الكيمياء الحيوية

Bio-Chemistry

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المقرر: الكيمياء الحيوية

الفرقة الثالثة تربية كيمياء عام العام الدراسي ٢٠٢٣-٢٠

اعداد د. احمد جابر محمد طه المدرس بكلية العلوم – جامعة جنوب الوادي

Introduction:

Biochemistry is concerned with the chemical composition of cell parts and knowledge how the biochemical reactions occur, as well as the chemical and physical nature of different types of nutrients, the biological function of these substances from cells and their intermediate metabolism.

Our course is focused on studying the chemical compounds that are components of living cells and the materials that can be used in their biosynthesis, including **carbohydrates**, **lipids**, and **proteins**.

Bio-Chemistry

التمثيل الغذائي Metabolism Food الأكل

Anabolism

Catabolism

بناء

هدم

التمثيل الغذائي هو كل العمليات الحيوية التي تتم داخل الكائن الحي من عمليات هدم وبناء



Oxidizable

قابل للأكسدة

الكربوهيدرات CHO

الليبيدات Lipids

البروتينات Proteins

Non-oxidizable

غير قابل للأكسدة

الفيتامينات Vitamins

المعادن Minerals

الماء Water

في هذا المقرر سوف نتطرق للدراسة الكيميائية لكلا من الكربوهيدرات والليبيدات والبروتينات

Carbohydrates

Carbohydrates received their name from the fact that the general empirical formula for many members of the class can be written $C_n(H_2O)_n$, hydrated carbon. Sugars, starches, and cellulose-compounds which have important structural and energy functions in the living materials-are all carbohydrates. (Sugars are water soluble carbohydrates).

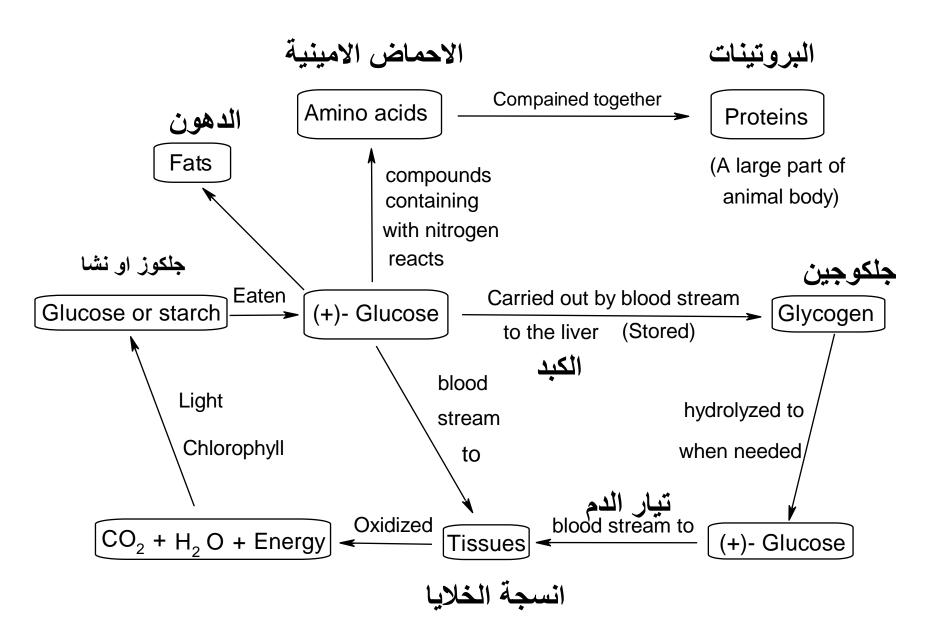
It would be difficult to overestimate the importance of human beings of carbohydrates.

Photosynthesis:

The production of carbohydrates in nature occurs in green palnts by a process called photosynthesis. Plants contain the green pigments chlorophyll which catalyzes the conversion of carbon dioxide and water into sugar. The reaction is thermodynamically unfavourable but proceed because the necessary energy is supplied by the sun in the form of sunlight.

While plants build up carbohydrates from carbon dioxide and water, animals degrade carbohydrates to carbon dioxide and water. The animal obtains carbohydrates by eating plants and combine the carbohydrates with oxygen from the air to carry out the reverse of the photosynthesis reaction. The oxidation of carbohydrates supplies the animal with the energy (according to the above equation) necessary to sustain life, and it also regenerates carbon dioxide for use by the plants in photosynthesis.

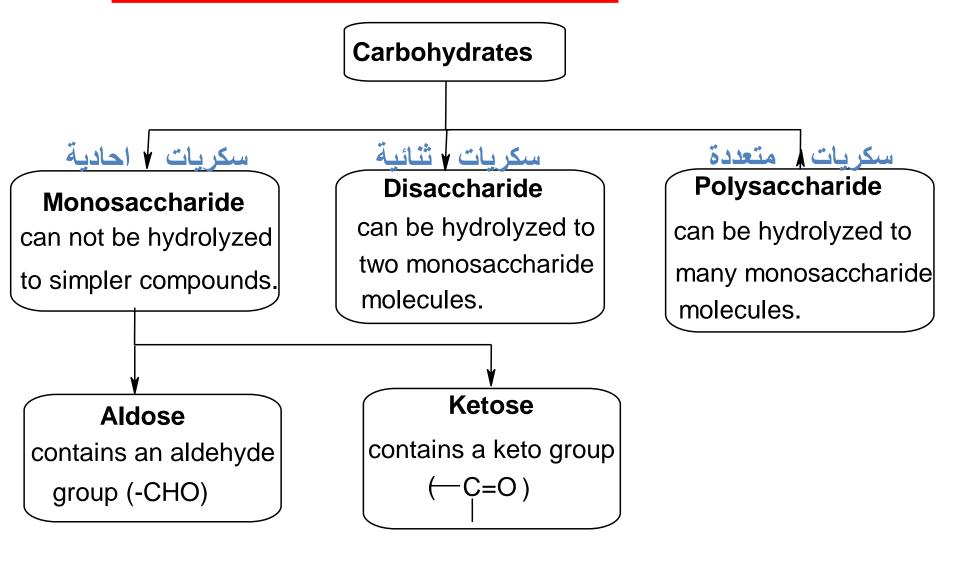
All carbohydrates are polyhydroxy aldehydes, polyhydroxy ketones, or molecules which yield polyhydroxy aldehydes or ketones on hydrolysis. Monosaccharides are the smallest carbohydrate molecules and include the four-, five-, and six-carbon sugars. Sucrose, table sugar, is one of the disaccharides; disaccharides can hydrolyse to two monosaccharides. Polysaccharides, which include starch and cellulose, yield many monosaccharides molecules upon hydrolysis.



