Plant Biochemistry

Photosynthesis:

Definition: Utilization of solar energy by plant cells for the biosynthesis of cell components.

- The overall process of photosynthesis involve the absorption and retention of light energy, its conversion into chemical energy, and the storage of this chemical energy in the final products of photosynthesis.

- The flow of carbon through the biosphere begins with photosynthesis.

- Organisms capable of photosynthesis produce carbohydrate, molecular oxygen from CO_2, H_2O, ATP and NADPH.

- The net reaction of photosynthesis:

$$6CO_2 + 6H_2O \xrightarrow[\text{synthesis}]{\text{photo-}} [CH_2O]_6 + 6O_2$$

The 1st is the capture of light energy by light absorbing pigments and its conversion into the chemical energy of ATP and certain reducing agents particularly NADPH. (as seen below).

$$H_2O + NADP^+ + Pi + ADP \xrightarrow{\text{light}} \text{oxygen} + NADPH + H^+ + ATP$$

IN the 2nd phase of photosynthesis the energy rich products of the 1st phase NADPH, ATP are used on the sources of energy to bring about the reduction of CO_2 to yield glucose (as seen below).

$$CO_2 + NADPH + H^+ + ATP \longrightarrow \text{glucose} + NADP^+ + ADP + Pi$$

Photosynthesis requires the interaction of two light reactions, both of them can be driven by light of wave length less than 680 nm but only one of them light of longer wave length.

Photosynthesis has two phases, the light phase [or light reactions] which are directly dependent on light energy, and the dark reactions/phase which can occur in the absence of light. However, the term dark reactions should not be taken to mean that it takes place only in the dark or at night, in living plants they take place together with the light reactions, in the day time.

Photosynthetic Organisms:

- The capacity to carry out photosynthesis is found in a wide range of organisms in both the pk and Ek domains.

    Ek: higher green plants, multicellular green, brown, and red algae.

    pK: blue green algae, sulfar bacteria, purple bacteria.

Chlorophylls:

Higher plants contain two forms of chlorophyll, designated chloropyll a and chlorophyll b.

- Chlorophyll a, a substituted tetrapyrrole, the four nitrogen atoms of the pyralies are coordinated to a Mg atom to form an extremely stable essentially planar complex.

- Chlorophyll b differs from chlorophyll a in having a formyl gr in place of a methyl group on one of its pyrroles.

- Another distinctive feature of chlorophyll is the presence of phythol, a highly hydrophobic 20-carbon alcohol, esterified to an acid sick chan.

- The chlorophylls are very effective photo receptors because they contain networks of alternating single and double bonds. Such compounds are called polyenes.

- The absorption spectra of chlorophylls `a' and 1b' are different, light that is not appreciably absorbed by chlorophyll a at certain wave length (460 nm for example) is chlorophyll b.

When light strikes the chlorophyll molecule, one of the electrons in it is raised to a higher energy level and is said to be in an "exited state", the chlorophyll molecules are arranged in such away that the exited electrons don't immediately return to their ground but are transferred to other molecules resulting in an increase in the free energy or the chemical potential, of the acceptor molecule. Thus, the light energy is converted into chemical energy. The electron `hole' left in the chlorophyll molecule is replaced by an electron donated by water; in this process the water is oxidized and molecular oxygen given off. Chlorophyll, is an intermediate in the pathway of electrons from a low energy level in water to a high energy level in the final electron acceptor.

Light reactions of photosynthesis depends on the interplay of two photosystems. Photosystem I, which can be exited by light of wave length shorter than 700 n.m. generates a strong reductant that leads to the formation of O_2.

<u>Photosystem II:</u>

A transmembrane assembly of more than 10 polypeptide chains [>600 kd], catalyzes the light-driven transfer of electrons from water to plastoquinone.

It consists of a light-harvesting complex, a core with a reaction center and an oxygen evolving complex.

The light harvesting complex [Ohc II] contains some 200 molecules of chlorophyll a and chlorophyll b bound to several polypeptide chains. The core contains and additional 50 molecules of bound chlorophylla.

LHC II 200 chr. a and b attached to proteins

Core 50 ch. a. b.

Water splitting E. No. 99-405

(2) Mn^{++} at catlysis

Photosystem II Photosystem I

2 $NADP^+$

Sun light Antena chlo. O_2 Ferrodoxin

H_2O 2 NADPH Fe-S-

680-I pigment A2

p680 Ao

e- e-

Bound pheophytin Ao

p700

Plastoquinone-QA e-

QB plastoquine-e- LHC1

Plastocyanin (Pc e-)

Cyt bf.

Electrons are extracted from water by intermediate called "Z", water are splitted by the water splitting enzymes a constituent of photosystem II, contains a cluster of four managanese ions at catalytic cetner.

