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# CRASH COURSE



All living bodies are composed of several lifeless substances which are present in their cells in a very complex but highly organised form. These are called biomolecules. Some common examples are carbohydrates, proteins, enzymes, nucleic acids, lipids, amino acids, fats etc:

Living organisms  $\to$  Organs  $\to$  Tissues  $\to$  Cells  $\to$  Organelles  $\to$  Biomolecules.

### **Carbohydrates**

The carbohydrates are naturally occurring organic substances. They are present in both plants and animals.

"Carbohydrates are defined as a class of compounds that include polyhydric aldehydes or polyhydric ketones and large polymeric compounds that can be broken down (hydrolysed) into polyhydric aldehydes or ketones."

Carbohydrates contain > C = O and -OH groups. A carbonyl compound reacts with an alcohol to form hemiacetal.

The name of simpler carbohydrates end is —ose. Carbohydrate with an aldehydic structure are known as aldoses and those with ketonic structure as ketoses. The number of carbon atom in the molecule is indicated by Greek prefix.

Table : 31.1

Number of carbon atoms in the molecule	Aldose	Ketose
3	Aldotriose	Ketotriose
4	Aldotetrose	Ketotetrose
5	Aldopentose	Ketopentose
6	Aldohexose	Ketohexose
7	Aldoheptose	Ketoheptose

#### **Monosaccharides**

These are the simplest one unit non-hydrolysable sugars. They have the general formula  $C_nH_{2n}O_n$  where n varies from 3 to 9 carbon atoms. About 20 monosaccharides occur in nature. The simplest are trioses (n=3)

$$\begin{array}{c|cccc} & H-C=O & CH_2OH \\ & & & & \\ & C_3H_6O_3 & ; & H-C-OH & ; & C=O \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & & \\ & & \\ & & & \\ & &$$

The most important naturally occurring monosaccharides are pentoses and hexoses. A common pentose is ribose and two common hexoses are glucose and fructose.

Except ketotriose {dihydroxyacetone}, all aldose and ketoses {monosaccharides} contain asymmetric carbon atoms and are optically active.

#### Glucose; $(C_6H_{12}O_6)$ or Aldo-hexose

Glucose is known as **dextrose** because it occurs in nature as the optically active dextrorotatory isomer. It is also called grape sugar as it is found in most sweet fruits especially grapes.

- (1) **Preparation:**
- (i) Laboratory method

$$\begin{array}{c} C_{12}H_{22}O_{11} + H_2O \xrightarrow{\quad H^+ \quad} C_6H_{12}O_6 + C_6H_{12}O_6 \\ \text{Cane sugar} \\ \text{(Sucrose)} \end{array}$$

HCI (dil.) is used for hydrolysis. Glucose being much less soluble in alcohol than fructose separates out by crystallising on cooling.

(ii) *Manufacture*: It is obtained on a large scale by the hydrolysis of starch (corn starch or potato starch) with dilute sulphuric acid or hydrochloric acid.

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow[320^{\circ}C, 2^{-3}]{H^+} nC_6H_{12}O_6$$
Starch

A thin paste of starch is boiled with dilute acid till the hydrolysis is complete. The excess of acid is neutralised with chalk (calcium carbonate) and the filtrate containing glucose is decolourised with animal charcoal. The solution is concentrated and evaporated under reduced pressure. Glucose is obtained in crystalline form.

- (2) *Physical properties*: It is a colourless crystalline solid, melts at  $146^{\circ}$  C. It is readily soluble in water. From aqueous solution, it separates as a crystalline monohydrate  $(C_6H_{12}O_6.H_2O)$  which melts at  $86^{\circ}$  C. It is sparingly soluble in alcohol but insoluble in ether. It is less sweet (three-fourth) than cane sugar. It is optically active and the ordinary naturally occurring form is (+) glucose or dextro form. It shows **mutarotation**.
  - (3) Chemical properties
  - (i) Alcoholic reactions (Reactions due to -OH group):
  - (a) Reaction with acid chlorides and acid anhydride

$$CHO \qquad CHO \\ | \qquad | \qquad | \\ (CHOH)_4 + 5CH_3COCl \xrightarrow{ZnCl_2} (CHOOCCH_3)_4 + 5HCl \\ | \qquad | \qquad | \\ CH_2OH \qquad CH_2OOCCH_3 \\ Glucose \qquad Glucose penta-acetate$$

This shows that a molecule of glucose contains 5 - OH groups.

(b) Reaction with PCl

$$CHO \qquad CHO \\ | \qquad | \qquad | \\ (CHOH)_4 + 5PCl_5 \longrightarrow (CHCl)_4 + 5POCl_3 + 5HCl \\ | \qquad | \qquad | \\ CH_2OH \qquad CH_2Cl \\ \text{Glucose} \qquad Penta-chloroglucose} \\ \text{(Glucose penta-chloride)}$$

(c) Reaction with metallic hydroxides

$$C_6H_{11}O_5 + OH + HO - Ca - OH \longrightarrow$$
Glucose

 $C_6H_{11}O_5 + OH + HO - Ca - OH \longrightarrow$ 

 $\square$  Glucose behaves as a weak acid. Instead of  $Ca(OH)_2$  we can take other metallic hydroxide like  $Ba(OH)_2$ ,  $Sr(OH)_2$ ,  $Cu(OH)_2$  etc to form glucosate which is soluble in water.

(d) Formation of glycosides

$$C_{6}H_{11}O_{5} \stackrel{\vdash}{-}OH + H_{1}OCH_{3} \stackrel{HCl}{\longrightarrow} C_{6}H_{11}O_{5}OCH_{3} + H_{2}O$$

$$C_{6}H_{11}O_{5}OCH_{3} + H_{2}O$$

$$C_{7}OH \qquad CHOH, \qquad CHOH, \qquad CHOH$$

CHOH

This reaction shows the presence of ring structure in glucose.

One thy glucoside

- (ii) Reactions of carbonyl group (Aldehydic group)
- (a) Reduction

$$CH_2OH(CHOH)_4 CHO + 2H \xrightarrow{Na-Hg} H_2O$$

CH<sub>2</sub>OH(CHOH)<sub>4</sub> CH<sub>2</sub>OH

On prolonged heating with concentrated  $\it HI$  and red phosphorus at  $110^{o}\,\it C$  , glucose forms a mixture of 2-iodohexane and  $\it n$ -hexane.

(b) Oxidation

Reaction with Fehling solution

$$CH_2OH(CHOH)_4CHO + 2CuO \longrightarrow$$

$$\begin{array}{c} CH_2OH(CHOH)_4 \ COOH + Cu_2O \ . \\ \text{Gluconic acid} & \text{(red ppt.)} \end{array}$$

☐ Reaction with Tollen's reagent

$$CH_2OH(CHOH)_4\,CHO + Ag_2O \longrightarrow \\ CH_2OH(CHOH)_4\,COOH + \underbrace{2Ag}_{\text{(Mirror)}}_{\text{[or black ppt.]}}$$

☐ Reaction with Bromine water

$$CH_2OH(CHOH)_4 CHO + [O] \xrightarrow{Br_2/H_2O}$$

$$CH_2OH(CHOH)_4COOH$$
.

Gluconic acid

☐ Reaction with Nitric acid

$$CH_2OH(CHOH)_4 CHO + 3[O] \xrightarrow{HNO_3}$$
  
Glucose  $(C_6)$ 

 $COOH(CHOH)_4 COOH + H_2O$ . Saccharic acid $(C_6)$ 

(c) Reaction with HCN

$$CH_2OH(CHOH)_4CHO+HCN$$

(d) Reaction with hydroxyl amine

$$CH_2OH(CHOH)_4CHO + NH_2OH \rightarrow$$

$$CH_2OH(CHOH)_4CH = NOH + H_2O$$
.
Glucose oxime

(e) Reaction with Phenyl hydrazine (Fischer's mechanism): When warmed with excess of phenyl hydrazine, glucose first forms phenylhydrazone by condensation with - CHO group.

Glucose Glucose phenyl *hydrazone* The adjacent – *CHOH* group is then oxidised by a second molecule of phenyl hydrazine.

$$CH = NNHCH$$

$$CHOH + HNNHCH$$

$$(CHOH)$$

$$CHOH$$

$$CHOH$$

$$CHOH$$

$$CHOH$$

$$CHOH$$

$$CHOH$$

$$CHOH$$

$$CHOH$$

$$CHOH$$

The resulting carbonyl compounds Ketacto WRAP I differ molecule of phenyl hydrazine to yield glucosazone. Glucose phenyl hydrazone

$$CH = NNHCH$$

$$C = O + HNNHCH$$

$$CHOH$$

$$CHOH$$

$$CHOH$$

$$CHOH$$

$$CHOH$$

$$CHOH$$

$$CHOH$$

$$CHOH$$

(iii) Miscellaneous reactions

Glucosazone

(a) Fermentation

$$\begin{array}{ccc} C_6 H_{12} O_6 & \xrightarrow{Zymase} & 2 C_2 H_5 OH + 2 CO_2 \\ & \text{ Ethanol} \end{array}$$

- (b) *Dehydration*: When heated strongly or when treated with warm concentrated sulphuric acid, glucose is dehydrated to give a black mass (sugar carbon).
- (c) Reaction with alkalies: When warmed with concentrated alkali, glucose first turns yellow; then brown and finally gives a resinous mass.