Definition and Classification

Carbohydrates are polyhydroxy aldehydes, polyhydroxy ketones or compounds that can be hydrolyzed to them. There are three major classes of carbohydrates:

Definition and Classification:



General properties of carbohydrates

- Carbohydrates act as energy reserves, also stores fuels, and metabolic intermediates.
- Ribose and deoxyribose sugars forms the structural frame of the genetic material, RNA and DNA.
- Polysaccharides like cellulose are the structural elements in the cell walls of bacteria and plants.
- Carbohydrates are linked to proteins and lipids that play important roles in cell interactions.

Monosaccharides

 $(C_6H_{12}O_6)$

Monosaccharides

- The word "Monosaccharides" derived from the Greek word "Mono" means Single and "saccharide" means sugar
- Monosaccharides are polyhydroxy aldehydes or ketones which cannot be further hydrolysed to simple sugar.
- Monosaccharides are simple sugars. They are sweet in taste.
 They are soluble in water. They are crystalline in nature.
- They contain 3 to 10 carbon atoms, 2 or more hydroxyl (OH) groups and one aldehyde (CHO) or one ketone (CO) group.

Classification of Monosaccharides

Monosaccharides are classified in two ways. (a) First of all, based on the number of carbon atoms present in them and (b) secondly based on the presence of carbonyl group. The naturally occurring monosaccharides contain three to seven carbon atoms per molecule. Monosaccharides of specific sizes may be indicated by names composed of a stem denoting the number of carbon atoms and the suffix *-ose*. For example, the terms *triose*, tetrose, pentose, and hexose signify monosaccharides with,

Monosaccharides

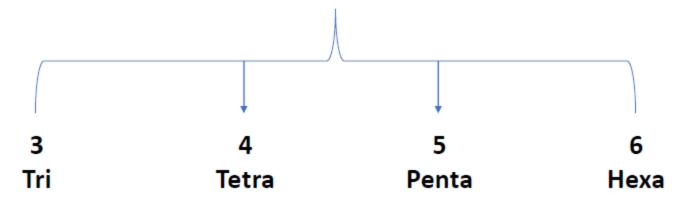
Polyhydroxy aldehyde or ketone
ose

 $(C \cdot H_2O)_n$

n = 3,4,5,6



According to no. of carbon atom



Trioses

Aldotriose

Glyceraldehyde جلیسرالدهید **Ketotriose**

$$CH_2OH$$

 $C=O$
 CH_2OH

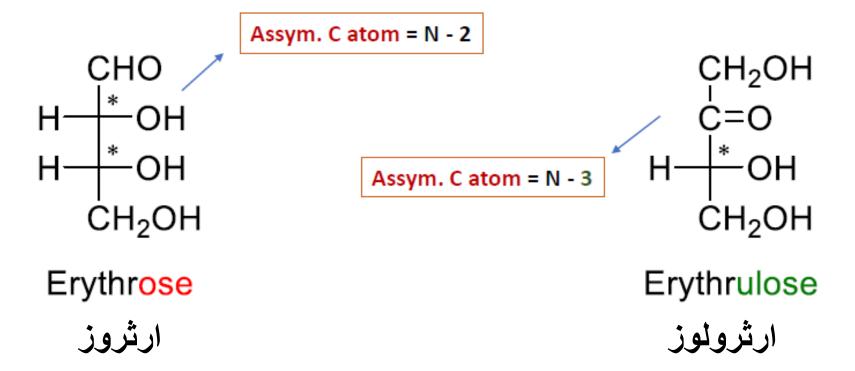
Dihydroxy acetone ثنائي هيدروكسي أستون

Tetroses



Aldotetrose

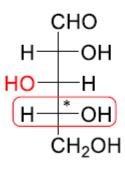
Ketotetrose



Pentoses

Aldopentose

CHO H—OH H—OH H—*OH CH₂OH

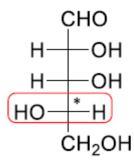


D-Xylose

زيلوز

D-Ribose

ريبوز

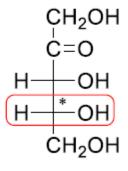


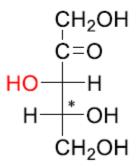
CHO H—OH HO—H HO—*H CH₂OH

L-Ribose

L-Xylose

Ketopentose





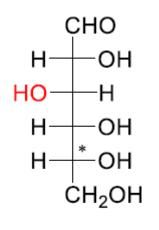
D-Ribulose ریبیلوز D-Xylulose زیلیلوز

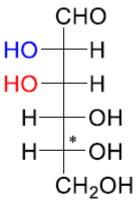


ماهو شكل اليساري لكلا من الريبوز والزيلوز؟

Hexoses

Aldohexose

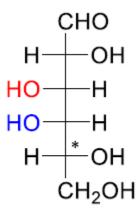




D-جلوكوز

D-Glucose

D-مانوز



D-Galactose

D-جلاكتوز

Ketohexose

$$\begin{array}{c} \mathsf{CH_2OH} \\ \mathsf{C} = \mathsf{O} \\ \mathsf{HO} \longrightarrow \mathsf{H} \\ \mathsf{H} \longrightarrow \mathsf{OH} \\ \mathsf{H} \longrightarrow \mathsf{OH} \\ \mathsf{CH_2OH} \end{array}$$

D-Fructose **D-فرکت**وز



الفعالية البصرية للسكريات الأحادية

Optical activity of monosaccharides

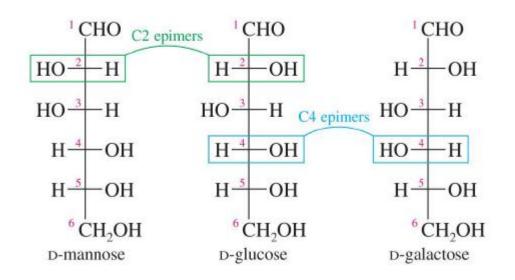
إذا احتوى المركب على ذرة كربون أو أكثر غير متناظرة Asymmetric وتسمى أيضا كيراليه Optically (ذرة كربون تحتوى على أربع استبدالات مختلفة) فالمركب يكون فعالاً بصرياً Optically (عدرة كربون تحتوى على أربع استبدالات مختلفة) فالمركب يكون فعالاً بصرياً ومدنانه ودلناه والأحماض الأمينية.

