COURSE CODE: CHM 321

COURSE TITLE: CHEMISTRY OF MACROMOLECULES.

NUMBER OF UNITS: 3 Units

COURSE DURATION: 3 hours per week

COURSE DETAILS:

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COURSE CONTENT:

Introduction, symmetry, conformations and configurations. Charity and resolutions of racemic mixtures. Stereochemistry and biological activities. Stereochemistry and stereospecificity in synthesis. The structure and brief chemistry of mono-saccharides, polysaccharides, amino acids, proteins, nuclei and acid and DNA, synthetic polymers and detergents, physical methods in the determination of the structures and properties of Macromolecules, bimolecular spectroscopy and interaction in biological macromolecules. Purification of biological macromolecules.

COURSE REQUIREMENTS:

This is a compulsory course for all 300 level chemistry students in the University. In view of this, students are expected to participate in all course activities and have minimum of 75% attendance to be able to write the final examination.

READING LIST:

1. Osuntogun B. A., Familoni O. B and Alo B. I. (2006) Basic Organic Chemistry. University of Lagos Press
2. Charles D. Winter- Chemistry of Macromolecules.
3. Elias H.G. (1987). Mega Molecules, Springer-Verlag, Berlin.
4. Jenkins A.D. and Loening K.L. (1989). Nomenclature in Comprehensive Polymer Science, Pergamon Press, Oxford.
5. Morawetz H (1985). Polymers – The origins and Growth of a Science, John Wiley, New York.

LECTURE NOTES

Examples of macromolecules: textile, ceramics e.t.c.

Symmetry, conformation & configuration

Chirality & resolution of racemic mixtures

Stereo-selectivity & stereo specificity in synthesis

Chemistry of monodarride, polysaccharides, protein, amino acids, nucleic acid and DNA

Synthesis of polymer soap & detergents

Structure & properties of biological molecules.

Stereoisomers

When you look in a mirror, you see a reflection or mirror image of yourself. Suppose your mirror image becomes a 3-dimensional object; we could there ask that what is the relationship between you and your mirror image. By relationship, we mean "can your reflection be superposed on the original". The answer is that you and your mirror image are not super-posable.

If you have a ring on the idle finger of your right hand for example, your mirror image has the ring on the little finger on the left hand. Also if you part your hair on the right side, the part will be on the left side on the mirror image. This simply means that you and your reflection are different object. That is, you cannot super-pose one on each other.

Stereoisomers: have the same m.f and the same order of attachment of atom in their molecules but different 3-dimensional orientation of their atoms in space.

Enantiomers

These are stereoisomers that are non-superposable mirror images of each other. The significance of enantiomerism is that expect for inorganic and few simple organic compounds, the vast majority of molecules in the biological world show this type of isomerism. As an example of molecule that exhibit isomerism, let us consider two buthanol. Your attention will be focused on carbon-2 (c-2).

For stereoisomers to occur, the center carbon must be bonded to four different atoms..

(c-2) the carbon bearing the OH group (2-butanol). What makes this carbon different is that it has four different groups bonded to it. The most common cause of enantiomerism among organic compounds is a carbon with 4- different groups bonded to it.

$CH_3CHOHCH_2CH_3$: The structural formula drawn does not show the shape of 2-butano; or the orientation of it atom in space to this, we must consider the molecule ass a 3 dimensional object. On the left is what we call the original molecule while on the right is the mirror image.

To the right is the mirror image of the original molecule. Every molecule and in fact every object in the world around us as a mirror image. The questions we now need to write is what is the relationship of the original 2-butanol and it mirror-image. To answer this question; you need to imagine that you can pick up the mirror image and move the mirror image in space

and find that it fits over the original so that every bond, atom and detail of the mirror image exactly matches the bonds, atoms and details of the original the two are vsuper-posable.

In this case, the mirror image and the original represent the same molecule. They are only oriented differently in space. If however, no matter how you turn the mirror. Image in space it will not fit exactly on the original with every detail matching i.e. the atom, bond e.t.c then the two are non-super-posable meaning that they are different molecules.

Imagine you hold the mirror-image by the C-OH bond and rotate the bottom part of the molecule by 180^0 about this bond, the OH group retains it position in space but the CH_3 group which was to the right and in the plane of the paper is still in the plane of the paper but now to the left . similar, the CH_2CH_3 group which was in front to the plane of the paper and to the left is now behind the plane of the paper and to the right.

Summarily, we can rotate the mirror-image of 2-butanol in space in any way we what but as long as no bond is broken or re-arranged.

Only 2 of the 4 groups bonded to carbon -2 of the mirror image can be made fto coincide with those of the original. Because 2-butanol and it mirror image are not superposable, they are enantiomers. Enantiomers always occurs in pairs.