A dilute solution of glucose, when warmed with dilute solution of alkali, some glucose is converted into fructose and mannose. **D-glucose** and **D-mannose** are **epimers**.

$$CH = O \qquad CH - OH \qquad CHOH$$

$$H - C - OH \qquad C = O$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$Glucose \qquad Enol \qquad Fructose$$

$$HO - CH \qquad CH = O$$

$$\parallel \qquad \qquad HO - C - H$$

$$\vdots \qquad \qquad \vdots$$

$$O \qquad H \qquad Enol \qquad HO - C - H$$

$$H - C - OH$$

$$CHOH$$

$$D(+) Glucose \qquad D(+) Mannose$$

(d) Action of concentrated hydrochloric acid Epimers  $C_6H_{12}O_6 \xrightarrow{Conc.HCl} \rightarrow$ 

$$CH_3COCH_2CH_2COOH + HCOOH + H_2O$$
Laevulicacid

On treatment with conc. HCl, glucose can also form hydroxymethyl furfural.

$$CHO \longrightarrow CH - CH + 3HO$$

$$HOCH - C \qquad C - CHO$$

$$Hydroxymethyl$$

This on acid treatment gives laevulic acid

#### (4) *Uses*

- (i) In the preservation of fruits and preparation of jams and jellies.
- (ii) In the preparation of confectionary and as a sweetening agent.
- $\left(iii\right)$  As a food for patients, invalids and children.
- (iv) In the form of calcium glucosate as medicine in treatment of calcium deficiency.
  - (v) As a reducing agent in silvering of mirrors.
  - (vi) As a raw material for alcoholic preparations.
  - (vii) In industrial preparation of vitamin-C.
  - (viii) In the processing of tobacco.
- (ix) As an intravenous injection to the patients with lower glucose content in blood.

# (5) Test of glucose

- (i) When heated in a dry test tube, it melts, turns brown and finally black, giving a characteristic smell of burnt sugar.
- (ii) When warmed with a little conc.  $\boldsymbol{H}_2\boldsymbol{SO}_4$  , it leaves a charred residue of carbon.
- (iii) When it is boiled with dilute NaOH solution, it first turns yellow and then brown.
- (iv) **Molisch's test**: This is a general test for carbohydrates. Two or three drops of alcoholic solution of  $\alpha$ -naphthol is added to 2mL of glucose solution. 1 mL of concentrated  $H_2SO_4$  is added carefully along the sides

of the test tube. The formation of a violet ring, at the junction of two liquids confirms the presence of a carbohydrate.

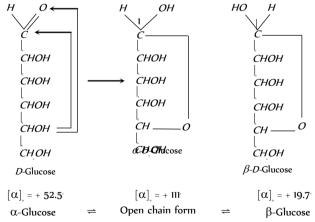
- (v) Silver mirror test: A mixture of glucose and ammonical silver nitrate is warmed in a test tube. Appearance of silver mirror on the inner walls confirms glucose.
- (vi) Fehling's solution test: A little glucose is warmed with Fehling's solution. A red precipitate of cuprous oxide is formed.
- (vii) <code>Osazone formation</code> : Glucose on heating with excess of phenyl hydrazine in acetic acid gives a yellow crystalline compound, m.pt.  $205^{o}\,C$  .

#### (6) Structure of glucose

(i) Open chain structure: The structure of D-glucose as elucidated by Emil Fischer is,

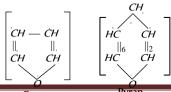
(b) Ordinary { (Specific rotation =  $52.5^{\circ}$ ) resh aqueous solution has specific rotation,  $[\alpha]_D + 111^{\circ}$ . On keeping the solution for some time;  $\alpha$ -glucose slowly changes into an equilibrium mixture of  $\alpha$ -glucose (36%) and  $\beta$ -glucose (64%) and the mixture has specific rotation +  $52.5^{\circ}$ .

Similarly a fresh aqueous solution of  $\beta$ -glucose having specific rotation,  $[\alpha]_D + 19.7^o$ , on keeping (standing) gradually changes into the same equilibrium mixutre (having, specific rotation  $+52.7^o$ ). So an aqueous solution of glucose shows a physical property, known as **mutarotation**, i.e., a change in the value of specific rotation (muta=change; rotation = specific rotation) is called **mutarotation**.

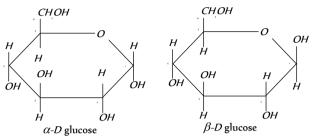


 $(c^3)^6\%$  Fischer and Tollen's proposed that the ring or the internal hemiacetal is formed between  $C^1$  and  $C^4$ . It means the ring is **Furantype** or 5-membered ring; this is called **Furanose structure**,

However according to Haworth and Hirst the ring is formed between  $C^1$  and  $C^5$ . It means the ring is **Pyran type** or 6-membered ring, this is called **Pyranose structure.** 



(d) *Haworth structure*: The two forms of D-glucose are also shown by **Haworth** projection formula which are given below,



# Fructose, fruit sugar (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) or ketohexose

It is present in abundance in fruits and hence is called **fruit sugar**. It is also present in cane sugar and honey alongwith glucose in combined form. The polysaccharide **inulin** is a polymer of fructose an gives only fructose on hydrolysis. Since naturally occurring fructose is laevorotatory, it is also known as **laevulose**.

- (1) Preparation:
- (i) Hydrolysis of cane sugar

$$C_{12}H_{22}O_{11}+H_2O \xrightarrow{\quad H_2SO_4(\text{dil.})\quad} C_6H_{12}O_6+C_6H_{12}O_6$$
 Cane sugar Varm Carbon Sugar Variations D-Fructose

The solution having equal molecules of D-glucose and D-fructose is termed **invert sugar** and the process is known as **inversion**.

☐ The excess of sulphuric acid is neutralised by adding milk of lime. A little more of lime is added which converts both glucose and fructose into calcium glucosate and calcium fructose respectively.

(ii) Hydrolysis of Inulin with dilute sulphuric acid

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\quad H_2SO_4(\text{dil.}) \quad} nC_6H_{12}O_6$$
Fructose

(2) **Properties :** The anhydrous fructose is a colourless crystalline compounds. It melts at  $102^{o}\,C$ . It is soluble in water but insoluble in benzene and ether. It is less soluble in water than glucose. It is the **sweetest** of all sugars and its solution is laevorotatory. Like glucose, it also shows **mutarotation.** 

$$CHOH \qquad HOHC \qquad OH$$

$$C=O \qquad CHOH \qquad C$$

$$HO-C-H \qquad GO$$

$$H-C-OH \qquad GO$$

$$H-C-OH \qquad GO$$

$$CHOH \qquad H-C-OH \qquad GO$$

$$CHOH \qquad H-C-OH \qquad GO$$

$$CHOH \qquad CHOH$$

$$D-Fructose \qquad \alpha-D-Fructose$$

$$[\alpha]_D=-92^\circ \qquad [\alpha]_D=-21^\circ$$

Table: 31.2 Comparison between glucose and fructose

Property	Fructose	
Molecular formula	Glucose $C_6 H_{12} O_6$	$C_6H_{12}O_6$
Nature	Polyhydroxy aldehyde.	Polyhydroxy ketone
Melting point	146° <i>C</i>	102° <i>C</i>
Optical activity of natural form	Dextrorotatory	Laevorotatory
With ethyl alcohol	Almost insoluble	More soluble
Oxidation		
(a) With bromine water	Gluconic acid	No reaction
(b) With nitric acid		
	Saccharic acid (Glucaric acid)	Mixture of glycollic acid, tartaric acid and trihydroxy glutaric acid
Reduction	Sorbitol	Mixture of sorbitol and mannitol
Calcium hydroxide	Forms calcium glucosate, soluble in water	Forms calcium fructosate, insoluble in water
Molisch's reagent	Forms a violet	Forms a violet ring
Fehling's solution	Gives red precipitate	Gives red precipitate
Tollen's reagent	Forms silver mirror	Forms silver mirror
Phenyl hydrazine	Forms osazone	Forms osazone
Resorcinol + HCl (dil.) (Selivanoff's test)	No colouration	Gives red or brown colour or precipitate
Freshly prepared ammonium molybdate sol. + few drops of acetic acid ( <b>Pinoff's test</b> ).	Light blue colour	Bluish green colour on heating
Alcoholic α-naphthol + HCl (conc.) (Furfural test)	No colouration	A purple colour (violet) on boiling

 $\square$  Fructose gives reactions similar to glucose. The difference in properties is due to the fact that it contains a ketonic group while glucose contains an aldehydic group.

#### Interconversions :

- (1) Chain Lengthening of Aldoses (Killiani-Fischer synthesis) : The conversion of an aldose to the next higher member involves the following steps :
  - (i) Formation of a cyanohydrin.
  - (ii) Hydrolysis of CN to COOH forming aldonic acid.
  - (iii) Conversion of aldonic acid into lactone by heating.
- (iv) The lactone is finally reduced with sodium amalgam or sodium borohydride to give the higher aldose.

$$CHO \qquad CN \qquad COOH$$

$$(CHOH) \qquad HCN \qquad CHOH \qquad HO/H \qquad CHOH$$

$$Arabinose \qquad CHOH \qquad (CHOH) \qquad Ba(OH) \qquad (CHOH) \qquad$$

(i) An aldose can be converted to the next lower member by **Ruff Degradation**.