Electronic excitation energy is funneled from antenna chlorophylls to a reaction center chlorophyll called p680 I Pigment 680 wavelength]. This pigmant become exited p680 and an electron is transferred from p680 to bound pheophytin, the electron flow from reduced pheophytin to a plastoquinone bound to a protein site called Q_A, and finally to a second plastoquinone on site Q_B.

AT THIS POINT THE ENERGY OF TWO PHOTONS HAS BEEN SAFELY STORED IN THE REDUCING POTENTIAL OF QH_2 reduced plastoquinone.

Cytochrome of Complex

- Electrons flow through this complex from photosystem II to photosystem I.
- Cytochrome bf catalyzes the transfer of electrons across the thylakoid membrane to plastocyanine 9pc].
- It is a transmembrane protein complex.
- After electrons are pumped through bf complex to pc, pc becomes reduced.

Photosystem I:

- A transmembrane complex consisting of at least 13 polypeptide chains (> 800 kd).
- Light is funneled from an accessory antenna protein [LHC I] containing 70 chlorophyll a and chlorophyll b molecules and a core antenna with 130 chlorophyll a molecules to p700, the reaction center.
- An electron is transferred from p700*, the excited state of the reaction-center chlorophyll, to an acceptor chlorophyll called Ao to form A-o.
- The very high-potential electron of A-o is transferred to A and then to a series of iron-sulfar centers within photosystem I.
- The final step is the reduction of ferrodoxin. This reaction occurs on the stromal side of the thylakoid membrane.
- The high-potential electrons of two molecules of ferrodoxin are then transferred to $NADP^+$ to form NADPH. This reaction is catalyzed by ferrodoxin – $NADP^+$ reductase.

Two molecules of reduced ferredoxin 2 electrons to one $NADP^+$

THE NET REACTION carried out by photosystem II, cyt. bf and photosystem I is:

$$2H_2O + 2NADP+ \xrightarrow{\text{light}} O_2 + 2\ NADPH + 2H^+$$

CYCLIC ELECTRON Flow: "Cyclic phosphorelation"

- An alternative pathway for electrons arising from p700, the reaction center of photosystem.
- Electrons passed from p700 – don't pass to $NADP^+$
- The high potential electron in ferrodoxin can be transferred to the cyt. bf complex rather than to $NADP^+$.
- This electron flows back to the oxidized form of p700 through plastocyanin to Fd. Thus, immumination of photosystem I can cause e- to cycle continuously out of the reaction center of photosystem I and back to it, each e- being propelled around the cycle by the energy yielded by absorption of one photon.
- This cyclic flow of electrons leads solely to proton pumping by the cytochrome bf complex.
- The proton gradient then drives the synthesis of ATP.
- ATP synthase of chloroplasts [CF1-Cfo complex] catalyzes the formation of ATP from ADP and Pi.

- About 3 protons flow through CF1-Cfo complex per ATP synthesized.

- The newly synthesized ATP is released into the stromal space.

- NADPH formed by photosystem I is released into the stromal space.
  Thus, ATP and NADPH, the products of light reactions of photosynthesis, are appropriately positioned for the subsequent dark reactions, in which CO_2 is converted to carbohydrate.

- Cyclic electron flow involves only photosystems.

- The overall reaction equation for cyclic electron flow and photophosphorelation is simply:

$$ADP + Pi \xrightarrow{light} ATP + H_2O$$

- There is no NADPH or O2 evolution.

- Cyclic flow and photophosphorelation are believed to occur when the plant cell is already amply supplied with reducing power in the form of NADPH but requires additional ATP other metabolic needs.

- By regulating the partitioning of electrons between $NADP^+$ reduction and cyclic photophosphorelation, a plant adjust the ratio of NADPH and ATP produced in the light reaction to match its needs.

- Electron transferring molecules in the connecting chain between photosystem I and are oriented assymetrically in the thylakoid membrane, so that photo induced electron flow results in the net movement of protons across the membrane, from the outside of the thylakoid membrane to the inner component.

Figure

DARK REACTIONS

- Photosynthetic carbohydrate synthesis: Plants and photosyntheatic organisms can make carbohydrates from CO_2 and water. They synthesize glu, sucrose and other carbohydrates by reducing CO_2 at the expense of energy furnished by the ATP and NADPH generated in the light phase of photosynthesis.

- Green plants contain their chloroplasts unique enzymatic machinery to catalyze the conversion of CO_2 $\longrightarrow$ simple reduced organic compounds, [a process called CO_2 fixation]. Plants convert there simple products of photosynthesis into more complex biomolecules including sugars, polysaccharides and metabolites derived from them.

