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went on to explain how pigments are molecularly structured, linked through a single and double-bond alternating linkage or chromophore and how this can be shortened by photonic weakening of one of the double-bonded linkages and causing a reduction in colouration (eg. fading) and how a lengthening of the chromophore causes darkening. He mentioned the carotenoids as examples and how the various forms of carotene (α - β - γ - δ - &c) had slightly longer or shorter chromophores and therefore showed different colours. He showed how the blood pigmenting agent Haem – an iron-based tetrapyrrole (with carboxyl groups) can change its composition out of the bloodstream as it loses the iron ion and changes to biliverdin and bilirubin which explains how bruises change colour. He also showed how the magnesium tetrapyrrole, more familiar as chlorophyll, can similarly lose its magnesium ion to change to phaeophytin A and B becoming brown which is why marine brown algae, need only a small amount of sunlight to photosynthesize, hence the kelp niche largely in the lowest intertidal zone. Another example is of porphyrins (found in deep sea jellyfish) which are dissolved by alkalis by removing the iron ion, just as acidified acetone removes haem from haemoglobin. He then ventured into anthocyanins and the families of phenolic –OH (hydroxyl) groups that react with amines and iron, especially ferric iron, to produce very strong pigments but how phenolics are prone to fading through oxidation. He told us how a strongly-pigmented flower can change from bright pink to green or blue when a burning cigarette, combining heat and tobacco smoke, is held very close. He also mentioned the litmus test using anthocyanins and how the red oxonium and the blue (basic) quinone colour reactions are reversible.

He then talked about xanthopterin in insects (with other pterins) and how these too can change colour through oxidation, also how lignin will oxidise in sunlight causing furniture to fade. Fungi contain polyalkynes with triple-bonded carbon atoms but that these triple bonds are amazingly weak and can easily break causing fading, something I have found with some, but not all, of the freeze-dried Hampshire fungal collection.

Papers Given at the Biochemistry Seminar, Jodrell Lab, Kew 9.11.2006

Basic Biochemicals - David Lampard

Biochemistry is the branch of organic chemistry that deals with the molecules involved in biological processes and structures. Before describing some of the main groups of biochemicals it is worth defining some of the terms most frequently used when describing biochemicals and their reactions

There are three types of chemical bond that connect atoms and molecules together;

1. **Covalent Bond**, formed by the sharing of one or more electrons, especially pairs of electrons, between atoms.
2. **Ionic Bond**, formed by two ions with opposite charges, characteristic of salts. Also called *electrovalent bond*.
3. **Hydrogen Bond**, a hydrogen atom of one molecule is attracted to an electronegative atom, especially a nitrogen, oxygen, or fluorine atom, usually of another molecule.

Covalent bonds between carbon atoms help form the long chains of biochemicals. Hydrogen bonds are often involved in determining the shape of large molecules

Displaying formulae

A molecular formula shows the relative abundance of the atoms more electrons, especially pairs of elec-

trons, between atoms.

Structural formulae show the relative position of atoms and bonds.

ISOMERS

Isomers are chemicals with the same molecular formula, but different structural formulae.

Biochemicals exist in right handed and left handed forms called dextro and levo, d and l. usually only the d forms are biochemically active.

Some groupings of atoms in a molecule have characteristic reactions independent of the rest of the molecule. These groupings are called **functional groups**.

Formula	Functional group	Comments
C=O	carbonyl	A carbonyl group on a non-terminal carbon atom is called a ketone group
CH	alkyl	
C=HO	aldehyde	
C=C	alkene	
-OH	hydroxyl (alcohol)	
-COOH	carboxylic acid	
-COOR	ester	'R' stands for any alkyl group
-NH ₂	amine	

FAMILIES OF BIOCHEMICALS

SACCHARIDES are also known as carbohydrates or sugars

Monosaccharides, or simple sugars e.g., glucose

Disaccharides, polymers of two monosaccharides e.g. maltose, lactose

Polysaccharides, long chain polymers of monosaccharides e.g. cellulose, starch

LIPIDS Fats, oils, waxes etc.

Fatty acids and glycerides

AMINO ACIDS are the building blocks of polypeptides and proteins.

Saccharides or carbohydrates are:

- A source of energy for the body e.g. glucose and a store of energy, e.g. starch in plants
- Building blocks for polysaccharides (giant carbohydrates), e.g. cellulose in plants and glycogen in the human body.
- Components of other molecules e.g. nucleic acids, glycolipids, glycoproteins, Adenosine triphosphate.