It involves two steps.

(CHO.COCH)

$$CHO \qquad COOH$$

$$CHOH \qquad CHOH \qquad CHOH$$

$$CHOH) \qquad Br \qquad (CHOH), \qquad HO+Fe \qquad (CHOH), \qquad CHOH$$

$$CHOH \qquad CHOH \qquad CHOH \qquad CHOH$$

$$Aldonic acid \qquad Aldopentose$$

$$(ii) \textit{By Wohl's method} \qquad (D-Arabinose)$$

$$O = CH \qquad CHOH \qquad (CHOH) \qquad (CHOH) \qquad (CHCO)O \qquad (CHOH) \qquad$$

(3) Conversion of an aldose to the risomeric Ketose Three steps are involved,

$$O = CH \qquad HC=NNHCH \\ CHOH \qquad CHNHNH \qquad C=NNHCH \\ (CHOH) \qquad CHOH \qquad CHOH \qquad (CHOH) \qquad (-2CHNHNH) \\ CHOH \qquad CHOH \qquad Osazone \\ HC=O \qquad CHOH \\ C=O \qquad 2H \qquad C=O \\ (CHOH) \qquad CHOH \qquad (CHOH) \qquad (CHOH) \\ C=O \qquad (CHOH) \qquad (CHOH) \qquad (CHOH) \qquad (CHOH) \\ CHOH \qquad (CHOH) \qquad (CHOH) \qquad (CHOH) \qquad (CHOH) \qquad (CHOH) \\ CHOH \qquad (CHOH) \qquad$$

(4) Conversion of a ketose to the isomeric aldown Fructose Osone СНОН СНО CHOHC=0 СНОН СНОН (CHOH) (CHOH) CHOH) СНОН СНОН CH OH Fructose Glucose **Disaccharides** 

The disaccharides yield on hydrolysis two monosaccharides. Those disaccharides which yield two hexoses on hydrolysis have a general formula  $C_{12}H_{22}O_{11}$ . The hexoses obtained on hydrolysis may be same or different.

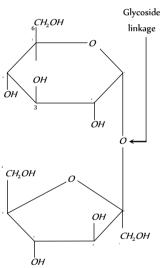
$$\begin{array}{c} C_{12}H_{22}O_{11} \xrightarrow{\quad H_2O\quad} C_6H_{12}O_6 + C_6H_{12}O_6 \\ \text{Sucrose} & H^+ & \text{Glucose} + \text{Galactose} \\ \\ \text{Lactose} & \xrightarrow{\quad H_2O\quad} \text{Glucose} + \text{Glucose} \\ \\ \text{Maltose} & \xrightarrow{\quad H_2O\quad} \text{Glucose} + \text{Glucose} \\ \end{array}$$

The hydrolysis is done by dilute acids or enzymes. The enzymes which bring hydrolysis of sucrose, lactose and maltose are *invertase*, *lactase* and *maltase*, respectively. Out of the three disaccharides, sucrose (canesugar) is the most important as it is an essential constituent of our diet.

In disaccharides, the two monosaccharides are joined together by glycoside linkage. A glycoside bond is formed when hydroxy group of the hemiacetal carbon of one monosaccharide condenses with a hydroxy group of another monosaccharide giving - O- bond.

- (1) Sucrose; Cane-sugar [CHO]: It is our common table sugar. It is obtained from sugar cane and sugarbeets. It is actually found in all photosynthetic plants.
- (i) \textit{Properties}: It is a colourless, odourless, crystalline compound. It melts at  $185-186\,C$ . It is very soluble in water, slightly soluble in alcohol

and insoluble in ether. It is dextrorotatory but does not show mutarotation. It is a non-reducing sugar as it does not reduce Tollen's or Fehling's reagent. Sucrose, on heating slowly and carefully, melts and then if allowed to cool, it solidifies to pale yellow glassy mass called 'Barley sugar'. When heated to 200 C it loses water to form brown amorphous mass called Caramel. On strong heating, it chars to almost pure carbon giving smell of burnt sugar. It is composed of  $\alpha\text{-D-}$ glucopyranose unit and a β-Dfructofuranose unit. These units are joined by α-β-glycosidic linkage between C -1 of the glucose unit and C-2 of the fructose unit.



(ii) *Uses* 

Structure of sucrose

- (a) As a sweetening agent for various food preparations, jams, syrups sweets, etc.
- (b) In the manufacture of sucrose octa-acetate required to denature alcohol, to make paper transparent and to make anhydrous adhesives.
- (2) **Inversion of cane-sugar :** The hydrolysis of sucrose by boiling with a mineral acid or by enzyme invertase, produces a mixture of equal molecules of D-glucose and D-fructose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
Sucrose Sucrose D-Glucose D-Fructose (This mixture is laevorotatory)

Sucrose solution is dextrorotatory. Its specific rotation is  $+66.5^{\circ}$ . But on hydrolysis, it becomes laevorotatory. The specific rotation of *D*-glucose is  $+52^{\circ}$  and of *D*-fructose is  $-92^{\circ}$ . Therefore, the net specific rotation of an equimolar mixture of *D*-glucose and *D*-fructose is.

$$\frac{+52^{\circ}-92^{\circ}}{2} = -20^{\circ}$$

Thus, in the process of hydrolysis of sucrose, the specific rotation changes from  $+66.5^{\circ}$  to  $-20^{\circ}$ , *i.e.*, from dextro it becomes laevo and it is said that inversion has taken place. The process of hydrolysis of sucrose is thus termed as **inversion of sugar** and the hydrolysed mixture having equal molar quantities of D-glucose and D-fructose is called **invert sugar**. The enzyme that brings the inversion is named as **invertase**.

Table: 31.3 Distinction between glucose and sucrose

Test	Glucose	Sucrose
With conc. HSO in cold	No effect	Charring occurs and turns black
Molisch's reagent	Violet ring is formed	Violet ring is formed
With NaOH	Turns yellow	No effect
With Tollen's Solution	Gives silver mirror	No effect
With Fehling's solution	Gives red precipitate of CuO	No effect
On heating with phenyl hydrazine	Gives yellow precipitate of glucosazone	No effect, i.e., does not form osazone
Aqueous resorcinol + conc. <i>HCl</i> solution	No effect	Reddish-brown precipitate which dissolves in ethanol.

#### Polysaccharide (Starch and cellulose)

Polysaccharides are polymer of monosaccharide. The most important polysaccharides are starch and cellulose. They have a general formula  $(C_6H_{10}O_5)_n$ . Starch (Amylum) is most widely distributed in vegetable kingdom. It is found in the leaves, stems, fruits, roots and seeds. Concentrated form of starch is present in wheat, corn, barley, rice, potatoes, nuts, etc. It is the most important food source of carbohydrates.

(1) **Starch and its derivatives :** Starch is a white amorphous substance with no taste or smell. When heated to a temperature between  $200-250^{\circ}\,C$ , it changes into dextrin. At higher temperature charring occurs. When boiled with dilute acid, starch ultimately yields glucose.

$$(C_6H_{10}O_5)_n \longrightarrow (C_6H_{10}O_5)_{n_1} \longrightarrow$$
Starch Dextrin

$$C_{12}H_{22}O_{11} \longrightarrow C_6H_{12}O_6$$
Maltose Glucose

Both n and  $n_1,\,$  are unknown, but n is believed to be greater than  $n_1$  .

When treated with enzyme, diastase, it yields maltose.

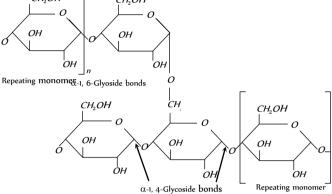
$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{} nC_{12}H_{22}O_{11}$$
Maltose

Starch solution gives a blue colour with a drop of iodine which disappears on heating to  $75-80^{\circ}\,C$  and reappears on cooling. The exact chemical nature of starch varies from source to source. Even the starch obtained from same source consists of two fractions

- (i) amylose and
- (ii) amylopectin.

Amylose is a linear polymer while amylopectin is a highly branched polymer. Both are composed of  $\alpha$ -D-glucose units linked by glycosidic linkages. The number of D-glucose units in amylose range from 60 - 300. It

is soluble in hot water, Amylopectin consists of D-glucose units from 300 – 600. It is insoluble in water.



Uses: Starch and its derivatives are used

 $\mbox{(i)}$  As the most valuable constituent of food as rice, bread, potato and corn-flour, etc.

Structure of amylopectin

- (ii) In the manufacture of glucose, dextrin and adhesives (starch paste).
  - (iii) In paper and textile industry.
  - (iv) In calico printing as a thickening agent for colours.
  - (v) Nitro starch is used as an explosive.
- $\mbox{(vi)}$  Starch-acetate is a transparent gelatin like mass and is used mainly for making sweets.
- (2) **Cellulose:** It is found in all plants and so is the most abundant of all carbohydrates. It is the material used to form cell walls and other structural features of the plants. Wood is about 50% cellulose and the rest is lignin. Cotton and paper are largely composed of cellulose.