CALVIN CYCLE

CARBON DIOXIDE FIXATION OCCURS IN 3 STAGES:

1. Condensation with a five carbon acceptor ribuloase-1,5 bisphosphate to form 2 molecules of 3-phosphoglycerate.

2. The 3-phosphoglycerate is reduced to glyceraldehyde-3-phosphte [6-molecules].

3. One molecule of this triose phosphate [gly-3-O] can either be used for energy production via glycolysis and citric a cycle, or condensed to hexose hosphate to be used in the synthesis of starch or sucrose.

In the 3rd stage 5 of the 6 molecules of gly-3 (p) are used to regenerate 3 molecules of ribulose-1,5-bisphosphate.

- Regeneration of ribulose 1,5 biphosphate; involves rearrangement of carbon skeleton of glyceraldehyde-3-phosphate and dihydroxyacetone phosphate produced in the first two stages of carbon fixation. The intermediates in the pathway include 3, 4, 5, 6, 7 carbon sugars.

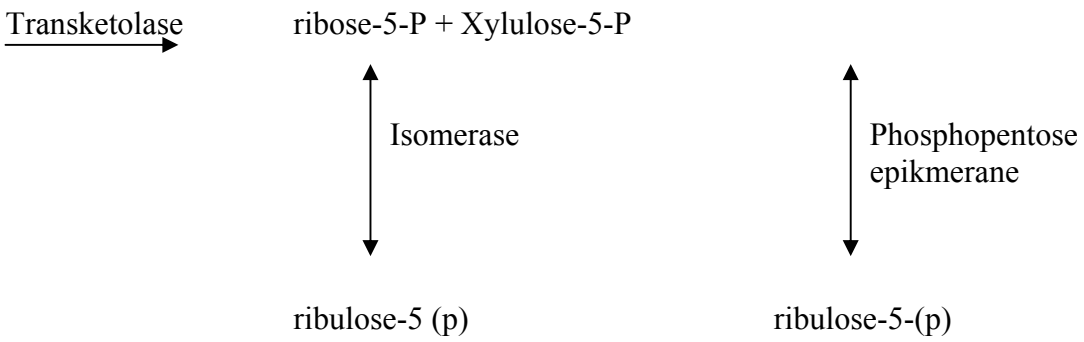
- Glyceraldehyde-3-p + Fructose – 6 – P $\xleftrightarrow{\text{transketolase}}$

  Xylose-5-p + Erythrose – 4- p

- Erythrose – 4 – p – dihydroxyaceton phosphazte aldose

  Sedoheptulose 1,7 biphosphate
  ↓ Sedoheptulose-1,7,biphosphatase
  Sedoheptulose 7- (p)

- Sedoheptulose-7-phosphate + glyceraldehyde-3-p



Calvin Cycle:

$3\ CO_2 + H_2O$

Ribulose 1,5 bi phosphate carboxylase

3 (Ribulose-1,5,bisphosphate — 6 (3-phosphoglycerate)