Monosaccharides

Have the general formula (CH₂O)_n where n usually equals 3,5 or 6

Monosaccharides can be classified according to the number of carbon atoms in the molecule:

n = 3 **trioses**, have the formula C₃H₆O₃ e.g. glyceraldehyde

n = 5 **pentoses**, have the formula C₅H₁₀O₅ e.g. ribose and deoxyribose

('pent' indicates 5)

$n = 6$ **hexoses**, have the formula $C_6H_{12}O_6$ e.g. fructose, glucose and galactose ('hex' indicates 6)

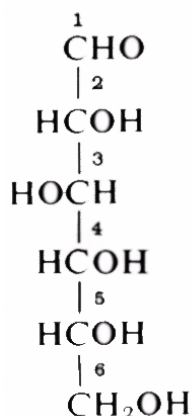


Fig.1 numbering of carbon atoms in glucose

When describing reactions in sugars the carbon atoms are numbered as above. All of the C_6 sugars are isomers.

Monosaccharides are formed in metabolic pathways from simpler compounds with fewer carbon atoms. All the sugars formed from glyceraldehyde e.g. ribose, glucose, galactose, mannose are called aldoses because the functional group is an aldehyde $C=HO$. Aldoses are also known as reducing sugars.

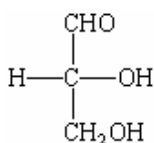


Fig.2 structure of glyceraldehyde

However sugars derived from dihydroxyacetone such as fructose are called ketoses because the functional group is a ketone $C=O$

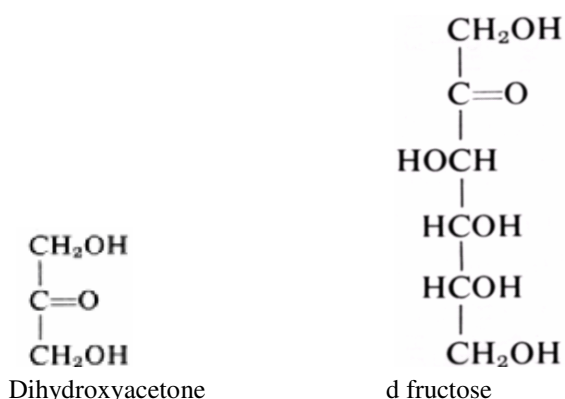


Fig.3 formation of ketose sugars from dihydroxyacetone.

If the carbon chain is long enough, the hydroxyl group at one end of a monosaccharide can react with the carbonyl group at the other end to form a cyclic compound. When a six-membered ring is formed, the product of this reaction is called a pyranose ring.

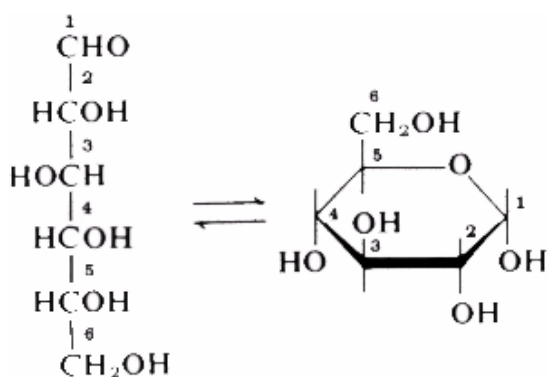


Fig. 4 equilibrium between chain and ring form of glucose

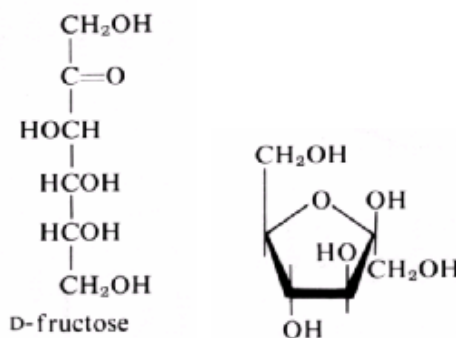


Fig. 5 chain and ring forms of fructose
Fructose forms a five sided ring called a furanose ring

A sugar may transform from the straight chain to the ring structure in an equilibrium state. There are two forms of the pyranose ring named after the position of the hydroxyl group on the first carbon atom.