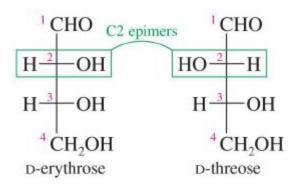
وعليه فعندما تمر حزمة لضوء مستقطب من جهاز مقياس الأستقطاب polarimeter على المحلول فإن شعاع الضوء المستقطب إما يدور يميناً فيكون المركب أيمن الدوران ويرمز له (+) أو (D) أو يدور يساراً فيكون أيسر الدوران ويرمز له (-) أو (L)

السكر الثلاثي الألدهيدي جليسرالدهيد توجد به ذرة كربون واحدة غير متماثلة أو غير متناظرة هى ذرة الكربون رقم 2 (نجمه) والتى بإستطاعتها تدوير الضوء المستقطب لذلك يوجد هذا المركب بشكل إيزومرين Stereo isomers هما L،D

- All D-sugars have the hydroxyl group at the lowest chiral carbon atom on the right.
- All L-sugars have the hydroxyl group at the lowest chiral carbon atom on the left.

Epimers



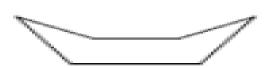


Epimers are carbohydrates which vary in one position for the placement of the -OH group

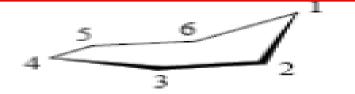
• السكريات التي تختلف في شكلها الفراغي في ذرة كربون واحدة فقط

Chair Conformation for Glucose شکل الکرسی للجلوکوز





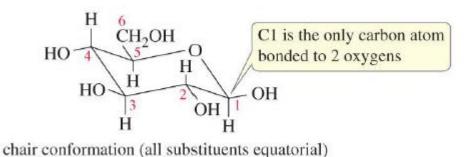
The chair-form of cyclohexane



The boat-form of cyclohexane



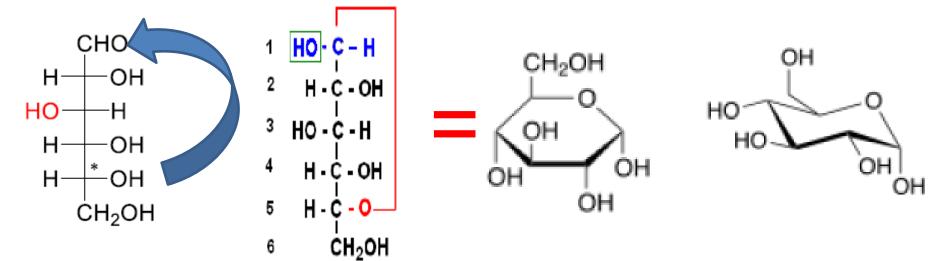
The half-chair form of cyclohexane



The twist-boat form of of cyclohexane

$$\begin{array}{c|c} H & 6 \\ CH_2OH \\ HO & H \\ \hline \\ HO & H \\ \hline \\ H & OH \\ \end{array}$$

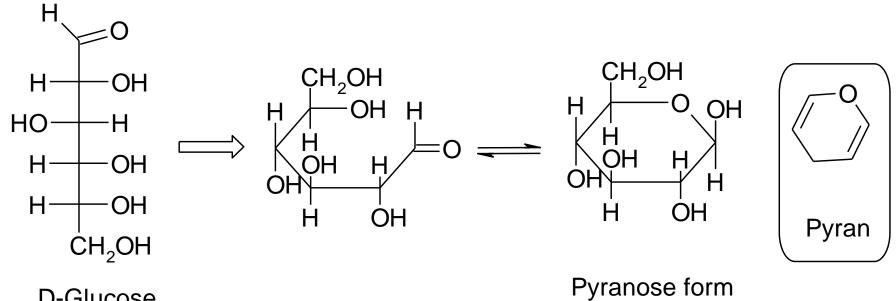
chair conformation (OH on C1 axial)



D-Glucose

D-جلوكوز

يوجد الجلكوز في الفراغ في شكل الكرسي لانه الاكثر ثبات و اقل طاقة



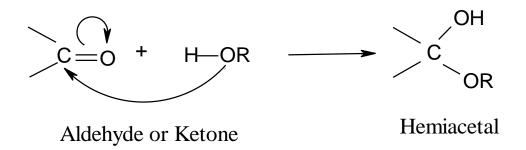
D-Glucose (Fischer projection)

Pyranose form (Haworth projection)

Anomers of Glucose

$$\begin{array}{c} \text{Anomeric carbon} \\ \text{HO} \xrightarrow{\text{4}} \xrightarrow{\text{6}} \\ \text{HO} \xrightarrow{\text{4}} \xrightarrow{\text{0}} \\ \text{HO} \xrightarrow{\text{1}} \xrightarrow{\text{5}} \\ \text{H} \\ \text{OH} \xrightarrow{\text{1}} \\ \text{H} \\ \text{OH} \xrightarrow{\text{1}} \\ \text{OH} \\ \text{OH$$

- The hydroxyl group on the anomeric (hemiacetal) carbon is down (axial) in the α anomer and up (equatorial) in the θ anomer.
- The β anomer of glucose has all its substituents in equatorial positions.
- The hemiacetal carbon is called the anomeric carbon, easily identified as the only carbon atom bonded to two oxygens.



- تكون مجموعة الهيدروكسيل الموجودة على الكربون غير المتماثل hemiacetal لأسفل
 (محوري) في انومر α وأعلى (استوائي) في β انومر.
 - ❖ يحتوي anomer β للجلوكوز على جميع بدائله في المواقع الاستوائية.
- يُطلق على الكربون الهيمي أسيتال اسم الكربون الأنومريك، ويمكن التعرف عليه بسهولة على
 أنه ذرة الكربون الوحيدة المرتبطة باثنين من الأكسجين.