Object that are not superposable on their mirror images are said to be chiral. Chirality is encountered in 3-dimensional object of all sort. Your left hand is chiral and so it your right hand.

The most common cause of enantiomerism in organic molecule is the presence of a carbon with four different group bonded to it. Let us examine the statement by considering a molecules of 2-propanol which has no such carbon.

In 2-propanol, carbon-2 (C-2) is bonded to 3-different groups but no carbon is bonded to 4 different groups. The questions we ask is; “is the mirror image of 2-propanol superposable on the original”.

Answer: the mirror image of 2-propanol is superposable on it original image

In the diagram shown above, it is a 3-dimensional represent of 2-propanol with it mirror image. If we ask the question what is the relationship of the mirror image to the original if we rotate the mirror image by 120^0 about the C-OH and then compare it with the original, then we can see that all atoms and bond of the mirror image fix exactly on the original. This means that the original structure and it mirror image are infact the same molecule viewed from different perspective.

If an objective and it mirror image are superposable, then the object and it mirror image are the same meaning that the objective does not exhibit enantiomerism. i.e. such an objective is achiral. A achiral objective as at least one plane of symmetry. A achiral object as at least one plane of symmetry. A plane of symmetry is also called are mirror plane which is an

imaginary plane passing through an object and dividing so that one part of the object is the reflection of the other half.

The most common cause of chirality in organic molecule is a tetrahedral carbon atom with 4 groups bonded with it. We call such a carbon atom a stereo-center. 2 – butanol as one stereo-center whereas 2-propanol as non. Another example of a molecule with a stereo-center is 2-hydroxy propanioc acid commonly known as lactic acid. Lactic acid is a product of anaerobic glycolysis and it what gives sour cream/sour taste.

Drawing of enantiomers

We now need to think on how to represent the three dimensioner structure on a 2-dimensional page. Let us consider 2-butanol as an example.

Review structure to show the tetrahedral geometry of 2-butallol and its stereo center. In structure (1), two groups are in the plance of the paper. One is coming out of the plane towards us and is behind the plane i.e. away from us.

Instructure (1), if you turn it slightly in space and tip it a bit to place the carbon framework in the plane of the paper. Doing this will give us a representation with structure (2) in which we still have 2 groups in the plane of the paper i.e. one coming towards us and one going away from us.

For an abbrevative representation of this structure (2), we can turn it into a line angle formula and that gives us structure (3). Although we don't normally show hydrogen in the line angle formula. We do it in (3) just to remind course increase that the 4^{th} group of this stereo-center is really there and it is hydrogen. Finally we can carry the abbreviation a step further and write 2-butanol as structure (4). Here in structure (4), we have omitted hydrogen from the stereocentre because we know it is there since carbon needs for groups.

Clearly, the abbreviated structure (3) and (9) are the easiest to write. For the purpose of stereo-isomerism we are going to be using structure (3) and (4).

Assignment: read on naming in stereoisomerism clockwise- R,S – anticlockwise.

The cahn-ingold- prelog R-S Notational system

This system was devised in the E-□ system which was used to distinguished between E-□ stereoisomers of alkenes where substituents are ranked by atomic number.

The system was introduced by R.S.Cahn, Sir Christopher ingold, and Vladimir Prelog. Actually, Cahn, Ingold and Prelog first developed their ranking system to deal with the problem of the absolute confuration at a chirality center, and this is the system's major application.

The table below shows how the system called the sequence rules, is used to specify the absolute configuration at the chirality center m (+)-2-butanol.

1. Identify the substituents at the chirality center, and rank then in order of decreasing precedence. Precedence is determined by atomic number. Working outward from the point of attachment and the chirality center.	In order of increasing precedence, the for substitutes attached to the chirality center of 2-butanol are; $HO \rightarrow CH_3CH_2 \rightarrow CH_3 \rightarrow H$- (highest) (lowest)
2. Orient the molecule so that the lowest ranked substituents points. Away from you 3. Draw the 3 highest substituents as they appear to you when the molecule is oriented so that the lowest ranked group points away from you. 4. If the order of decreasing precedence of the 3 highest ranked substitents appears in a clockwise sence, the absolute configuration is R (latin: rectus, "right", "correct"). If the order of decreasing precedence is counterclockwise, the absolute configuration is S (latin sinister, "left")	Hydrogen is the lowest ranked atom attached to the chirality center and points. Away from us. The order of increasing precedence is counterclockwise. The configuration at the durality center is S.

Often, the R or S configuration and the sign of rotation are incorporated into the name of the compound, as in (R) – (-) -2-butanol and (S)-(+)-2- butanol.