Pure cellulose is obtained by successively treating cotton, wool, flax or paper with dilute alkali, dilute HCl or HF. This treatment removes mineral matter, water, alcohol and ether. Cellulose is left behind as a white amorphous powder.

Cellulose is insoluble in water and in most of the organic solvents. It decomposes on heating but does not melt. It dissolves in ammonical copper hydroxide solution (Schwitzer's reagent). Cellulose also dissolves in a solution of zinc chloride in hydrochloric acid.

When it is treated with concentrated  $H_2SO_4$  in cold, it slowly passes into solution. The solution when diluted with water, a starch like substance amyloid is precipitated and is called **parchment paper**. When boiled with dilute  $H_2SO_4$ , it is completely hydrolysed into D-glucose.

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{} nC_6H_{12}O_6$$
Cellulose
Glucose

The cattle, goats and other ruminants can feed directly cellulose (grass, straw, etc.) as they have digestive enzymes (celluloses) capable of hydrolysing cellulose into glucose. Man and many other mammals lack the necessary enzymes in their digestive tract and thus cannot use cellulose as food stuff.

Cellulose is a straight chain polysaccharide composed of *D*-glucose units which are joined by *B*-glycosidic linkages between *C*-1 of one glucose

take because they cannot be synthesised in the body. The  $\alpha$ -amino acids are classified into the following four types and tasulabed as under,

unit and 
$$C$$
-4 of the next glucose unit. The number of  $D$ -glucose units in cellulose ranges from 300 to 50000.

**Uses**: Cellulose is used

- (i) As such in the manufacture of cloth (cotton), canvas and gunny bags (jute) and paper (wood, bamboo, straw, etc.)
- (ii) In the form of cellulose nitrates for the manufacture of explosives (gun-powder), medicines, paints and lacquers. The cellulose nitrates with camphor yield *celluloid* which is used in the manufacture of toys, decorative articles and photographic films.
- (iii) In the form of cellulose acetate for the manufacture of rayon (artificial silk) and plastics.

Table: 31.4 Distinction between glucose, sucrose, starch

Test	Glucose	Sucrose	Starch
With iodine solution	No effect	No effect	Blue colour
With Fehling's solution	Gives red precipitate	No effect	No effect
With Tollen's reagent	Gives silver mirror	No effect	No effect
With phenyl hydrazine	Forms yellow osazone	No effect	No effect
Solubility in water	Soluble	Soluble	Insoluble
Taste	Sweet	Sweet	No taste

#### **Amino acids**

Proteins are a class of biologically important compounds. They are crucial to virtually all processes in living systems. Some of them are hormones which serve as chemical messengers that coordinate certain biochemical activities. Some proteins serve to transport the substances through the organism. Proteins are also found in toxins (poisonous materials) as well as in antibiotics. All the proteins are made up of many amino acid units linked together into a long chain. An amino acid is a bifunctional organic molecule that contains both a carboxyl group, –*COOH*, as well as an amine group, – *NH*.

Carboxyl group

$$\begin{array}{c|c} & & & \\ R - & & \\ \hline & C & \\$$

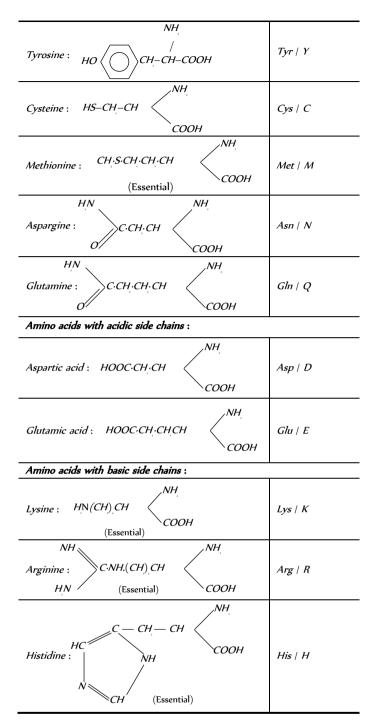
The proteins differ in the nature of R-group bonded to  $\alpha$ -carbon atom. The nature of R-group determines the properties of proteins. There are about 20 amino acids which make up the bio-proteins. Out of these 10 amino acids (non-essential) are synthesised by our bodies and rest are essential in the diet (essential amino acids) and supplied to our bodies by food which we

Table : 31.5

rable : 31.5			
Amino acids with non polar side chain :			
Name / Structure	Three letter symbol / One letter code		
Glycine: CH COOH	Gly   G		
Alanine : CHCH COOH	Ala   A		
Valine: (CH) CH-CH (Essential)	Val   V		
Leucine: (CH) CH-CHCH (Essential) COOH	Leu   L		
Isoleucine : CH-CH-CH COOH CH (Essential)	Ile   1		
Phenyl alanine : CHCHCH (Essential) COOH	Phe   F		
H,C —— CH, H,C —— CHCOOH Proline:	Pro   P		

### Amino acids with polar but neutral side chain :

Name   Structure	Three letter symbol   One letter code
Tryptophan:  N  CH  NH  C-CH-CH-COOH  (Essential)	Trp   W
Serine: HO-CH-CH COOH	Ser   S
Threonine : CHCHOH-CH (Essential)	Thr   T



#### (1) Methods of preparation of $\alpha$ -amino acids

#### (i) Amination of $\alpha$ -halo acids

#### Lab preparation of glycine

The ammonium salt so obtained is boiled with copper carbonate and cooled when blue colour needles of copper salt of glycine are obtained.

$$\begin{split} 2[H_2N-CH_2COONH_4] + CuCO_3 & \xrightarrow{\text{Boiled}} \\ & (H_2NCH_2COO)_2Cu + (NH_4)_2CO_3 \\ & \text{Copper salt of glycine} \end{split}$$

It is now dissolved in water and  $H_2\,S$  is passed till whole of the copper precipitates as copper sulphide leaving glycine as the aqueous solution.

$$(H_2N-CH_2COO)_2Cu+H_2S \rightarrow 2H_2NCH_2COOH + \underset{\text{Glycine}}{CuS} \downarrow$$

#### (ii) Gabriel pthalimide synthesis

Pot. phthalimide

CO

NCH COOCH

Chloro ethyl acetate

Pot. phthalimide

CO

NCH COOCH

+ CHNHCOOCH

Glycine

COOH

Synthesis

CH 
$$_3$$
COCOOH

Pyruvic acid

 $_{NH_3}$ 

CH  $_3$  C COOH

 $_{NH_3}$ 
 $_{NH_2}$ 

Alamine

#### (iv) Streker synthesis

$$\begin{array}{c} H \\ R-C = O \xrightarrow{HCN} R-C-OH \xrightarrow{NH_3} R-C-NH_2 \\ \hline CN \\ \text{Cyanohydri n} \end{array}$$

$$\begin{array}{c} CN \\ CN \\ \text{Amino nitrile} \end{array}$$

$$\begin{array}{c} H \\ + \\ -C-NH_2 \\ + \\ -COOH \\ \alpha-\text{Amino acid} \end{array}$$

(v) **From natural protein**: Natural proteins are hydrolysed with dil. HCl or  $H_2SO_4$  at 250°C in an autoclave when a mixture of  $\alpha$ -amino acids is obtained. This mixture is esterified and the various esters are separated by fractional distillation. The esters are then hydrolysed into respective  $\alpha$ -amino acids.

# (2) Physical properties

- (i) Amino acids are colourless, crystalline substances having sweet taste. They melt with decomposition at higher temperature (more than  $200^{\circ}$ C). They are soluble in water but insoluble in organic solvents.
- (ii) Except glycine, all the  $\alpha$ -amino acids are optically active and have an asymmetric carbon atom ( $\alpha$ -carbon atom). Hence, each of these amino acids can exist in two optical isomers. In proteins, however, only one isomer of each is commonly involved.
- (iii) Zwitter ion and isoelectric point : Since the  $-NH_2$  group is basic and -COOH group is acidic, in neutral solution it exists in an internal

ionic form called a **Zwitter ion** where the proton of -COOH group is transferred to the  $-NH_2$  group to form **inner salt**, also known as **dipolar ion**.

$$\begin{array}{c|c} R \\ H_2 \stackrel{\bullet \bullet}{N-CHCOOH} \stackrel{\text{In water}}{\longrightarrow} \\ & \stackrel{\alpha\text{-Amino acid}}{\longrightarrow} \\ R & R & R \\ & \stackrel{\bullet \bullet}{\longrightarrow} \begin{vmatrix} R & R \\ R & + & | & - \\ N-CH-COO+H & \rightarrow H_3 \stackrel{\bullet}{N-CH-COO} \\ \text{Zwitterion} \\ \text{(Dipolar ion)} \end{array}$$

The Zwitter ion is dipolar, charged but overall electrically neutral and contains both a positive and negative charge.