MUTAROTATION:

D-Glucose exists in two crystalline forms; one melts at 150°C,

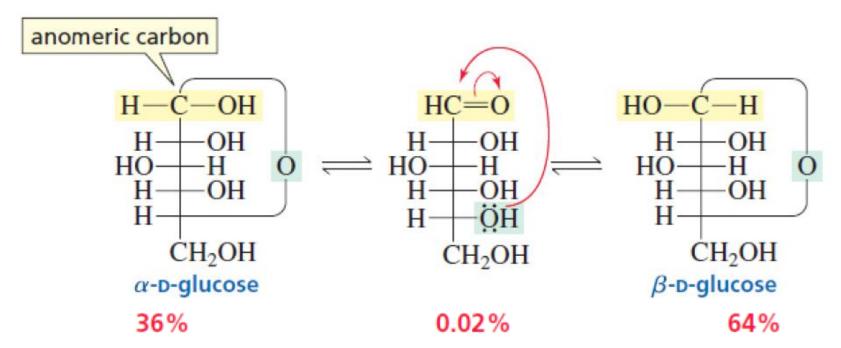
frequency in the infrared suggests that these two crystalline forms are the α - and β -hemiacetals. X-ray diffraction studies confirm that this is indeed the case. The crystals melting at 150°C are β -D-glucose, and they show the anomeric hydroxyl group to be in the equatorial position. The crystals of α -D-glucose melt at 146°C, and crystallography shows the same

the other at 146°C. The fact that neither form shows a carbonyl

molecular structure except for the anomeric hydroxyl, which here is in the axial position. A solution freshly prepared by dissolving β -D-glucose crystals in water gives a specific rotation of + 18.7°. This value slowly rises with time to +52.5°. The α -D-glucose shows a rotation, determined immediately upon dissolution, of +112°, but this value also changes slowly with time to a final value of +52.5°.

ظاهرة الدون التلقائي Mutarotation

وهي ظاهرة تغير الدوران النوعي للسكر في محلوله المائي نتيجة حصول حالة توازن بين الصيغة المفتوحة للسكر والصيغ الحلقية له بشكليها (α , β) ولكون لكل من الصيغ أعلاه دوران نوعي مختلف ويكون الدوران النوعي النهائي للسكر هو محصلة للدوران النوعي للصيغ الثلاثة له وتدعى هذه الظاهرة بـ ظاهرة تغير الدوران النوعي أو الدوران التلقائي Mutarotation وهي صفة مميزة للسكريات المختزلة Reducing Sugars (الاحادية والثنائية) بسبب وجود مجموعة كاربونيل

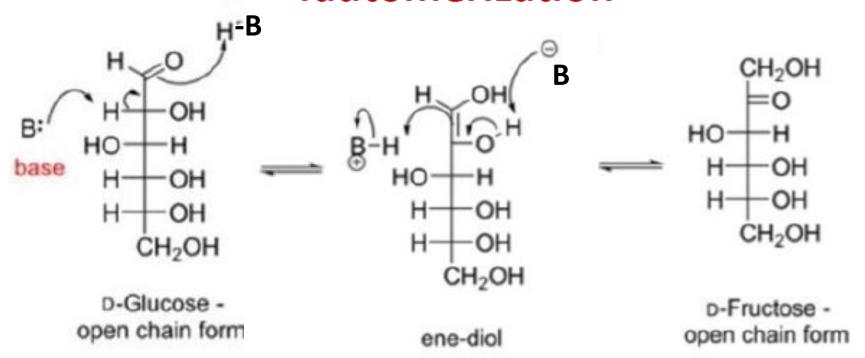


Tautomerization

Tautomerization is a net process by which protons are transferred from one site to another by a series of steps in which the solvent is an intermediary.

هو انتقال الالكترون من مكان الي اخر عن طريق عدة خطوات التي يكون فيها المذيب وسيطا

Tautomerization



Reactions of Monosaccharides

تفاعلات السكريات الأحادية

تفاعلات السكريات الأحادية

Oxidation Sugar acids الأكسده

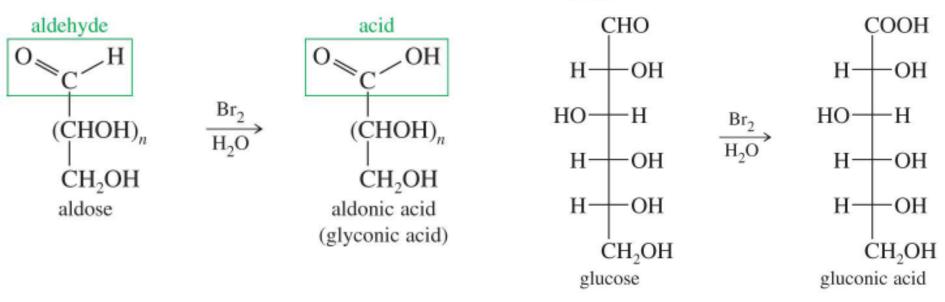
Reduction Sugar alcohols الاختزال

Or De-oxy sugar

Reaction with NH₃ Sugar amine التفاعل مع الآمونيا

الأكسدة بماء البروم



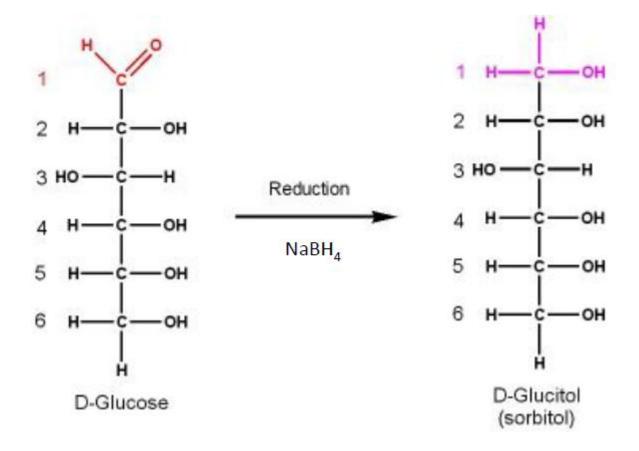


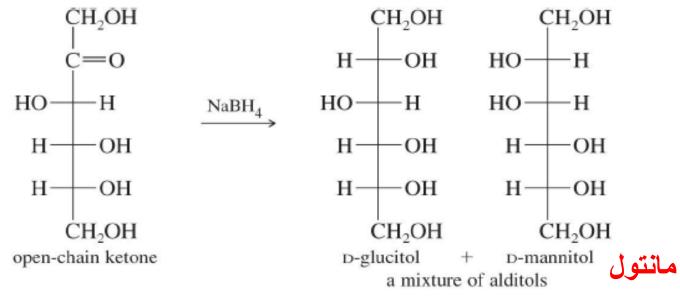
جلكونيك

- يتم أكسدة مجموعة الألدهيد إلي مجموعة كربوكسيل بإستخدام ماء البروم.
- ماء البروم يقوم بأكسدة الألدهيد فقط ولا يستطيع أكسدة مجموعات الكحول ولا مجموعات الكيتون.