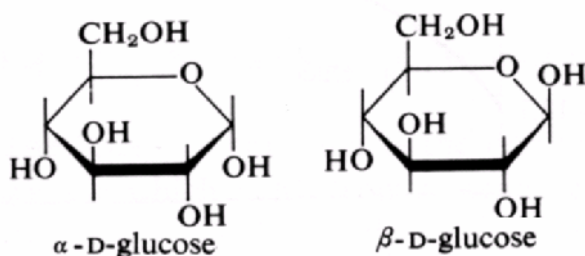


Fig. 6 the two positions of the hydroxyl group in glucose

The nature of the bonds in the ring configuration also means that the ring structure is three dimensional. In the ring configuration there are two shapes, known as the chair form and the boat form. The sugar is constantly changing between forms.

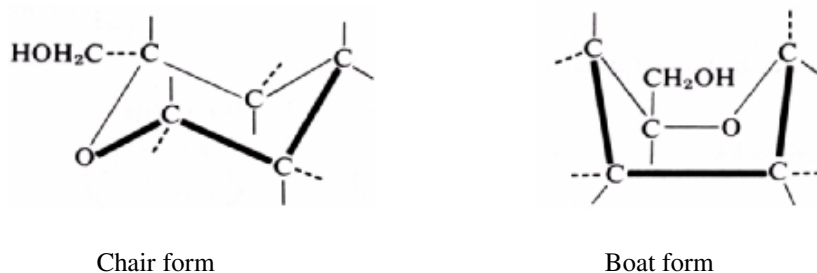


Fig. 7 three dimensional forms of the glucose ring

DISACCHARIDES

The reactive groups on the carbon atoms make it possible for monosaccharides to react together to form polymers, long chain molecules consisting of repeating units. In sugars polymerisation takes place only in the ring configuration

The simplest polymers are DISACCHARIDES, the three most common are

maltose = glucose + glucose

lactose = glucose + galactose

sucrose = glucose + fructose

Lactose and maltose are also reducing sugars because they are derived from aldose sugars.

Disaccharides are more common than simple sugars but cannot pass through cell walls.

Disaccharides are formed through a reaction that is called a condensation reaction, one which releases a water molecule. The resultant bond is called a glycoside bond. This takes energy to form.

The type of polymer formed is described according to the carbon atoms involved and the configuration of the monosaccharides.

Maltose for example has a 1,4, bond in the alpha position. I.e. the hydroxyl group on the first carbon of the first glucose molecule reacts with the hydroxyl group on the fourth carbon of the second glucose.

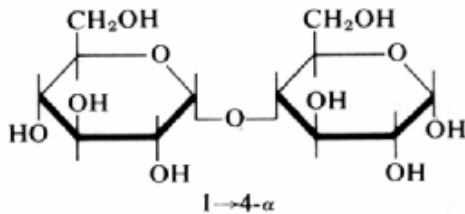


Fig. 8 Maltose showing the 1-4 alpha glycoside bond

The reverse reaction to split the bond is called hydrolysis and releases energy.

POLYSACCHARRIDES

Monosaccharides can undergo a series of condensation reactions, adding one unit after another to the chain until very large molecules (polysaccharides) are formed. This is called condensation polymerisation, and the individual building blocks are called monomers. The properties of a polysaccharide molecule depend on:

It's length (though they are usually very long)

The extent of any branching (addition of units to the side of the chain rather than one of its ends)

Any folding, which results in a more compact molecule

Whether the chain is 'straight' or 'coiled'

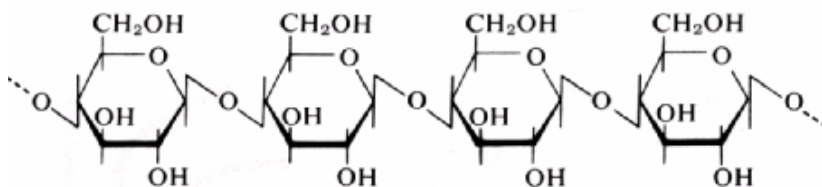


Fig. 9 cellulose showing glycoside bonds

Cellulose is formed by units of glucose, joined by 1-4 beta glycoside bonds.

Another common polysaccharide, starch, consists of a mixture of amylose and amylopectin

Amylose is a straight chain molecule of linked glucose units linked by 1-4 alpha glycoside bonds.

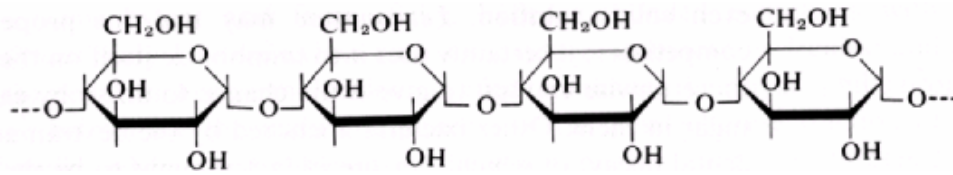


Fig. 10 amylose

The chain configures into coils.