(3) **Chemical properties :** Amino acids are amphoteric in nature. Depending on the pH of the solution, the amino acid can donate or accept proton.

$$R-CH-C-OH \begin{tabular}{c} & O & & O & \\ & R-CH-C-OH & \begin{tabular}{c} & H & & O & \\ & NH_2 & & & \\ & NH_3 & & \\ & NH_3 & & \\ & PH=0 \\ & (Cation in fairly acidic medium) \\ \hline \\ & & & \\$$

When an ionised form of amino acid is placed in an electric field, it will migrate towards the opposite electrode. Depending on the pH of the medium, following three things may happen

- ullet In acidic solution (low pH), the positive ion moves towards cathode.
  - In basic solution (high pH), the negative ion moves towards anode.
  - The Zwitter ion does not move towards any of the electrodes.

The intermediate pH at which the amino acid shows no tendency to migrate towards any of the electrodes and exists the equilibrium when placed in an electric field is known as **isoelectric point**.

This is characteristic of a given amino acid and depends on the nature of R-linked to  $\alpha$ -carbon atom.

#### (i) Action of heat

(a) For  $\alpha$ -amino acids

(b) For 
$$\beta$$
-amino acids

$$\begin{array}{c|c} CH_2-CH-COOH & \xrightarrow{\text{heat}} CH_2 = CH-COOH \\ \hline |NH_2 & H \\ \hline |NH_2 & H \\ \hline |\beta\text{-Amino propionic acid} \end{array}$$

$$CH_{3} - CH - CH - COOH \xrightarrow{\text{heat}} CH_{3}CH = CHCOOH$$

$$\downarrow NH_{2} H \downarrow \qquad \qquad Crotonic acid$$

$$\downarrow NH_{2} H \downarrow \qquad \qquad Crotonic acid$$

$$\downarrow \beta \text{-Amino butyric acid}$$

(c) For  $\gamma$  and  $\delta$  amino acids

$$CH_2 - CH_2 - CH_2 - CO \xrightarrow{\text{heat}} CH_2 - CH_2 - CH_2 - CO$$

$$NH \ H - H - O$$

$$\gamma$$
-Amino butyric acid 
$$\gamma$$
-Butyrolac tam

$$CH_{2}CH_{2}CH_{2}CH_{2}CO \xrightarrow{\text{heat}} CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CO$$

$$NH \stackrel{\bullet}{\mid} H \xrightarrow{O-H} O-H$$

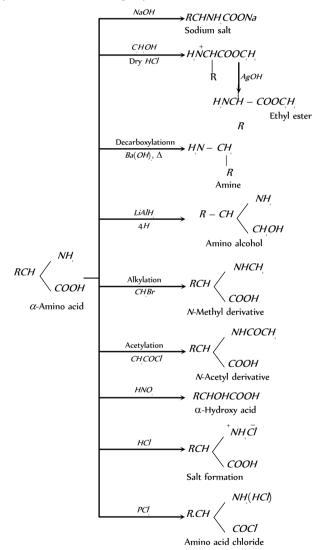
$$\stackrel{\delta \text{ Amino pulsorgoid}}{\longrightarrow} O-H$$

$$\stackrel{\delta \text{ Amino pulsorgoid}}{\longrightarrow} O-H$$

$$\stackrel{\delta \text{ Amino pulsorgoid}}{\longrightarrow} O-H$$

These lactams have stable five or six membered rings.

(ii)  $\alpha$ -amino acids show the reactions of -NH group, -COOH groups and in which both the groups are involved.



- $\square$  Proline is the only natural  $\alpha$ -amino acid which is a secondary amine.
  - $\square$  Only achiral  $\alpha$ -amino acid found in protein is glycine.
- (iii) *Formation of proteins-peptide bond*: Proteins are formed by joining the carboxyl group of one amino acid to the  $\alpha$ -amino group of another amino acid. The bond formed between two amino acids by the elimination of a water molecule is called a peptide linkage or bond. The peptide bond is simply another name for amide bond.

The product formed by linking amino acid molecules through peptide linkages, -CO-NH-, is called a **peptide**. Peptides are further designated as *di, tri, tetra* or *penta* peptides accordingly as they contain two, three, four or five amino acid molecules, same or different, joined together in the following fashions.

$$\begin{array}{c|c}O & H & O \\ \parallel & | & C \\ H_2N - CH - C - OH + H - N - CH - C - OH \xrightarrow{-(H_2O)} \\ R & R\end{array}$$

$$\begin{array}{c|c} O & H & O \\ \parallel & \parallel & \parallel \\ H_2N-CH-C-N-CH-C-OH \\ \stackrel{|}{R} & \begin{array}{c} \text{Peptide linkage } \\ \text{(Dispetide)} \end{array} \end{array}$$

When the number of amino molecules is large, the product is termed polypeptide which may be represented as,

$$H_2N-CH-C-\begin{bmatrix}O\\||\\-NH-CH-C-\\|\\R'\end{bmatrix}-NH-CH-COOH$$

(4) Composition: Composition of a protein varies with source. An approximate composition is as follows:

Carbon 50-53%; hydrogen 6-7%; oxygen 23-25%; nitrogen 16-17%; Sulphur about 1%. Other elements may also be present, *e.g.*, phosphorus (in nucleoproteins), iodine (in thyroid proteins) and iron (in haemoglobin).

(5) **Structure of proteins:** The structure of proteins is very complex. The **primary structure** of a protein refers to the number and sequence of the amino acids in its **polypeptide chains** (discussed in the formation of proteins). The primary structure is represented beginning with the amino acid whose amino group is free (the *N*-terminal end) and it forms the one end of the chain. Free carboxyl group (*C*-terminal end) forms the other end of the chain.

Left hand side 
$$\begin{array}{c|c} O & O & \text{Right hand side} \\ H_2N-CH-C-NH-CH-C-NH... CH-COOH} \\ \text{One end} & R & R' & R'' & \text{Other end} \\ \text{($N$-terminal end)} & (R,R',R'') \dots \text{may be same or different)} & (C\text{-terminal end}) \end{array}$$

Side chains may have basic groups or acidic groups as  $-NH_2$  in lysine and -COOH in aspartic acid. Because of these acidic and basic side chains, there are positively and negatively charged centres. Though the peptide linkage is stable, the reactivity is due to these charged centres in the side chains.

Primary structure tells us nothing about the shape or conformation of the molecule. Most of the bonds in protein molecules being single bonds can assume infinite number of shapes due to free rotation about single bonds. However, it has been confirmed that each protein has only a single three dimensional conformation. The fixed configuration of a polypeptide skeleton is referred to as the **secondary structure** of a protein. It gives information:

- About the manner in which the protein chain is folded and bent;
- About the nature of the bonds which stabilise this structure.

Secondary structure of protein is mainly of two types

(i)  $\alpha$ -helix: This structure is formed when the chain of  $\alpha$ -amino acids coils as a right handed screw (called  $\alpha$ -helix) because of the formation of **hydrogen bonds** between amide groups of the same peptide chain, *i.e.*, *NH* group in one unit is linked to carbonyl oxygen of the third unit by hydrogen bonding. This hydrogen bonding between different units is responsible for holding helix in a position. The side chains of these units project outward from the coiled backbone.

Such proteins are elastic, *i.e.*, they can be stretched. On stretching weak hydrogen bonds break up and the peptide chain acts like a spring. The hydrogen bonds are reformed on releasing the tension. Wool and hair have  $\alpha$ -helix structure.

(ii)  $\beta$ -pleated sheet: A different type of secondary structure is possible when polypeptide chains are arranged side by side. The chains are held together by a very large number of hydrogen bonds between C=O and NH of different chains. Thus, the chains are bonded together forming a sheet. These sheets can slide over each other to form a three dimensional structure called a beta pleated sheet. Silk has a beta pleated structure.

Globular proteins possess tertiary structure. In general globular proteins are very tightly folded into a compact spherical form.

- (6) **Classification of proteins:** According to chemical composition, proteins are divided into two classes
- (i) Simple proteins: Simple proteins are composed of chains of amino acid units only joined by peptide linkages. These proteins on hydrolysis yield only mixture of amino acids. Examples are:

Egg albumin, serum globulins, glutenin in wheat, coryzenin in rice, tissue globulin, etc.

(ii) *Conjugated proteins*: The molecules of conjugated proteins are composed of simple proteins and non protein material. The non-protein material is called **prosthetic group** or **cofactor**. These proteins on hydrolysis yield amino acids and non-protein material. Examples are

Mucin in saliva (prosthetic group, carbohydrate), casein in milk (prosthetic group, phosphoric acid), haemoglobin in blood (prosthetic group, iron pigment), etc.

#### According to molecular shape, proteins are divided into two types

- (i) *Fibrous proteins*: These are made up of polypeptide chains that run parallel to the axis and are held together by strong hydrogen and disulphide bonds. They can be stretched and contracted like a thread. These are usually insoluble in water. Examples are:  $\alpha$ -keratin (hair, wool, silk and nails); myosin (muscles); collagen (tendons, bones), etc.
- (ii) *Globular proteins*: These have more or less spherical shape (compact structure).  $\alpha$ -helics are tightly held up by weak attractive forces of various types: Hydrogen bonding, disulphide bridges, ionic or salt bridges. These are usually soluble in water. Examples are: Insulin, pepsin, haemoglobin, cytochromes, albumins, etc.