Compounds in which chirality center is part of a ring are handled in an analogous fashion. To determine, for example, for example, whether the configuration of (+)-4-methyl-cyclohexene is R or S, treat the right and left hand around the ring as if they were independent substituents.

With the lowest ranked group (hydrogen) directed away from us, we see that the order of increasing sequence rule precedence is clockwise. The absolute is R.

Carbohydrates.

They are the most abundant organic compounds in the plant world. The act as store houses of chemical energy (glucose, starch, glycogen) and of component of supportive structures in plant (cellulose). Carbohydrates accounts for ≃3. 4^{th} of the dry wet of plants. Animals including humans get their carbohydrates by eating plants but do not store much of what they consume. In fact, less than 1% of the body weight of animals is made up of carbohydrates. The word carbohydrates means (hydrate of carbon) and derived from the formular $Cn(H_2O)m$ where n = m at times.

Two examples of carbohydrates that can be written alternatively as hydrate of carbon are

1. Glucose (blood sugar) with formula $C_6H_{12}O_6$ and can be written as $C_6\ (H_2O)_6$
2. Sucrose (table sugar) with formula $C_{12}H_{22}O_4$ and can be written as $C_{12}(H_2O)$

Not all carbohydrates have this general formular because some contain few O_2, many and some even contain nitrogen.

Most carbohydrate are poly hydroxyaldehyde or polyhydroxy ketone or compounds that yields them after hydrolysis. i.e. the chemistry of carbonhydrates is essentially chemistry hydroxyl and carbonyl groups.

Monosaccahrides

They have the general formaula CnH_2nOn. With one of the carbon atoms being a carbonyl of either a aldehyde and ketone. The most common monosaccharides having from 3-9 carbon atoms. The simplest form of monosaccharides is triosc ($C_3H_6O_3$) with structural formula

The suffix "-ose" indicate that the molecule is a monosaccharide (carbohydrate) and the prefix tri, tetra, penta e.t.c. indicates number of carbon atoms in the chain. Monosaccharide contain an aldehyde are termed "Aldose". While those containing kentone group are termed

“ketoses”. There are only, two triose’s. the first one is glyceraldehydes / aldo-triose while the second one is called dihydroxy acetone and it is a ketriose.

Often the designation aldo and ketrio are omitted and the molecules are simply referred to as triose, pentose, octose e.t.c.

Stereoisomerism

In, aldo-triose the stereo-carbon possess for different substituents and is therefore non-supersable and the same applies to dihydroxy acetone.

Fishser projection formula

Chemist commonly use two dimensional representation called fisher projection to show the structure of carbohydrate. To draw a fisher projection, draw a 3-dimensional representation with the most oxidized carbon atoms toward the top and molecule oriented so that the vertical bonds from the stereocenter away from you and the horizontal bonds are directed towards you.

D & L monosaccharides

The R&S naming system as being widely accepted as standard for designating the configuration of stereo-centers. We still designate the configuration of carbohydrate by D&L system proposed by Fischer in 1891. He assign the dextropotatory & levorotatory enantiomers of glyceldehyde by following the configuration & naming them D-glycelaldehyde & L-glycelaldehysde.

D&L glycelaldehyde serves as reference point for the assignment of relative configuration to other aldoses and ketoses. The reference point is the stereo-centre farest from the carbonyl group. Because this stereo-center is the next to the last carbon atom in the chain, it is called penultimate.

Almost all monosaccharides in the biological world belong to the D-series and majority of them are either hexose’s or pentose’s

<u>Names & structure of Aldo: triose’s pentose’s & hexose’s.</u>

Amino sugars

Amino sugars contain an “NH_2 group in place of an “OH” group. Only 3 amino sugars are common in nature. They are D-glucosamine, D-manosamine & D-galactosamine. N –acetyl. D-glucosamine is a derivative of D-glucosamine & is a component of many polysaccharides including connecting tissue such as cartilage. It is a component of chic

In which is the hard shell-like exoskeleton of lobsters, craps, shrimps and other shell fish.

Several other amino-sugars are components of naturally occurring anti-bodies.

Physical properties of monosaccharides

1. They are colourless crystalline solids. Because hydrogen bonding is possible between their polar OH group & H_2O, all monosaccharides are very soluble in H_2O.
2. They are slightly soluble in ethanol & insoluble in non-polar solvents e.g diethyl ether, dichloromethane & benzene.

Cyclic structure of monosaccharides

We know that aldehydes & ketone reactions are alcohol to form hemiacetals. Cyclic hemiacetals are readily formed when hydroxyl and carbonyl group interact to form 5 or 6 membered ring, e.g. 4-hydroxy pentanal formed a five membered cyclic hemiacetal. Note that a second stereocenter is generated at carbone one as a result of hemiacetal formation.