Amylopectin is also made of glucose units but branches every 24 to 30 units

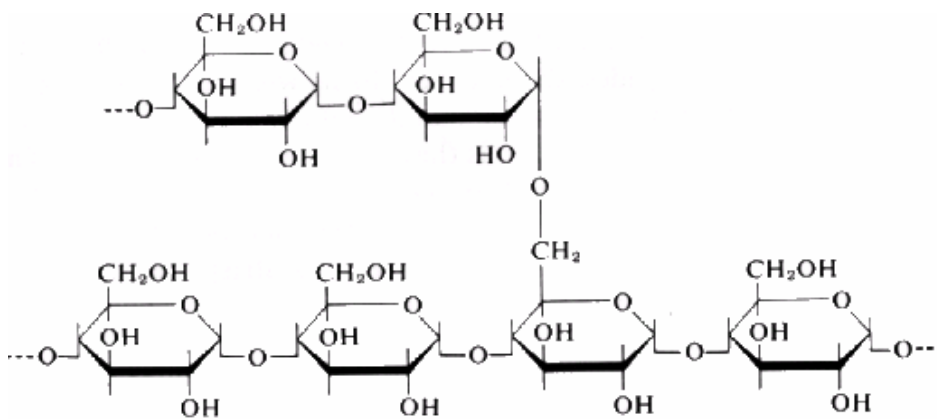


Fig. 11 amylopectin

In animals glycogen is the equivalent of amylopectin, however it branches every 8 -12 units

Chitin is a more complex polymer of glucose. It is constructed from units of N-acetylglucosamine (more completely, N-acetyl-D-glucos-2-amine).

These are linked together in 1-4- β fashion (in a similar manner to the glucose units which form cellulose).

In effect chitin may be described as cellulose with one hydroxyl group on each monomer replaced by an acetylamino group.

LIPIDS

The collective name for fats, oils, waxes and fat like molecules i.e. steroids.

Their roles include:

- components of cell membranes (phospholipids and cholesterol)
- energy stores
- chemical messengers (steroid 'hormones')
- protection, waterproofing, insulation and buoyancy agents.

The basic building blocks of lipids are a glyceride molecule, formed from glycerol (propane 1,2,3, triol) and fatty acids.

The glycerol molecule has three reactive alcohol groups.

If **one** fatty acid chain attaches a monoglyceride is formed. If **two** a diglyceride If **three** a triglyceride

The reaction is a condensation reaction between a hydroxyl group of glycerine and a hydroxyl group of the fatty acid releasing water, the resultant compound is an ester. In the resultant glyceride, the glycerol component is hydrophilic and the fatty acid component is hydrophobic.

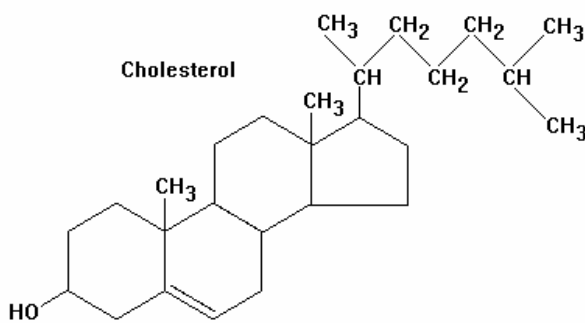


Fig. 15 Cholesterol showing the steroid unit structure

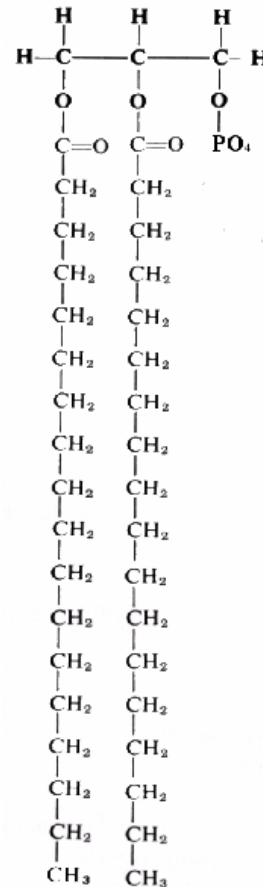


Fig. 16 phospholipid structure

If one of the glycerol groups reacts with phosphoric acid the result is a phospholipid. Phospholipids are an important component of cell membranes. There are a number of lipids based around structure consisting of three six carbon and one five carbon fused rings, the steroids. One of these is cholesterol.