Reduction of Simple Sugars

- C=O of aldoses or ketoses can be reduced to C-OH by NaBH₄ or H₂/Ni.
- Name the sugar alcohol by adding -*itol* to the root name of the sugar.
- Reduction of D-glucose produces **D-glucitol**, commonly called **D-sorbitol**.
- Reduction of D-fructose produces a mixture of D-glucitol and D-mannitol.





فركتوز

Reaction with NH₃

Glucose

Glucosamine

Disaccharides

Disaccharides are formed when two monosaccharides are joined together **by an O-glycosidic linkage** and a molecule of water is removed.

Among the most common disaccharides are:

- **❖** Maltose (Malt sugar)
- **❖** Lactose (Milk sugar)
- **Sucrose (Cane or beet sugar)**

Disaccharides

$$C_6H_{12}O_6 + C_6H_{12}O_6$$
 \longrightarrow $C_{12}H_{22}O_{11} + H_2O$
Monosaccharides Disaccharide

<u>Sucrose</u>

(Cane sugar or Beet sugar C₁₂H₂₂O₁₁)

Sucrose
$$C_{12}H_{22}O_{11}$$

$$C_{12}H_{14}O_{3}(OCH_{3})_{8}$$
Octamethyl sucrose
$$H_{2}O$$

$$H^{\dagger}$$

$$C_{12}H_{22}OCH_{3}$$

$$H^{\dagger}$$

$$H^{\dagger}$$

$$C_{12}H_{14}O_{3}(OCH_{3})_{8}$$

$$C_{12}H_{14}O_{14}O_{14}$$

$$C_{12}H_{14}O_{14}O_{14}$$

$$C_{12}H_{14}O_{14}O_{14}$$

$$C_{12}H_{14}O_{14}O_{14}$$

$$C_{12}H_{14}O_{14}O_{14}O_{14}$$

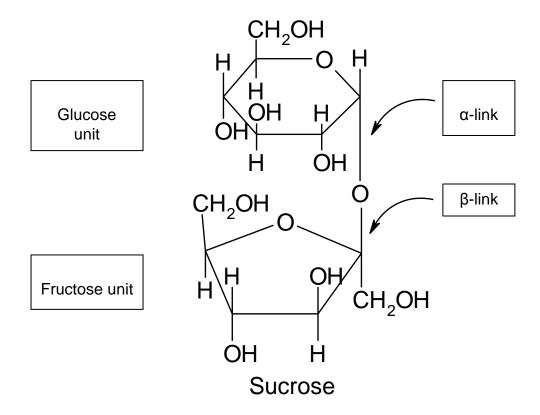
$$C_{12}H_{14}O_{14}O_{14}O_{14}$$

$$C_{12}H_{14}O_{14}O_{14}O_{14}O_{14}$$

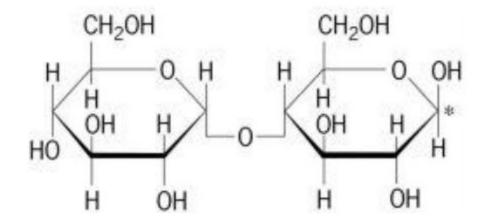
$$C_{12}H_{14}O_{14}O_{14}O_{14}O_{14}O_{14}O_{$$

2,3,4,6-Tetramethyl-D-Glucopyranose (α -and β -forms)

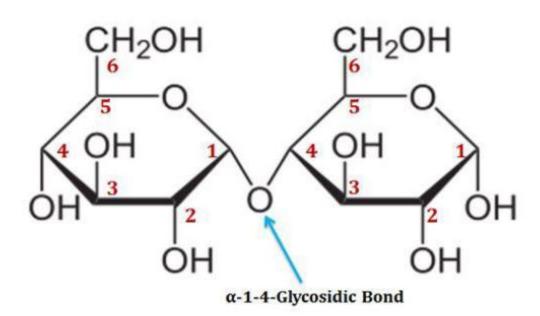
1,3,4,6-Tetramethyl-D-fructofuranose furanose (α -and β -forms)



Maltose (C₁₂H₂₂O₁₁):



MALTOSE



$\frac{\text{Lactose}}{\text{(milk sugar C}_{12}\text{H}_{22}\text{O}_{11}\text{)}}$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} HOH + OHOH + OHO$$

1) Oxidation:

Lactose aldehyde form

Lactonic acid

Polysaccharides

Polysaccharides contain hundreds or thousands of carbohydrate units. Polysaccharides are *not* reducing sugars, since the anomeric carbons are connected through glycosidic linkages.

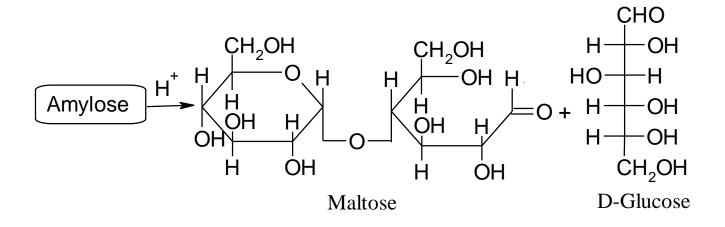
Nomenclature:

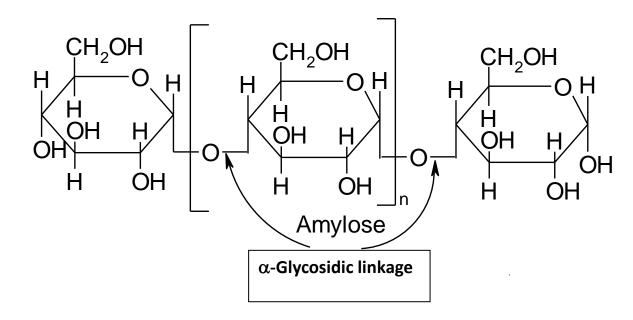
Homopolysaccharide- a polysaccharide is made up of **one type** of monosaccharide unit

Heteropolysaccharide- a polysaccharide is made up of more than **one type** of monosaccharide unit.