Proteins can also be classified on the basis of their function

Table : 31.6

Protein	Function	Examples
Enzymes	Biological catalysts, vital to all living systems.	Trypsin, pepsin.
Structural proteins	Proteins that hold living systems together.	Collagen.
Harmones	Act as messengers.	Insulin.
Transport proteins	Carry ions or molecules from place to another in	Haemoglobin.

	the living system.	
Protective proteins (antibiotics)	Destroy any foreign substance released into the living system.	Gamma globulin.
Toxins	Poisonous in nature.	Snake venom.

#### (7) General and physical characteristic of proteins

- (i) Most of them (except chromoproteins) are colourless, tasteless, and odourless. Many are amorphous but few are crystalline. They are nonvolatile and do not have a sharp melting point .
- (ii) Most of them are insoluble in water and alcohol. But many of them dissolve in salt solutions, dilute acids and alkalies. Some proteins such as keratins (skin, hair and nails) are completely insoluble.
- (iii) Protein molecules are very complex and possess very high molecular masses. They are hydrophilic colloids which cannot pass through vegetable or animal membrane. On addition of sodium chloride, ammonium sulphate magnesium sulphate, etc., some proteins are precipitated. The precipitate can be filtered and redissolved in water.
- (iv) The solution of proteins are optically active. Most of them are laevorotatory. The optical activity is due to the presence of asymmetric carbon atoms in the constituent  $\alpha$ -amino acids.
- (v) *Isoelectric point*: Every protein has a characteristic isoelectric point at which its ionisation is minimum. Like amino acids, proteins, having charged groups ( $\stackrel{+}{NH}_3$  and  $COO^-$ ) at the ends of the peptide chain, are amphoteric in nature. In strong acid solution, protein molecule accepts a proton while in strong basic solution it loses a proton. The *pH* at which the protein molecule has no net charge is called its isoelectric point. This property can be used to separate proteins from mixture by electrophoresis.
- (vi) **Denaturation:** The structure of the natural proteins is responsible for their biological activity. These structures are maintained by various attractive forces between different parts of the polypeptide chains. The breaking of these forces by a physical or a chemical change makes the proteins to lose all or part of their biological activity. This is called denaturation of proteins. The denaturing of proteins can be done by adding chemicals such as acids, bases, organic solvents, heavy metal ions, or urea. It can also be done with the help of heat and ultraviolet light. Denaturation can be irreversible or reversible. In irreversible denaturation, the denaturated protein does not return to its original shape. For example, the heating of white of an egg (water soluble) gives a hard and rubbery insoluble mass.

#### (8) Chemical properties

- (i)  $\it Salt\ formation$ : Due to presence of both  $\it -NH_2$  and  $\it -COOH$  groups in proteins, they form salts with acids and bases. Casein is present in milk as calcium salt.
- (ii) *Hydrolysis*: The simple proteins are hydrolysed by acids, alkalies or enzymes to produce amino acids. Following steps are involved in the hydrolysis and the final product is a mixture of amino acids.

 $\begin{array}{c} {\rm Protein} \to {\rm Proteose} \to {\rm Peptone} \to {\rm Polypeptide} \to {\rm Simple} \ {\rm peptide} \\ \to {\rm Mixture} \ {\rm of} \ {\rm amino} \ {\rm acids} \end{array}$ 

(iii) *Oxidation*: Proteins are oxidised on burning and putrefaction. The products include amines, nitrogen, carbon dioxide and water. The bad smell from decaying dead animals is largely due to the formation of amines by bacterial oxidation of body proteins.

#### (9) Test of proteins

- (i) *Biuret test*: On adding a dilute solution of copper sulphate to alkaline solution of protein, a violet colour is developed. This test is due to the presence of peptide (-CO-NH-) linkage.
- (ii) *Xanthoproteic test*: Some proteins give yellow colour with concentrated nitric acid (formation of yellow stains on fingers while working with nitric acid in laboratory). The formation of yellow colour is due to reaction of nitric acid with benzenoid structures. Thus, when a protein solution is warmed with nitric acid a yellow colour may be developed which turns orange on addition of  $NH_4OH$  solution.
- (iii) *Millon's test*: When millon's reagent (mercurous and mercuric nitrate in nitric acid) is added to a protein solution, a white precipitate which turns brick red on heating, may be formed. This test is given by proteins which yield tyrosine on hydrolysis. This is due to presence of phenolic group.
- (iv) *Ninhydrin test*: This test is given by all proteins. When a protein is boiled with a dilute solution of ninhydrin, a violet colour is produced.
- (v) *Nitroprusside test*: Proteins containing -SH group give this test. When sodium nitroprusside solution is added to proteins having -SH group, a violet colour is developed.

Ninhydrin 
$$O$$
  $OH$ 
 $\begin{vmatrix} & & & & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\$ 

- (vi) *Molisch's test*: This test is given by those proteins which contain carbohydrate residue. On adding a few drops of alcoholic solution of  $\alpha$ -naphthol and concentrated sulphuric acid to the protein solution, a violet ring is formed.
- (vii) *Hopkins-Cole test*: On adding concentrated sulphuric acid down the side containing a solution of protein and glyoxalic acid, a violet colour is developed.

#### (10) **Uses**

- (i) Proteins constitute as essential part of our food. Meat, eggs, fish, cheese provide proteins to human beings.
- (ii) In textile: Casein (a milk protein) is used in the manufacture of artificial wool and silk.
- (iii) *In the manufacture of amino acids*: Amino acids, needed for medicinal use and feeding experiments, are prepared by hydrolysis of proteins.

- (iv) *In industry*: Gelatin (protein) is used in food products, capsules and photographic plates. Glue (protein) is used as adhesive and in sizing paper. Leather is obtained by tanning the proteins of animal hides.
- (v) *In controlling body processes*: Haemoglobin present in blood is responsible for carrying oxygen and carbon dioxide. Harmones (proteins) control various body processes.
- (vi) **As enzymes**: Reactions in living systems always occur with the aid of substances called enzymes. Enzymes are proteins produced by living systems and catalyse specific biological reactions.

Important enzymes tabulated as under,

Table : 31.7

Enzymes	Reaction catalysed
Urease	Urea $\rightarrow CO_{,} + NH_{,}$
Invertase	Sucrose → Glucose + Fructose
Maltase	Maltose → 2 Glucose
Amylase	Starch $\rightarrow n$ Glucose
Pepsin	Proteins $ o$ Amino acids
Trypsin	Proteins $\rightarrow$ Amino acids
Carbonic anhydrase	$H_iCO_i \rightarrow H_iO + CO_i$
Nuclease	DNA, RNA $ ightarrow$ Nucleotides

# **Nucleic acids**

In every living cell there are found nucleo-proteins which are made up of proteins and natural polymers of great biological importance called nucleic acids.

Two types of nucleic acids are found in biological systems, these are Deoxyribonucleic acid (DNA) and Ribonucleic acid (RNA)

The nucleic acid was first isolated by Friedrich Miescher in 1868 from the nuclei of pus cells and was named nuclein. The term nuclein was given by Altman.

- (1) **Composition :** Nucleic acids like proteins and carbohydrates are polymer. The simple units that make up the nucleic acid are called **nucleotides**. Nucleotides are themselves composed of following three simple molecules.
- (i) *Nitrogenous base*: These are heterocyclic organic compound having two or more nitrogen atoms in ring skeleton. These are called bases because the lone pairs of electrons on the nitrogen atoms make them as Lewis bases.

Their structures are given below

(a) Pyrimidine derivatives

(b) Purine derivatives

5-Hydroxy methyl cytosine

DNA, RNA
(ii) Five carbon sugar (Pentose): In RNA, the sugar is ribose where as in DNA, the sugar is deoxyribose.

(iii) **Phosphoric acid, HPO**: Phosphoric acid forms esters to -OH groups of the sugars to bind nucleotide segments together. A molecule called **nucleoside** is formed by condensing a molecules of the base with the appropriate pentose. (*i.e.*, Base + Sugar).

A **nucleotide** results when the nucleoside combined with phosphoric acid mainly at carbon 5' of the pentose. (*i.e.*, Base + Sugar + Phosphoric acid).

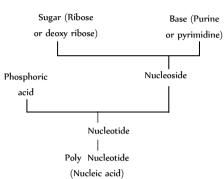
OH

$$HO - P - O - {5' \atop CH} O$$
 $N = N$ 
 $N =$ 

Nucleotide-adenosine 5'-phosphoric acid

This nucleotide is the building block of both DNA and RNA. The nucleic acids are condensation polymers of the nucleotide monomers and are formed by the creation of an ester linkage from phosphoric residue on one nucleotide to the hydroxy group on carbon 3' in the pentose of the second nucleotide. The result is a very long chain possessing upto a billion or so nucleotides units in DNA.

Thus, the formation of a nucleic acid can be summarised in the following general way  $% \left( 1\right) =\left( 1\right) \left( 1\right) \left($ 





(2) **Structure:** The sequence of bases along the DNA and RNA chain establishes its primary structure which controls the specific properties of the nucleic acid. An RNA molecule is usually a single chain of ribosecontaining nucleotides. DNA molecule is a long and highly complex, spirally twisted, double helix, ladder like structure. The two polynucleotide chains or

strands are linked up by hydrogen bonding between the nitrogenous base molecules of their nucleotide monomers. Adenine (purine) always links with thymine (pyrimidine) with the help of two hydrogen bonds and guanine (purine) with cytosine (pyrimidine) with the help of three hydrogen bonds.