Haworth protection

A common way of representing the cyclic structure of monosacchide is the Haworth projection named after the English chemist: Sir Watter Haworth in 1937 Nobel Lawretha in Haworth projection; a 5 or 6 membered cyclic hemiacetal is represented as a planar pentagon or hexagon respectively. Groups bonded to the carbon of the ring are either draw to lie above or below the plance of the ring. The new stereocenter created in forming the cyclic structure is called the "Anomeric carbon". Stereo-isomers that differ in configuration only at the anomeric carbon are called Anomers.

In aldose, the anomeric carbon is carbon one. In D-fructose, & Ketose, the anomeric carbon is carbon 2. Note that groups on the right handside of fisher projection are writtrn pointing down in Haworth projection. Groups on the left in fisher projection are written pointing up in the Haworth.

For a D-monosaccharide, determiner CH_2OH points up in the Haworth projection. The configuration of the anomeric –OH group is the Harworth projection. The configuration of the anomeric –OH group is relative to determiner CH_2OH group. If the anomeric OH group is on the same side as determiner CH_2OH, its configuration is called β. If the anomeric OH group is on the opposite side, the configuration is called ∝.

Six membered hemiacetal ring is denoted as pyranand a five membered hemiacetal is denoted as furan.

The terms furanose & pyranose are used because monosaccharide 5&6 membered ring corresponond to the heterocyclic compound pyranal furan

The ∝ &β forms of glucose are 6 member cyclic hemiacetals. They are named ∝-D-Glucopyranose & β-D-glucopyranose.

Hint: Aldopentoses also formed cyclic hcmiacetal. The most prevalent form of aldopentoses in biological world are furanose. The cyclic structure of furanose is as follows:

Conformation

The 5-memberd ring is so dose to being planar that Haworth projections are adequate to represent furanoses. For pyranoses, the six membered ring are more adequately represented as a chair conformation on with strain is a minimum.

Muta rotation

This is the change in specific rotation that accompanies the interconversion of ∝ & β anomers in aqueous solution. For examples, a solution prepared by dissolving crystalline ∝-D-glucopyranose in H_2O shows an initial rotation of + 112^0 with gradually increases to an equilibrium value of $+52.7^0$ as ∝-D-glucopyranose reaches an equilibrium with β-D-glucopyranose. A solution of β-D-glucopyranose also undergoes muta rotation during with the rotation angles from an initial values of 18.7^0 to the same equilibrium value of 52.7^0

The equilibrium mixture consists of 64% β-D-glucopyranose with 0.03% traces of open chain form. Muta rotation is common to all carbohydrates that exist in hemiacetyl form.

Reactions of monosaccharides

We are going to talk about reaction of monosacc with alcohol, reducing agent & oxidizing agent.

Formation of glycosides

Treating aldehyde or ketone with one molecule of alcohol yield a hemiacetal & treating with a molecule of alcohol yields an acetyl.

Treating all forms of monosaccharides that exist in a cyclic hemiacetal with alcohol will give an acetyl. For example, β-D-glycopyranose.

A cyclic acetyl derived from a monosaccharides is called glycoside & the bond from anomeric carbon to O-R group is called a glycocylic bond. Muta-rotation is not possible in glycoside because unlike in hemiacetylacetal an acetyl is no longer on equilibrium with the open chain carbonyl, containing compound in neutral or alkaline solution. Glycosides are stable in H_2O & aqueous base but undergo hydrolysis in aqueous acid to an alcohol & a monosaccharide.

We name glycosides by listing the alkyl or aryl bonded to O_2 followed the name of the carbohydrate involved in which ending ‘e’ is replaced by ‘ide’. For example, glycosides derived from β-D-glucopyranose are named as β-D-glucopyranosides. Those derived from β-D-glucofuranose are named as β-D-glucofuranoside Hydrolysis of Glycoside will give hemiacetyl of Alkanol.

Reduction of monosaccharides to Alditols

The carbonyl group of monosaccharides is reduce to hydroxyl group using reducing agents with $NaBH_4$. Reduction product is Alditols. Reduction of D-glucose gives D-glucitol / D-sorbitol.

Name alditols by replacing ‘ose’ with ‘itol’ sorbitol is found in plants, berries, apples, e.t.c. 60% sweet as sucrose (table sugar) to make candies and sugar substances for diabetes. Other Albitols are:

Xylitol is used as sweeting agents in chewing gum, candies and sweet cereal.

Monosaccharide oxidation to aldonic acid

Some agent including O_2 will oxidize aldehyde to carboxylic acids. Under basic conditions, the aldehyde group of an aldose can be oxidized to a carboxylate group. D-glucose for example, will be oxidized to D-gluconate.