PROTEINS

Are naturally occurring **polypeptides**. They:

- contribute to the mechanical structure of animals, including humans, e.g. keratin in hair and fingernails, and fibrous proteins such as collagen in tendons
- enable animals to move, e.g. myosin in muscle
- facilitate transport of smaller molecules around animals' bodies, e.g. haemoglobin
- control the types and rates of chemical reactions in living things; then they are called **enzymes**, e.g. amylase

- are important components of the human immune system, e.g. immunoglobins

AMINO ACIDS

- Amino acids are the building blocks (monomers) of proteins.
- Amino acids have the general structural molecular formula $\text{NH}_2\text{CHR}\text{COOH}$.
- They have two important functional groups (regardless of the rest of the molecule):
- A carboxylic acid group- COOH and an amide group- NH_2
- There are twenty different amino acids used to make protein in the human body. Of these nine are called **essential** (meaning they can only be obtained from the food we eat) and eleven are **non-essential** (they may be synthesised in the body though they are usually obtained from food).

Essential amino acids		
Name	Abbreviation	Linear Structure
Histidine	his H	$\text{NH}-\text{CH}=\text{N}-\text{CH}=\text{C}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH}$
Isoleucine	ile I	$\text{CH}_3-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}(\text{NH}_2)-\text{COOH}$
Leucine	leu L	$(\text{CH}_3)_2-\text{CH}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH}$
Lysine	lys K	$\text{H}_2\text{N}-(\text{CH}_2)_4-\text{CH}(\text{NH}_2)-\text{COOH}$
Methionine	Met M	$\text{CH}_3-\text{S}-(\text{CH}_2)_2-\text{CH}(\text{NH}_2)-\text{COOH}$
Phenylalanine	Phe F	$\text{Ph}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH}$
Threonine	thr T	$\text{CH}_3-\text{CH}(\text{OH})-\text{CH}(\text{NH}_2)-\text{COOH}$
Tryptophan	trp W	$\text{Ph}-\text{NH}-\text{CH}=\text{C}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH}$
Valine	val V	$(\text{CH}_3)_2-\text{CH}-\text{CH}(\text{NH}_2)-\text{COOH}$

Non-essential amino acids		
Name	Abbreviation	Linear Structure
Alanine	ala A	$\text{CH}_3-\text{CH}(\text{NH}_2)-\text{COOH}$
Arginine	arg R	$\text{HN}=\text{C}(\text{NH}_2)-\text{NH}-(\text{CH}_2)_3-\text{CH}(\text{NH}_2)-\text{COOH}$
Asparagine	asn N	$\text{H}_2\text{N}-\text{CO}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH}$
Aspartic Acid	asp D	$\text{HOOC}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH}$
Cysteine	cys C	$\text{HS}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH}$
Glutamic Acid	glu E	$\text{HOOC}-(\text{CH}_2)_2-\text{CH}(\text{NH}_2)-\text{COOH}$
Glutamine	gln Q	$\text{H}_2\text{N}-\text{CO}-(\text{CH}_2)_2-\text{CH}(\text{NH}_2)-\text{COOH}$
Glycine	gly G	$\text{NH}_2-\text{CH}_2-\text{COOH}$
Proline	pro P	$\text{NH}-(\text{CH}_2)_3-\text{CH}-\text{COOH}$
Serine	ser S	$\text{HO}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH}$
Tyrosine	tyr Y	$\text{HO}-\text{Ph}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH}$

Peptides and polypeptides

Two amino acids can undergo a condensation reaction to form a **dipeptide**.

The carboxyl group of one reacts with the amide group of the other, producing water. The amino acid units are linked by **peptide bonds** (sometimes called **peptide links**).