Hence, the two strands extend in opposite directions, *i.e.*, are antiparallel and complimentary. The following fundamental relationship exist.

- ☐ Thymine combines only with deoxyribose sugar and uracil only with ribose sugar. Other bases can combine with either of the two sugars.
  - The sum of purines equals the sum of pyrimidines.
  - The molar proportion of adenine equals to that of thymine.
  - The molar proportion of guanine equals to that of cytosine.
- ☐ The double helix is 20 Å. It completes a spiral at every 10 nucleotide pairs at a length of 34 Å. Sequences of monomers (nucleotides) may present innumerable variations. Evidently, innumerable varities of DNA exist in the organism.
- ☐ Watson, Crick and Witkins were awarded Noble prize in 1962 for suggesting the structure of DNA.

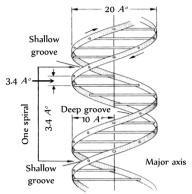


Fig :31.1 Helical structure of DNA as suggested by Watson and Crick

Table : 31.8	Difference	between	DNA	and	RNA
--------------	------------	---------	-----	-----	-----

DNA	RNA
It has a double helix structure.	It has a single helix structure.
Sugar unit is deoxyribose.	Sugar unit is Ribose.
Base units are adenine, guanine, thyamine and cytosine.	It contains uracil base instead of thyamine, other bases being same as those in DNA.
Responsible for inheritance of character.	It is responsible for protein synthesis.

- (3) Functions of nucleic acid : Nucleic acid have two important functions
  - (i) Replication and (ii) Protein synthesis.
- (i) *Replication*: The genetic information for the cell is contained in the sequence of the bases A, T, G and C (adenine, thymine, guanine and cytosine) in the DNA molecule. The sequence of bases in one chain of the double helix controls the sequence in other chain. The two chains fit together like a hand and a glove. They separate and about the hand is formed a new glove, and inside the glove is formed a new hand. Thus, the pattern is preserved in the two new molecules of DNA.
- [If one strand of DNA has the sequence ATGCTTGA, then the sequence of complimentary strand will be TACGAACT].
- (ii) *Synthesis of proteins*: The DNA contains the genetic code and directs protein synthesis through RNA. The double helix of DNA partially uncoils and about the individual strands are formed chains of RNA. The new chains contain ribose instead of deoxyribose and the base sequence is different which is determined by DNA, *i.e.*, opposite each adenine of DNA, there appears on RNA a uracil; opposite guanine, cytosine; opposite thymine, adenine, opposite cytosine, guanine. Thus, AATCAGTT on DNA becomes UUAGUCAA on RNA.

One kind of RNA, called messenger RNA, carries a message to the ribosome, where protein synthesis actually takes place. At the ribosome,

messenger RNA calls up a series of transport RNA molecules, each of which is loaded with a particular amino acid. The order in which the transport RNA molecules are called (–the sequence in which the amino acids are arranged to form the protein chain) depends upon the sequence of bases along the messenger RNA chain. Thus GAU is the code for aspartic acid; UUU, phenyl alanine; GUG, valine. There are 64-three letter code words (codons) and only 20-odd amino acids, so that more than one codon call the same amino acid.

The relation between the nucleotide triplets and the amino acids is called Genetic code. Nirenberg, Hollay and Khorana presented the genetic code for which they were awarded Noble prize in 1968.

(4) **Mutation :** A mutation is a chemical or physical change that alters the sequence of bases in DNA molecule. Anything that causes mutation is called **mutagen**. A mutation results from ultraviolet light, ionisation radiations, chemicals or viruses. The changes in sequence of bases in DNA are repaired by special enzymes in the cell. If it is not, the protein produced has no biological activity and the cell dies.

These mutations often prove harmful and give rise to symptoms that cause diseases. Sickle-cell anaemia is one such example. Such disease is passed on from one generation to the next generation.

## Lipids

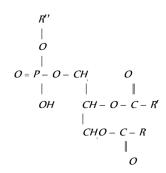
Lipids are constituents of plants and tissues which are insoluble in water but soluble in organic solvents such as chloroform, carbon tetrachloride, ether or benzene. They include a large variety of compounds of varying structures such as oils and fats; phospholipids, steroids, etc. Lipids are mainly made of carbon, hydrogen and oxygen. The number of oxygen atoms in a lipid molecule is always small as compared to the number of carbon atoms. Sometimes small amounts of phosphorus, nitrogen and sulphur are also present. They have a major portion of their structure like a hydrocarbon (aliphatic or fused carbon rings). Lipids serve as energy reserve for use in metabolism and as a major structural material in cell membranes for regulating the activities of cell and tissues.

Simple lipids are esters of glycerol with long chain monocarboxylic acids which can be saturated or unsaturated. These are generally called glycerides of fats and oils. Waxes are esters of fatty acids with certain alcohols, not glycerol. Fats and oils have biological importance but waxes have no value as these are not digested.

The functions of triglycerides are the following

- (1) They are energy reserves in the cells and tissues of living system. When digested, triglycerides are hydrolysed to fatty acids and glycerol.
- (2) Catabolism of fatty acids form acetyl-coenzyme-A. Most of the energy of fatty acids is converted into ATP.
- (3) Acetyl coenzyme is the starting material for the synthesis of many compounds.
- (4) Fats deposited beneath the skin and around the internal organs minimize loss of body heat and also act as cushions to absorb mechanical impacts.

Another very important class of lipids are the phospholipids. These are polar lipids and like the fats, are esters of glycerol. In this case, however, only two fatty acid molecules are esterified to glycerol, at the first and second carbon atom. The remaining end position of the glycerol is esterified to a molecule of phosphoric acid, which in turn is also esterified to another alcohol. This gives a general structure.



The alcoholic compound linked to phosphoric group may be choline, ethanol, amine, serine or inositol. The phosphate groups forms a polar end, *i.e.*, hydrophilic (water-attracting) and the two fatty acid chains constitute the non-polar tail, *i.e.*, hydrophobic (water repelling). This structure gives the phospholipids good emulsifying and membrane forming properties.

Cell membranes are composed of phopholipids and proteins in about equal, proportion. The phospholipids in the membrane appear to be arranged in a double layer or bilayer in which the non-polar tails face each other, thereby exposing the polar heads to the aqueous environment on either side of the membrane. Proteins found in the membrane are embedded in the mossaic formed by the lipids. Phospholipids facilitate the transport of ions and molecules in and out of the cell and regulate the concentration of molecules and ions within the cell. They provide structural support for certain proteins.

The above mentioned lipids are mainly straight chain compounds. There is a third class of lipids which are not straight chain compounds. They are called **Sterols**. The sterols are composed of fused hydrocarbon rings and a long hydrocarbon side chain. Cholestrol is most important compound of this class and is found in animals only. It exists either free or as ester with a fatty acid. Cholestrol is also the precursor of hormones. Cholestrol and its esters are insoluble in water. So they are deposited in the arteries and veins if the blood cholestrol rises. This leads to high blood pressure and heart diseases. Cholestrol is a part of animal cell membrane and is used to synthesized steroid hormones, vitamin-*D* and bile salts.

# **Energy cycle or metabolism**

A cell has small molecules (micromolecules) as well as large molecules (macromolecules). The chemical reactions of a living organism can be divided into main two types

- (1) The chemical reactions by which the large molecules are constantly broken down into smaller ones are called **catabolism**.
- (2) The chemical reactions by which the macromolecules are synthesised within the cell are called **anabolism**.

The two processes *i.e.*, degradation and synthesis are collectively called **metabolism**. Catabolism reactions are usually accompanied by *release of energy* whereas anabolism reactions require energy to occur.

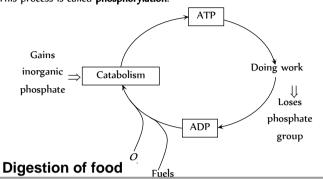
The primary energy found in living cells is chemical energy, which can be easily stored, transferred and transformed. For this, the living cells contain a chemical compound called **adenosine triphosphate** (ATP). It is regarded as **energy currency** of living cells because it can trap, store and release small packets of energy with ease.

ATP consists of a purine base called **adenine** linked to a five carbon sugar named **ribose** which is further attached to **three molecules of phosphate**.

ATP is energy rich molecule this is because of the presence of four negatively charged oxygen atom very close to each other. These four negatively charged *o*-atoms experience very high repulsive energy.

ATP  $\xrightarrow{\text{Hydrolysis}}$   $\xrightarrow{\text{Adenosine}}$   $\xrightarrow{\text{diphosphat e}}$  + Pi  $\Delta H = -30.93$  kJ mol  $\Delta DP$   $\xrightarrow{\text{Hydrolysis}}$   $\xrightarrow{\text{Adenosine}}$   $\xrightarrow{\text{Adenosine}}$  + 2Pi  $\Delta H = -28.4$  kJ mol  $\Delta DP$   $\Delta DP$   $\Delta H = -28.4$  kJ mol  $\Delta DP$   $\Delta DP$ 

ADP can change to ATP in the presence of inoraganic phosphate. This process is called **phosphorylation**.



Digestion is the process by which complex constituents of food are broken down into simple molecules by a number of enzymes in mouth, stomach and small intestine. The simple molecules thus formed are absorbed into blood stream and reach various organs.