Any carbohydrate that react with any oxidizing agent to form an aldonic acid is classified as a reducing sugar.

Oxidation to uronic acids

Enzyme catalysed oxidation of I^o alcohol at C-6 of a hexose will yield “uronic acid’. Enzyme catalysed oxidation of D-glucose for example will yield D-gluconic acid

D-glucuronic acid is widely distributed in both plants and animals. In humans, it is an important component of the acidic polysaccharides of connective tissues. The body also uses it to detoxify foreign phenols and alcohols. In the liver, this compounds are converted to glycocides of glucoronic acid to be excreted in the urine.

Assignment: testing for blood sugar, vit. c (ascorbic acid)

Disaccharides and oligosaccharides

Most carbohydrate in nature contain more than one monosaccharide unit. Those which contain two units are called disaccharides, 3 units; trisaccharides and so on. The more general term oligosaccharides is often used for carbohydrates that contain from 6-10 monosaccharides units. Carbohydrates containing large number of monosaccharide units are called polysaccharides. In a disaccharides, 2 monosaccharide units are jointed by a glucosidic bond between the anomeric carbon of 1 unit and hydroxyl of the other. Sucrose, maltose and lactose are 3 important disaccharides.

Sucrose

This the table sugar and is the most abundant disaccharide in the biological world. It is obtained principally from the juice of cane sugar and sugar beets. In sucrose, C-I of α-D-glucopyranose bond to C-2 of D-fructopuranose by an α - 1, 2 – glycosidic bonds.

Because the anomeric carbons of both the glucopyranose and fructofuranose units are involved in formation of glycosidic bond. Neither monosaccharides units is in ⟵ which is open chain form thus, making sucrose to be a non-reducing sugar.

Lactose

This is found in milk. It accounts for 5-8% of human milk and 4-6% of cows milk. This disaccharide consist of D-galactopyranose bonded by a β 1,4 glycosidic bond to C-4 of D-glucopyranose.

Lactose is a reducing sugar because the cyclic hemiacetal of D-glucopyranose is in ⟺ which his open chain form and can be oxidized to carboxyl group.

Maltose

It derives its name from its presense in malt. Maltose obtained from hydrolysis of starch. It consist of 2 units of D-glucopyranose joined by a glycosidic bind between C-I (the anomeric carbon of 1 unit) and C-4 of the other units.

Starch is broken-down into maltose by an enzymes in saliva called $\alpha\ 1{,}4\ glucan - 4 - glucanohydrolase$.

Polysaccharides

Consists of a large number of monosaccharide units joined together by glycosidic bond. 3 important polysaccharide that are all made of glucose units are; starch, glycogen and cellulose. Upon complete hydrolysis a polysaccharide will yield monosaccharide. Polysaccharide serves in the body in various ways and in various units. For examples, cellulose which gives:

1. Strength to the stems of plants and their branches
2. Also it gives structural component of insects
3. Serves as nutritional agent e.g. in potatoe, yam e.t.c. starch are readily available source of carbohydrates.

Starch

Consist of multiple repeat units of monosaccharides. It is found in all plant seeds and tuber and is the form in which glucose is stored for later use. Starch can be separated into two principle polysaccharide i.e amylase and amylopectin. Although the starch form each plants is unique, most starch consist of 20-75% amylase and 75% - 80% amylopectin. Complete hydrolysis of amylase and amylopectin yields only D-glucose. Amylase is composed of continous unbranched chains of as many as 4,000 D-glucose units joined by an ∝ 1,4 glycosidic bond. Amylopectin contains chains up to 10,000 D-glucose units and also joined by an ∝ 1,4 glycosidic bond.

Glycogen

Is the reserved carbohydrate for animals. Like amylopectin, glycogen is a branched polymer of D-glucose containing $\simeq 10^6$ glucose units joined by a α 1,4 and α 1,6 glycosidic bonds. The total amount of glycogen in the body of a well nourished adult human being is about 350g which is divided equally between liver and muscle.

Cellulose

As glucose is to animals, cellulose is to plants. Cellulose is the most widely distributed plants skeletal polysaccharides. Cellulose is the most abundant organic compound on earth. It constituents almost half of cell wall material of wood. Cotton is almost pure cellulose. Cellulose is a linear polymer of D-glucose units joined by β 1,4 glycosidic bonds. It has an average molar mass of 400,000gmol^{-1} corresponding to $\simeq$ 2,800 glucose units per molecule. Cellulose molecules act much like stiff rods, a future that enables them to aligne themselves side by side into well organized, water insoluble fibres in which the "OH" group form numerous intermolecular hydrogen bonds. This arrangement of parallel chains in bundles give cellulose fiber a high mechanical strength and explains why cellulose is insoluble in H_2O. when a piece of cellulose containing material is placed in H_2O, there are not enough "OH group" on the surface of the fibre to pull individual cellulose molecules away from the strongly hydrogen bonded fiber.