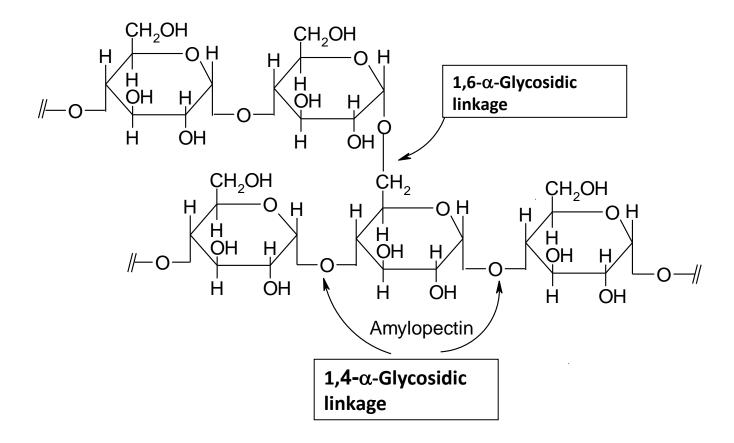
Starch

- ❖ Starch is a polymer consisting of D-glucose units.
- ❖ Starches (and other glucose polymers) are usually insoluble in water because of the high molecular weight, but they can form thick colloidal suspensions with water.
- Starch is a storage compound in plants, and made of glucose units
- ❖ It is a homopolysaccharide made up of two components: amylose and amylopectin.
- ❖ Most starch is 10-30% amylose and 70-90% amylopectin.
- * Amylose a straight chain structure formed by 1,4 glycosidic bonds between α-D-glucose molecules.



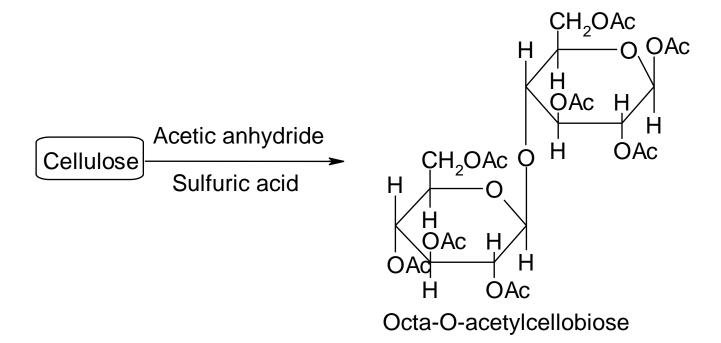


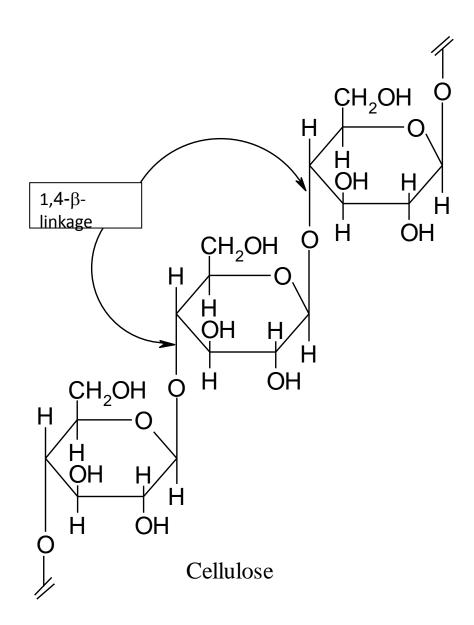
Structure of Amylopectin:



$$\frac{\text{Cellulose}}{(C_6H_{10}O_5)_n}$$

Structure of cellulose:





UNIT 2: LIPIDS

Introduction, Classification, Properties and Biological importance. Fatty acid nomenclature and structure, Triglycerides formation and its applications.

Introduction

There is a lot of interest these days on healthy diets as well as concerns about heart problems. There is also a strong market for the sales of omega-3 fatty acids, which are said to help lower fat levels in blood. But too many people rely on the supplements to help their hearts and don't understand the chemistry behind it all. Yes, taking omega-3 fatty acids will give you some of the fatty acids your body requires. No, this is not a substitute for eating a healthy diet and exercising. You can't sit in front of the TV set, eating your large pizza, and expect these pills to keep your health. You've got to do things the hard way eat your vegetables and get some exercise.

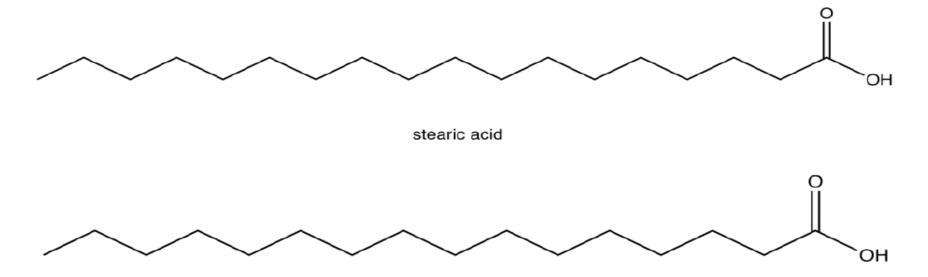
Fatty Acids

A lipid is an organic compound such as fat or oil. Organisms use lipids to store energy, but lipids have other important roles as well. Lipids consist of repeating units called fatty acids. Fatty acids are organic compounds that have the general formula

- $CH_3(CH_2)_nCOOH$, where n usually ranges from 2 to 28 and is always an even number.
- **❖** There are two types of fatty acids: saturated fatty acids and unsaturated fatty acids.

Saturated Fatty Acids

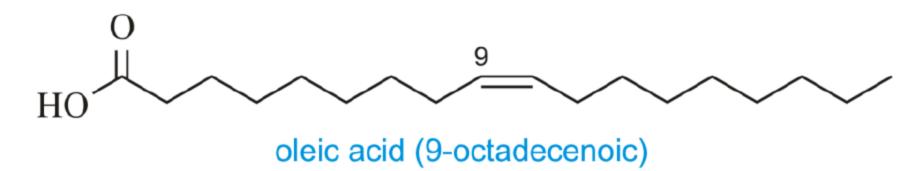
In saturated fatty acids, carbon atoms are bonded to as many hydrogen atoms as possible. This causes the molecules to form straight chains, as shown in the figure below. The straight chains can be packed together very tightly, allowing them to store energy in a compact form. This explains why saturated fatty acids are solids at room temperature. Animals use saturated fatty acids to store energy. For example: Stearic and palmitic



Unsaturated Fatty Acids

In unsaturated fatty acids, some carbon atoms are not bonded to as many hydrogen atoms as possible due to the presence of one or more double bonds in the carbon chain. Instead, they are bonded to other groups of atoms. Wherever carbon binds with these other groups of atoms, it causes chains to bend (see figure above). The bent chains cannot be packed together very tightly, so unsaturated fatty acids are liquids at room temperature. Plants use unsaturated fatty acids to store energy.

