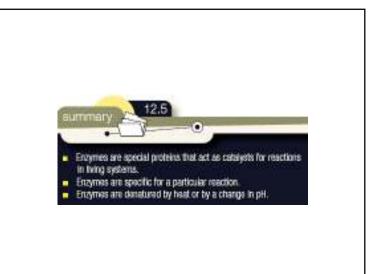


Not all enzymes have the same optimum pH.

The ionisation of amino acids is dependent on pH.

The bonds that determine the tertiary structure of the enzyme are altered as changes in pH alter the ionisation of the amino acid residues in the protein.







#### Proteins as markers for disease

Analytical techniques such as mass spectrometry (Chapter 8), infrared and NMR spectroscopy (Chapter 7) and advanced chromatographic techniques (Chapter 6) as well as two-dimensional electrophoresis are used to identify protein markers that indicate the presence of disease *e.g.* cancer; heart disease.

A raised level of these marker proteins in a patient's blood or tissue can be used to:

- identify a disease at early or advanced stages of development
- · monitor the progress of the disease
- · measure the effectiveness of treatment, and
- · test for the recurrence of the disease.

A raised level of a particular protein marker may indicate the presence of disease before physical symptoms are evident.

There is a continuing search for new, specific, protein markers for a range of diseases.

The study of protein structure and function is called proteomics and it has an increasingly important role in the identification of disease.