Textile fibres of cellulose

Both rayon and acetate rayon are made from chemically modified cellulose and are the first important synthetic textile fibres. In the production of rayon, cellulose fibres are treated with carbon disulphide in aqueous NaOH. In this reaction, some of the hydroxyl groups on the cellulose fibre are converted to the Na-salt of xanthate ester which causes the fibre to dissolve in alkaline as a viscous colloidal dispersion.

Amino acids and proteins

Are compounds whose chemistry is built on amines (-NH_2) and carboxylic acids (-COOH). Proteins are among the most important of all biological compounds. The acid base properties of amino acid is very important in determining the properties of proteins including the catalytic functions of enzymes. Some of the functions performed by amino acids and proteins includes the following:

1. Structure: structural proteins such as collagen and keratin are the chief constituents of skin, bones, hair and nails.
2. Catalysis: visually all reactions that takes place in living system are catalysed by special of protein called enzymes.
3. Movement: muscle fibres are made up of proteins called myosin and actin
4. Transport: the protein, haemoglobin is responsible for the transport of oxygen from the lungs to tissue. Other proteins transport molecules across cell membrance
5. Protection: a group of proteins called antibodies is one of the bodies defences against disease.

Amino acids

An amino acid is a compound that contains both the carbonyl group and an amine group. Although many types of amino acids are known, the α- amino acids are the most significant in the biological world because they are the monomers from which proteins are constructed.

A general structural formula of alpha amino acid is as shown;

Although structure (a) is a common way of writing structural formula for amino acids, it is not accurate because it shows an acid "COOH" and a base "NH_2" within the same molecule. These acidic and basic group reaction with each other to form an internal salt which is shown as structure (b) and is given a special name "z witterion".

A zwitterions has no net charge i.e. it contains one positive and one negative charge. Because they can exist as zwitterions, amino acids has many properties associated with salt. They are crystalline solid with high m. point and are fairly soluble in H_2O but insoluble in non-polar organic solvent such as ether and hydrocarbon solvents e.g. chloroform, benzene e.t.c.

The simplest anion acid is; "amino acetic acid" which is called "glycin". It has no side chain and consequently does not contain a chiral center.

NH_2CH_2COOH (glycin).

With the expection of glycin, all proteins derived from amino acid have at least one stereocenter and therefore are chiral. The common 20 amino acids;

a. Glycine
b. Alanine
c. Arginine
d. Asparagines
e. Aspartic acid
f. Cysteine
g. Glutamic acid
h. Glutamine
i. Histidine
j. Isoleucin
k. Leucine
l. Lysine
m. Methionine
n. Phenylalanine
o. Proline
p. Serine
q. Threonine
r. Tryptophan
s. Tyrosine
t. Valine

The structural formula of the

The standard 3-letter abbreviation and I-letter abbreviation are also shown. Amino acids are divided into 4 categories

1. Those with non-polar side chains
2. Those with polar side chain
3. Those with acidic side chain
4. Those with basic side chain

Note the following:

1. Also these proteins derived amine acids are ∝- amino acids i.e. the amino group is located on the carbon ∝ to the carbonyl group. For nineteen out of the 20, the amino group is 1^0. Only pronine has it amino group as 2^0.
2. With the exception of glycine, the ∝-carbon of each amino acid is a stereocentre.
3. Isoleucine and threoine contain a second stereocenter.

Name of some other common L-amino- acids

Although a fast majority of plant and animal proteins are constructed from this 20 amino acids, many other amino acid are also found in nature. Ornithine and citrulline are found predominantly in the liver are integral part of urea cycle, the metabolic path-way that convert ammonia to urea.

Thyroxine and triiodothyronine are two hormones derived from the amino acid thyroxine and are found in thyroid tissue. Their principal function is to stimulate metabolism in other cells and tissues.

4- amino-butanoic acid is found in high concentration in the brain. It is also called "GABA" and is synthesized in neutral tissue by decarboxylation of the ∝-carboxyl group of glutamic acid and is a neutron transmitter in the central nervous system of invertebrate and also in humans as well.

Properties of amino-acids

Among the most important properties of amino-acids are the acidic base properties.