Unsaturated fatty acids



Types of Lipids

Lipids may consist of fatty acids alone, or they may contain other molecules as well. For example, some lipids contain alcohol or phosphate groups. They include:

- 1- triglycerides (simple lipids): the main form of stored energy in animals.
- 2- **phospholipids**: the major components of cell membranes.
- 3- steroids: serve as chemical messengers and have other roles.

glycerol

3 fatty acids

triglyceride (triester of glycerol)

Applications of Fats and oils

Saponification reaction

Saponification of an ester with NaOH yields the sodium salt of a carboxylic acid. Saponification of a triglyceride yields a salt of a long-chain fatty acid, which is a soap.

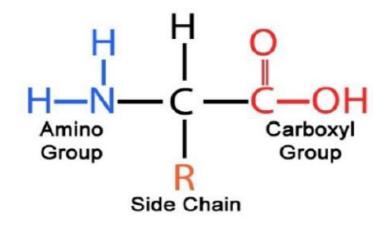
Amino acids and proteines

Amino acids

Amino acids are the building blocks of proteins. It has both an amino group (-NH₂) and an acid group (-COOH). There are more than 300 amino acids that occur in nature and many more yet to be characterized. Only 20 of the amino acids are found in the protein structure. The genetic code exists for only the 20 amino acids.

Structure of amino acids

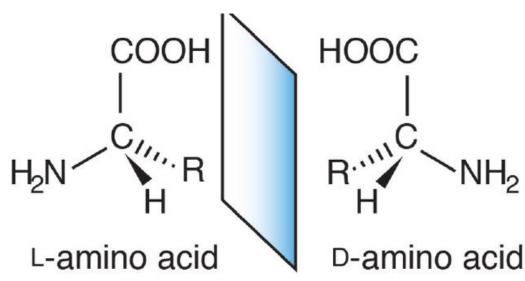
Each amino acid has 4 different groups attached to α -carbon (which is carbon atom next to carboxylic group – COOH).



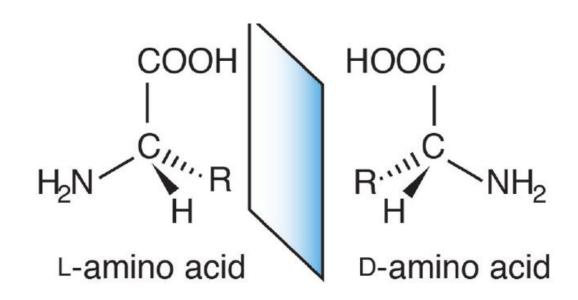
The properties of each amino acid are determined by its specific side chain (R-groups). R-groups vary in structure, size, electric charge, and solubility in water from one amino acid to other. Amino acids found in proteins are α -amino acids. The amino group is always found on the carbon adjacent to the carboxyl group.

Chirality – amino acids (except glycine) have a tetrahedral C_{α} bonded to four different chemical groups. As a result of this, amino acids are <u>optically active or chiral</u>. Common amino acids are all L stereoisomers. "CO-R-N" mnemonic is used for distinguishing L and D stereoisomers.

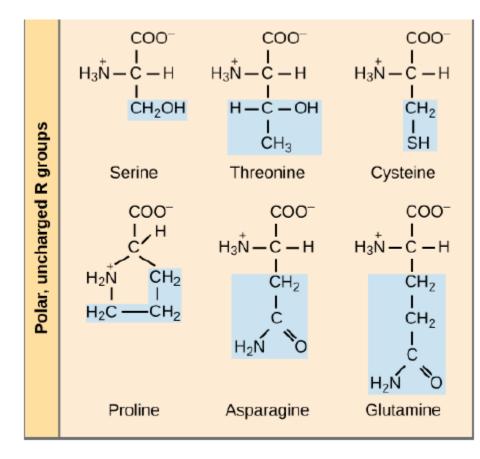
Looking down the H-C bond, CO-R-N spelled clockwise indicates the L stereoisomer.

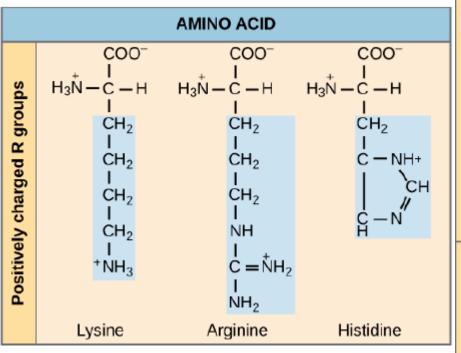


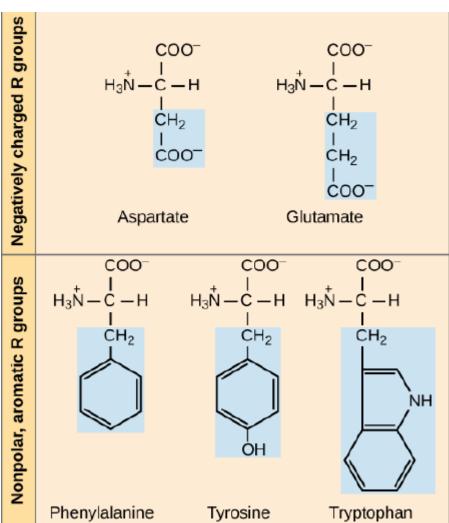
There is no definitive answer on why the L isomer is found in proteins. Both D and L isomers have identical energies.