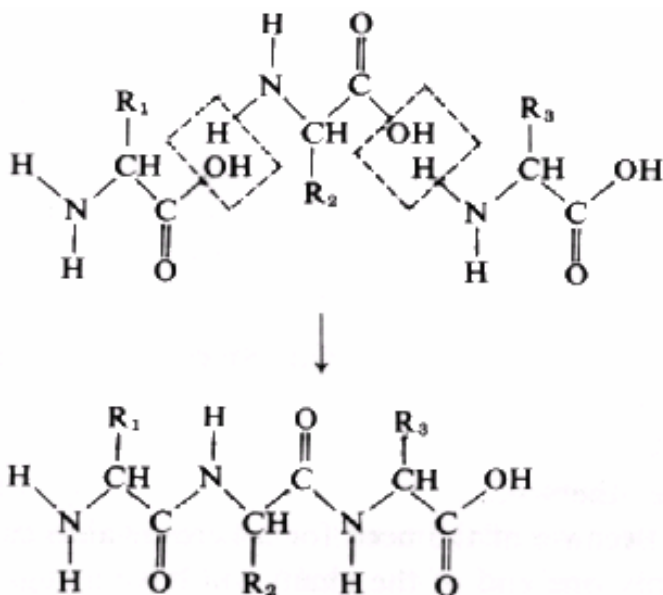


Fig 17. Formation of peptide bond

The addition of more amino acids through further condensation reactions result in a polypeptide. Long chain polypeptides are called proteins.

Protein Structure

Each protein has a characteristic sequence of amino acids in the chain. This sequence is called the primary structure. Further bonding can happen within a protein molecule (**intramolecular bonding**) and between protein molecules (**intermolecular bonding**). These bonds cause the molecules to adopt a three dimensional shape. Three types of bonds are involved, hydrogen bonds, covalent bonds and ionic bonds. Protein chains arrange themselves to maximise intra- and intermolecular bonding. This structure, when protein chains are held in place is called the **secondary structure**. This may be helical, e.g. keratin (the protein found in hair), or a pleated sheet, e.g. fibroin (the protein found in silk). These structures are held in place by hydrogen bonds.

The hydrogen atom of one peptide link is attracted to the oxygen of an adjacent peptide link.

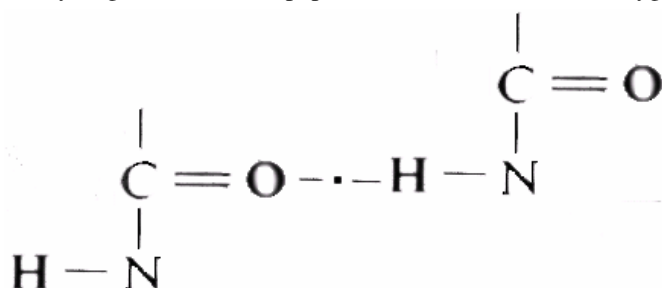


Fig. 18 Hydrogen bond formed between a carbonyl group and hydrogen from amine in adjacent protein chain

There may be further folding of protein chains e.g. into a globular shape.

This is the **tertiary structure** of a protein. Globular proteins include enzymes and immunoglobins. The structures are held in place by hydrogen bonds, disulfide bridges (sulphur – sulphur covalent bonds) and ionic bonds.

The precise structure of a globular protein is the key to specificity of enzymes. Similarly proteins that act as receptor sites on the cell surface can recognise specific molecules because of their shapes.

Finally proteins that contain more than one chain have a **quaternary structure**.

Examples are insulin and haemoglobin.

METABOLIC PATHWAYS

The formation and destruction of biochemicals takes place in metabolic pathways with the reactions being catalysed by enzymes.

Anabolism is biochemical processes involved in construction

I.e. the formation of complex molecules from simple ones

Anabolic processes require energy.

Catabolic processes involve the breakdown of larger molecules to smaller ones

They release energy.

Most biochemical metabolism take place in well defined sequences of reactions called metabolic pathways

Some important metabolic pathways

glycolysis – oxidation of glucose in order to obtain Adenosine triphosphate and producing pyruvic acid

citric acid cycle also called the **Krebs' cycle** or **tricarboxylic acid cycle**. part of respiration involving pyruvic acid eventually producing energy and releasing carbon dioxide.

oxidative phosphorylation – final part of respiration, disposal of the electrons released by glycolysis and citric acid cycle. Much of the energy released in this process can be stored as ATP.

pentose phosphate pathway - synthesis of pentoses (used in nucleic acids) from glucose and release of the electrons needed for anabolic reactions.

urea cycle - disposal of toxic ammonia into urea.

fatty acid b-oxidation - fatty acids breakdown into acetyl-coenzyme A, to be used by the Krebs' cycle. Coenzyme A is an important molecule involved in chemical reactions

Gluconeogenesis - glucose synthesis from smaller precursors, to be used by the brain.

Photosynthesis synthesis of glucose from carbon dioxide and water.

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<http://www.iubmb-nicholson.org/>