1. Acidity of ∝-carbonyl groups: the average value of Pka carbonyl group of a protonated amino-acid is 2.19. thus, the ∝- carbonyl group is a considerable stronger acid than acetic acid and other low molecular weight aliphatic carboxylic acid. The greater acidity is accounted for by the e^- withdrawing inductive effect of the adjacent NH_3^+ group.
2. Acidity of side-chain carbonyl group: due to the e^- withdrawing inductive effect of the NH_3^+ group, the side chain carbonyl group of protonated aspartic acid and glutamic

acid are also stronger acid than acetic acid. Note that this acid strengthening inductive effect increases with increasing distance of the COOH from the α-NH_3^+.

3. Acidity of α-amino groups: the average value of Pka for an α- ammonia group i.e α-NH_3^+ = 9.47 compared to an average value of 10.76 for 1^0 aliphatic ammonium ions. Thus, the α-ammonium group (α-NH_3^+) of an amino acid is a slightly stronger acid than a 1^0 aliphatic NH_3^+ is and converscingly, an α-NH_3^+ is a slightly weaker base than a 1^0 aliphatic amine is c
4. Basicity of Guaniddine group of arginine: the side chain guanidine group of arginine is a considerablely stronger base than an aliphatic amine is Guanidine is the strongest base of any neutral compound. The remarkable basicity group of arginine is attributed to the large resonance stabilization of the protonated from relative to the neutral form.
5. Basicity of the imidazole group of histidine: recall the imidazole group on the side chain of histidine contains $6= \pi^{e\text{-}s}$ in the planer fully conjugated ring, imidazole is classified as a heterocyclic aromatic amine. The unshared pair of e^- on one nitrogen is a part of the aromatic sexlet whereas that on the other nitrogen is not. It is the pair of e^- that is not part off the aromatic sexlet which is responsible for the basic properties of the imidazole ring. Protonation of this nitrogen produces a resonance stabilized ion.

Titration of amino acids

Values of Pka for the ionizable group of amino acid are most commonly obtained by acid-base titration and by measuring the P^H of the solution as a function of added base (or added acid depending on how the titration is done). To illustrate this exsperimental procedure, consider a solution containing Imol of glycin to which has being added enough strong acid so that both the amino and carbonyl agroup are fully protonated. Next, the solution is titrated with 1m NaOH, the volume of base added and P^H of resulting solution are recorded and then plotted.

The most acidic group and the one to react first added NaOH is the carbonyl group (C=o). when exactly 0.5m of NaOH has been added, the carbonyl group is half neutralized. At this point, the concentration of the Zwitterion equals that of the positive charged ion and the P^H of 2.35 equals the Pka the carbonyl group.

Isoelectric point

Titration curves permit us to determine Pka value for the ionizable groups of an amino acid. They also permit us to determine another important property i.e. the “isoelectric point” - P^I. the P^I is the P^H at which most of the molecules of amino acid in solution have a net charge of “zero” meaning that; “they are Zwitterion”. At P^H = 6.06, the predominant from of glycin molecules has a dipolar ion. Futhermoare, at this P^H, the concentration of positively charged glycin molecules equals concentration of negatively charged glycin molecules.

Given a value for the isoelectric point of an amino acid, it is ossible to estimate the charge on that amino acid at any $P^{H.}$ for example, the charge on tyrosine have P^H=5.63, the isoelectric point of tyrosine is zero. A small fraction of tyrosine molecule is positively charged at P^H=5 showing that we have 0.63 unit less than it isoelectric point.

Electrophoresis

This is a process of separating compounds on the basis of their electric charges. It is used to separate an identified mixture of amino acid and proteins. Electrophoretic separation can be carried out with; paper, starch, ager, certain plastics and cellulose acetate used as solid support.

In paper electrophoresis, a paper strip saturated with an aqueous buffer with predetermined P^H serves as a bridge between two electrode vessels. Then, a sample of amaino acid is applied as a colourless spot on the paper strip.

Note: that the amino acid mixture is colourless. When an electrical potential is applied to the electrode vessel, amino acid migrate toward the electrode carrying the charge opposite to their own. Molecules having a high charge density move more rapidly than those with a lower charge density.

Any molecule already at it isoelectric point remains at the origin. After the separation is complete, the paper strip is spaced with a dye that transforms each amino acid into a colour compound making the separate component visible. A dye commonly used to detect amino-acid is collect Ninhydrin" with lupac name: 1,2,3- indanetrione monohydrate. Nimhydrion react with $\propto$-amino acid to produce aldehyde, CO_2 and a purple colour anion.

This reaction is commonly used in both quantitative and qualitative analysis of amino acid.

19 of the 20 protein $\propto$-amino acid having 1^0 amino groups and gives the same purple coloured ninhydrin derived anion.

Proline a 2^0 amino gives a different orange coloured compound.