AMINO ACID			
Nonpolar, aliphatic R groups	COO [−] H ₃ N − C − H H	COO ⁻ I H ₃ N – C – H I CH ₃	COO- H ₃ N-C-H - CH CH ₃ CH ₃
	Glycine COO-	Alanine COO-	Valine COO-
lar, alipha	H ₃ N — C — H I CH ₂	H ₃ N — C — H I CH ₂	$H_3\overset{+}{N}-\overset{I}{C}-H$ $\overset{I}{H}-\overset{C}{C}-CH_3$
Nonpol	CH CH ₃ CH ₃	CH ₂ I S	CH ₂ I CH ₃
	Leucine	CH ₃ Methionine	Isoleucine

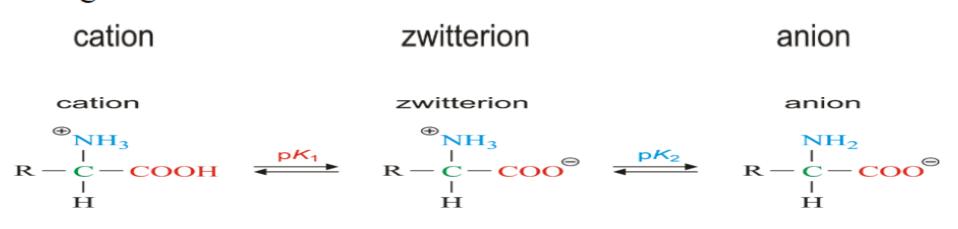






Zwitter Ions

At physiological pH of 7, the carboxyl group of an amino acid is in its conjugate base form (-COO⁻) and the amino group is in its conjugate acid form (-NH³⁺). Thus, each amino acid can behave as either an acid or a base. Such molecules which can behave both like an acid and a base are termed amphoteric molecules. Also, molecules that bear both positive and negative charges are called zwitter ions.



Classification of amino acids

- I) **Nutritional classification** Based on the ability of the body to synthesize amino acids, they can be classified as essential and non-essential amino acids.
- Essential amino acids These amino acids cannot be formed (synthesized) in the body and so,

it is essential to be included in the diet. Their deficiency in the body affects growth, health and protein synthesis. The following amino acids are essential:

- 1. Valine 5. Methionine.
- 2. Isoleucine 6. Tryptophan
- 3. Lysine 7. Threonine
- 4. Leucine 8. Phenyl alanine

- 2. <u>Semi-essential amino acids</u> These amino acids are formed in the body but not in sufficient amount for body requirements especially in children. The semi-essential amino acids are:
- 1. Arginine
- 2. Histidine
- **3.** <u>Non-essential amino acids</u> The amino acids that can be synthesized in the body by regular metabolism in enough amounts are called as non-essential amino acids. They need not be included in the diet. They are;

- 1. Glycine
- 2. Alanine
- 3. Cysteine
- 4. Tyrosine
- 5. Proline

- 6. Serine
- 7. Asparagine
- 8. Glutamine
- 9. Aspartic acid
- 10. Glutamic acid

Identification of amino acids by ninhydrin test as follow:

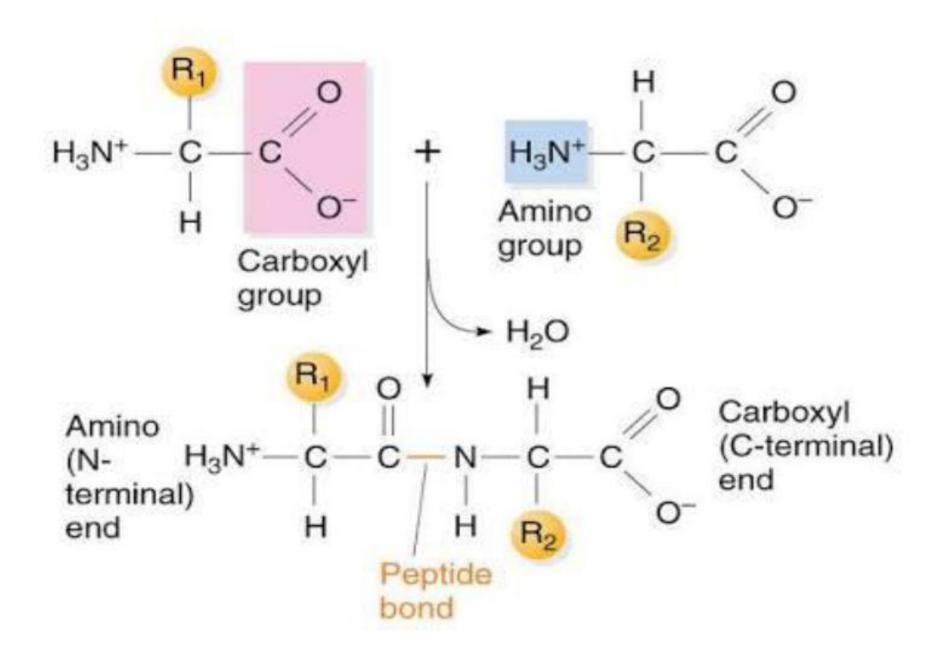
Proteins – Introduction

Proteins are polypeptides, which are made up of many α amino acids linked together through amide linkages called peptide bonds. The structure of an amino acid contains amino group, carboxyl group, and R group which is usually carbon based and gives the amino acid it's specific properties. These properties determine the interactions between atoms and molecules, which are: van der Waals force between temporary dipoles, ionic interactions between charged groups, and attractions between polar groups.

Proteins form the very basis of life. They regulate a variety of activities in all known organisms, from replication of the genetic code to transporting oxygen, and are generally responsible for regulating the cellular machinery and determining the phenotype of an organism. Proteins accomplish their tasks in the body by three-dimensional tertiary and quaternary interactions between various substrates. The functional properties depend upon the proteins threedimensional structure. The (3D) structures arise because particular sequences of amino acids in a polypeptide chain fold to generate, from linear chains, compact domains with specific structures. The folded domains either serve as modules for larger assemblies or they provide specific catalytic or binding sites.

Peptide Bonds

To make a protein, amino acids are connected together by a type of amide bond called a "peptide bond". This bond is formed between the alpha amino group of one amino acid and the carboxyl group of another in a condensation reaction. When two amino acids join, the result is called a dipeptide, three gives a tripeptide, etc. Multiple amino acids result in a polypeptide (often shortened to "peptide"). Because water is lost in the course of creating the peptide bond, individual amino acids are referred to as "amino acid residues" once they are incorporated. Another property of peptides is polarity: the two ends are different. One end has a free amino group (called the "Nterminal") and the other has a free carboxyl group ("Cterminal").



Protein Structure

It is convenient to discuss protein structure in terms of four levels (**Primary**, **secondary**, **tertiary**, **and quaternary**) of increasing complexity.

In primary structure _ Primary structure is simply the sequence of residues making up the protein. Thus, primary structure involves only the covalent bonds linking residues together.