Raw food may be taken as such or after cooking. It is chewed in the mouth and swallowed when it passes through a long passage in the body called alimentary canal. During this passage it gets mixed with various enzymes in different parts of the alimentary canal. The carbohydrates, proteins and fats are converted into simpler forms which are then carried by blood to different parts of the body for utilization. Digestion of food can be summarized in the following form

(1) Polysaccharide 
$$\xrightarrow{\text{Amylase}}$$
 Disaccharides  $\xrightarrow{\text{Pancreatic juice}}$  Disaccharides

Disaccharides (maltose, etc.) — Maltase Glucose (Intestine)

(2) Proteins 
$$\xrightarrow{\text{Pepsin}/HCl}$$
 Proteases and Peptones  $\xrightarrow{\text{Chemotryps in Pancreatic juice}}$  (Intestine)

Peptides — Peptidases — Amino acids (Intestine)

(3) Fats 
$$\xrightarrow{\text{Bilesalts}}$$
 Emulsified fat  $\xrightarrow{\text{Lipases}}$  Fatty acids  $\xrightarrow{\text{(From liver)}}$  Emulsified fat  $\xrightarrow{\text{Pancreatic and (intestine juice)}}$  + Glycerol

After digestion, there are present glucose, aminoacids, fatty acids along with vitamins and mineral salts. Undigested food and secretions are pushed forward into the rectum from where these are excreted.

#### **Vitamins**

In addition to air, water, carbohydrates, proteins, fats and mineral salts, certain organic substances required for regulating some of the body processes and preventing certain diseases are called **vitamins**. These compounds cannot be synthesised by an organism. On the basis of solubility, the vitamins are divided into two groups.

- (1) Fat soluble; Vitamin A, D, E and K.
- (2) Water soluble; Vitamin B and C.

Name	HO S	оулсея	Functions		Effects of defficiency
Water soluble vitamins					
Vitamin B	Rice polishings,	wheat flour, oat meal,	Major component of	of co-enzyme co-	Beri-beri, loss of appetite and vigour,
(Thiamine or Aneurin)	eggs, yeast, meat	t, liver, etc.	carboxylase re	equired for	constipation, weak heart beat, muscle
(CHNSOCĪ)			carbohydrate and	l amino acid	atrophy, even paralysis.

		metabolism.	
Vitamin B or G (Riboflavin or Lactoflavin) (C,H,N,O)	Cheese, eggs, yeast, tomatoes, green vegetables, liver, meat, cereals, etc.	Combines with phosphoric acid to form coenzyme FAD essential for oxidative metabolism.	Cheilosis, digestive disorders, burning sensations in skin and eyes, headache, mental depession, scaly dermatitis at angles of nares, corneal opacity, etc.
Vitamin B, (Pantothenic acid) (CHON)	All food; more in yeast, liver, kidneys, eggs, meat, milk, sugarcane, groundnut, tomatoes.	Important component of Co-A required for oxidative metabolism.	<b>Dermatitis</b> , in cocks; greying of hairs, retarded body and mental growth, reproductive debility.
Vitamin B or P-P (Nicotinic acid or Niacin) CHNO (CHN-COOH)	Fresh meat, liver, fish, cereals, milk, pulses, yeast, etc.	Active group in coenzyme NAD required for oxidative metabolism.	<b>Pellagra,</b> dermatitis, diarrhoea, demenia, muscle atrophy, inflammation of mucous membrane of gut.
Vitamin B. (Pyridoxine or Adermin) (CHON)	Milk, cereals, fish, meat, liver, yeast synthesised by intestinal bacteria.	Important coenzyme required in protein and amino acid metabolism.	<b>Dermatitis, anaemia,</b> convulsions, nausea, insomnia, vomiting, mental disorders, depressed appetite.
Vitamin H (Biotin) (CHNOS)	Yeast, vegetables, fruits, wheat, chocolate, eggs, groundnut synthesised by intestinal bacteria.	Essential for fat synthesis and energy production.	<b>Skin lesions</b> , loss of appetite, weakness, hairfall, paralysis.
Folic acid group	Green vegetables, soyabean, yeast, kidneys, liver, synthesised by intestinal bacteria.	Essential for synthesis of DNA and maturation of blood corpuscles.	Retarded growth, anaemia.
Vitamin B (Cyanocobalamine) (CyH_ONPCo)	Meat, fish, liver, eggs, milk synthesised by intestinal bacteria.	Required for chromosome duplication and formation of blood corpuscles.	Retarded growth, <b>pernicious anaemia</b>
Vitamin <i>C</i> (Ascorbic acid) ( <i>C</i> , <i>H</i> , <i>O</i> )	Lemon, orange and other citrus fruits, tomatoes, green vegetables, potatoes, carrots, pepper, etc.	Essential for formation of collagen, cartilage, bone, teeth, connective tissue and RBCs and for iron metabolism.	Wound-healing and growth retarded, scurvy, breakdown of immune defence system, spongy and bleeding gums, fragile blood vessels and bones, exhaustion, nervous breakdown, high fever.
Fat soluble vitamins Vitamin A (Retinol or Axerophthol) (C_H_O)	Synthesised in cells of liver and intestinal mucous membrane from carotenoid pigments found in milk, butter, kidneys, egg yolk, liver, fish oil, etc.	Essential for synthesis of visual pigments; growth and division of epithelial cells.	Xerophthalmia-keratini-zed conjunctive and opaque and soft cornea. Stratification and keratinization in epithelia of skin, respiratory passages, urinary bladder, ureters and intestinal mucosa, night-blindness, impaired growth, glandular secretion and reproduction.
Vitamin <i>D</i> (Ergocalciferol), (Sun shine vitamin) <i>C_H_O</i> and cholecalciferol	Synthesised in skin cells in sunlight from 7-dehydro-cholesterol also found in butter, liver, kidneys, egg yolk, fish oil, etc.	Regulates absorption of calcium and phosphorus in intestine, mineral deposition in bones and teeth.	<b>Rickets</b> with osteomalacia; soft and fragile teeth.
Vitamin $E$ group Tocopherols $(\alpha, \beta, \gamma)$ $(C_nG_pO_p)$	Green vegetables, oil, egg yolk, wheat, animal tissues.	Essential for proper spermatogenesis, pregnancy, lactation and muscular function.	<b>Sterility</b> (impotency) and muscular atrophy.
Vitamin $K$ (Phylloquinone) $(C_{\mathcal{H}}O)$	Carrots, lettuce, cabbage, tomatoes, liver, egg yolk, cheese; synthesized by colon bacteria.	Essential for synthesis of prothrombin in liver, which is required for blood clotting.	<b>Haemorrhages,</b> excessive bleeding in injury, poor coagulation of blood.

# **IMP POINTS**

- **E** Monosaccharides which differ in configuration at C and C in aldoses in ketoses are called **anomers**. Thus  $\alpha$ -D glucose and  $\beta$ -D glucose are anomers and so are  $\alpha$ -D fructose and  $\beta$ -D fructose.
- Monosaccharides which differ in configuration at a carbon atom other than the anomeric carbon are called epimers. Thus glucose and mannose which differ in configuration at C are called C epimers while glucose and galactose which differ in configuration at C are called C epimers.

- $\not$  In amino acids –COO group acts as the base while  $\stackrel{\scriptscriptstyle \top}{NH}_3$  acts as the acid.
- $\mathcal{L}$  Insulin is a protein harmone. It consists of 51 amino acids arranged in two polypeptide chains containing 21 and 30  $\alpha$  amino acids residues respectively. The two peptide chains are held together by two cystine disulphide cross links.
- 🗷 Certain enzymes are associated with coenzymes mostly derived from vitamins for their biological activity.
- Estable Each segment of a DNA molecule that codes for a specific protein or a polypeptide is called gene and the relationship between the nucleotide triplet and the amino acids is called the genetic code.
- M Phospholipids are major constituents of cell walls.
- ★ The deficiency of essential amino acids causes the disease called kwashiorkor.

- Lecithin (present in eggs) and cephalins are phospholipids in which two of the hydroxyl groups of glycerol are esterified with palmitic acid whereas the third OH group in lecithin is esterified with chlone (CH)N CHCHOH while in cephalin it is esterified with ethanolamine,
- $NH_3CH_2CH_2OH$ .
- Adenosine (ribose + adenine) is a nucleoside while adenosine monophosphate (AMP), adenosine diphosphate and adenosine triphosphate (ATP) are all nucleotides.
- A Haemoglobin is a globular protein and the red colour of haemoglobin is due to the iron protoporphyrin complex called the heme.
- ₤ The bicarbonate/carbonic acid system i.e., HCO/HCO acts as the buffer and maintains the pH of blood between 7.36-7.42.
- ☑ Vitamin C is a derivative of monosaccharide i.e., glucose while Vitamin D is derivative of steroid i.e. ergosterol.
- Vitamin K and Vitamin A contain isoprene units.
- A Of all the vitamins, Vitamin B<sub>i</sub> does not occur in plants but occurs only in animals and micro organisms. In fact, it is exclusively synthesized by the micro organisms and is conserved in the liver. Vitamin B<sub>i</sub> has been found in rain water where its presence is attributed to micro organisms sucked up by the winds.