Polypeptide and proteins

In 1902, Emyl fisher proposed that proteins are long chain of amino acid joined together by amide bonds between the alpha carbonyl group of one amino acid and the $\propto$ - amino group of another. For this amide bond, fischer proposed the spectial name; "Peptide bond".

Below is an example of peptide bond formed between serine and analine.

Peptide is the name giving to short polymer of amino acid. We classified peptide by the number of amino-acid in their chain. A molecule containing two amino acid joined by an amide bond is called a dipeptide, 3-tri, 4-tetra e.t.c. molecules containing more than 10 but fewer than 20 are called Oligopeptide. Those containing several dozens of amino acid are called "polypeptide".

Proteins are biological macromolecules with molecular weight 5000 or greater consisting on one or more polypeptide chain.

By convection, polypeptide are written from left-right beginning with the amino acid having the free amide ion and proceeding towards the amino acid is the COO^-.

I^0 structures of polypeptides and protein

I^0 structure of polypeptide or protein is the sequence of amino acid in it polypeptide chain. In this sense, the I^0 structure is a complete description of all covalent bonding in a polypeptide or protein. In 1953, Fredrick reported the I^0 structure of the two polypeptide chains of the hormone: insulin. This was a remarkable achievement in analytical chemistry. It also clearly established that the molecule of a given protein will all have the same amino acid composition and the same amino acid sequence. Nowadays, the amino acid sequence of over 20,000 different proteins are known.

Amino acid analysis

The first stop in determining the I^0 structure of a polypeptide is hydrolysis and quantitative analysis of it amino acid composition.

Samples of sproteins are hydrolyzed in 6M HCL in sealed glass at 100^0c for 24-72 hours (this hydrolysis can be done in a microwave oven in a shorter time). After the polypeptide is hydrolyzed, the resulting mixture of amino acid is analysed by ion-exchange chromatography.

In this process, the mixture of amino acid is passed through a specifically packed column. Each of the 20 amino acid requires a different time to pass through the column.

Amino acid are detected by reaction with Ninhydrin as they emerge, from the column polled by absorption spectroscopy. There are some current procedures that can determine the amino acid composition from as little as 50nmol ($50X10^{-7}M$) of a polypeptide.

Note: during hydrolysis, the side chain amide groups of asparagines and glutamine are hydrolysed and this amino acid are detected as aspartic acid and glutamine acid.

For each glutamine and asparagines hydroligeo an equivalent amount of NH_4CL is pumped.

Sequence analysis

Once the amino acid composition of a polypeptide has been determined, the next step is to determine the other in which the amino acid are joined in the polypeptide chain. The most common sequencing strategy is to cleaves the polypeptide at specific peptide bond (by using for example cyanogens bromide) determine the sequence of each fragment and then merge over lapping fragment to arrive at the sequence of the polypeptide.

Cyanogens bromide (Br CN) is specific for the cleavage of peptide bond formed by the carbonyl group of methionine. The product of this cleavage are substituted α- lactones derived from the N-terminal portion of the polypeptide and the second fragment containing C-terminal portion of the polypeptide.

Proteins

The word proteins is derived from the greek word “proteins” which means I^0.. protein are of I^0 and paramount importance in biologically word. Out of the dry body weight, ¾ are proteins made for the body. All the major structural and functional function of the body are carried out by protein molecules. Abnormality in protein structure will lead to molecular disability with consequence in alteration of body metabolism. Protein contains C,O,H & N as the major component while S,P are minor constituent.

Nitrogen is characteristics of protein. On an average, the N-content of ordinary protein is 16% by weight. All proteins are polymers of amino acid.

Classification of proteins

Protein can be classified in 3;

1. Fibrous proteins / structural protein
2. Globular proteins
3. Conjugated proteins

Fibrous protein

It forms skin, muscles, walls of arteries and hairs. Are composed of long threadlike molecules that are through and insoluble which are from fibrous protein.

Globular protein

They are small protein that a some how spherical in shape because of the following of the protein chains upon themselves. Globular proteins are H_2O soluble and performed various functions in organism. For examples, haemolobin transport O_2 to the cells, insulin aids in carbohydrate metabolism antibodies render foreign bacteria inactive.

Conjugated proteins

Proteins that are connected to a non-protein moiety such as a sugar performs various functions throughout the body. A common link between protein and non-protein is by a functional side chain of the protein e.g. an acidic side chain of the protein can form an ester with an hydroxyl group of sugar molecule.

Read on structure of protein, keratin, collagen.

Denature of protein: is the lost of it higher structural features by destruction of the hydrogen bonding and other bonding forces that holds it together. Denaturation of protein is the lost of many of proteins biological properties.

Factors responsible for denaturation

1. Temperature
2. Change in P^H
3. Read more.