3 ADP — 6 ATP

ribulose-5-(p) kinane — 3 phosphoglycerate kinane

3 ATP — 6 (1,3-biphosphoglycerate)

3 (Ribulose-5-phosphate

6 $NADPH+6H^+$

- transketolase
- aklolase
- transketose

2 Pi

glyceraldehyde-3-phosphate dehydrogenase

6 NADP

6 Pi

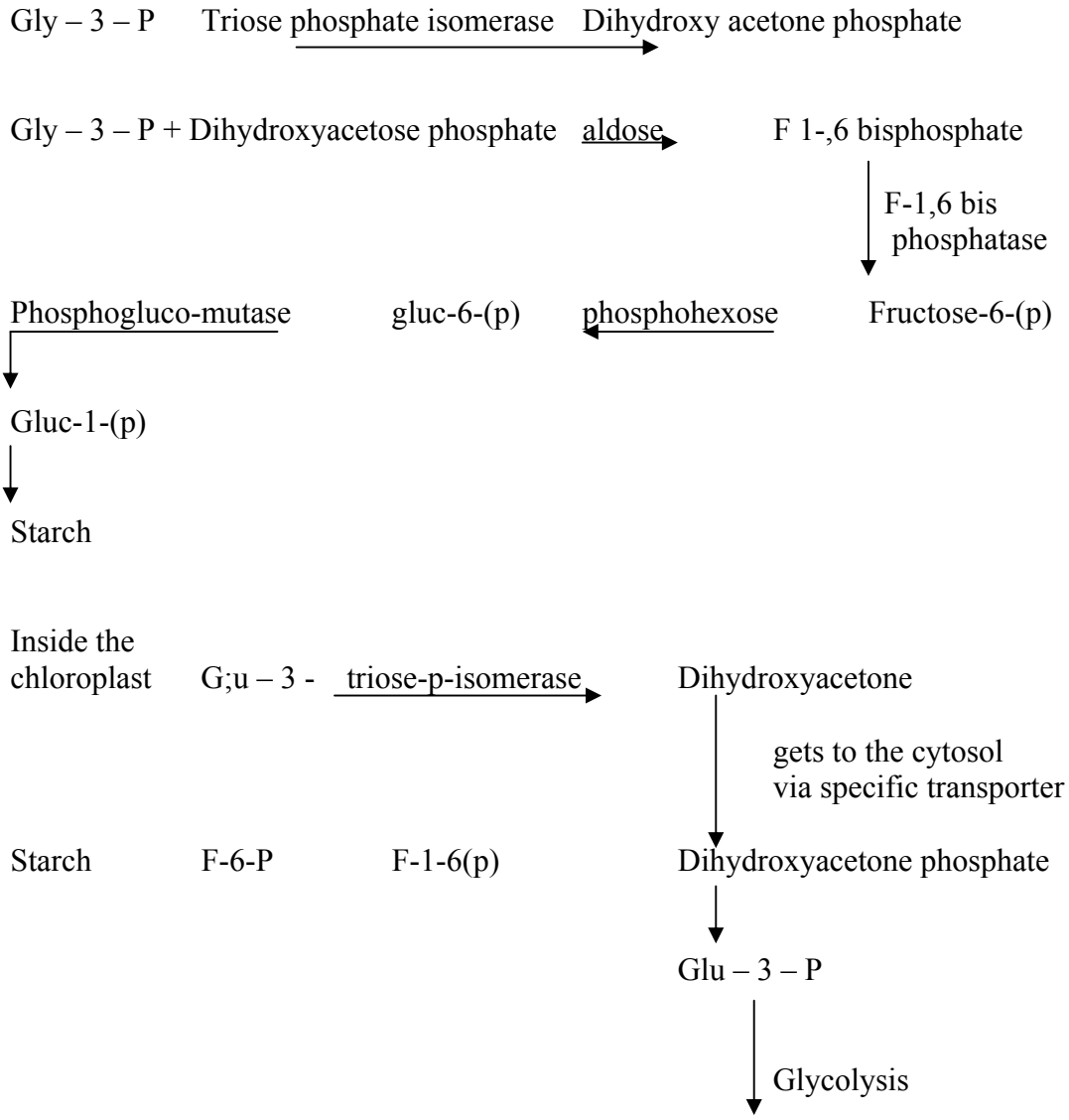
5 (Glyceradehyde-3-phosphate) — 6(Glyceraldehyde-3-phosphate)

1 (Glyceraldehyde-3-phosphate)

- Within the chloroplast stroma are all the enzymes necessary to convert the triose phosphate produces by CO^2 fixation [gly-3-p and dihydroxy acetone phosphate] in to starch, which is stored in the chloroplast as insoluble granules. Alddane condenses the trioses to fructokse-1-6-Bis phosphate, Fruc-1,6-bis (p) produces Fructose-6-P, phosphohexose isomerase yields glucose-6-phosphate, and

phosphoglycomutase produces glucose-1-phosphate, the starting material for starch synthesis.

Inside the chloroplast:



Activation of some enzymes of Calvin Cycle:

Some enzymes of the Calvin Cycle are indirectly activated by light.

Illumination of chlorophyll, leads to the transport of protons across the thylakoid membrane, makes the stromal compartment alkaline an is accompanied by a flow of Mg^{2+} out of the thylakoid compartment into the stroma. Some ensymes present in the stroma e.g. ribulose-1,5-bisphosphate carboxylation [Rubisco], is activated by alkaline pH and Mg^{2+}.

Fructose-1,6-bisphophatase requires Mg^{2+} and very dependent upon pH.

Ribulose-5-(p) kinase, Fruc-1,6-bisphosphatase, sedoheptulose-1,7-bisphosphatase can exist in either of two forms, differing in the oxidation state of Cys residues essential to their catalytic activity when there Cys residues are oxidized as disulfide bonds, the enzymes are inactive. This is the normal situation in the dark. With illumination, electrons flow from photosystem I to ferrodoxin, which passes electrons to a small, soluble, disulfide-containing protein called thioredoxin, thioredoxin donates electrons for the reduction of the disulfide bridges of these light activated enzymes and is then reactivated in a disulfide-exchange reaction catalyzed by thioredoxin reductase.

The balanced equation for the net reaction of the Calvin cycle is:

$6CO_2 + 18\ ATP + 12\ NADPH + 12\ H_2O \longrightarrow C_6H_{12}O_6 + 18\ ADP + 18\ Pi +$

$12\ NADP+ + 6H+$

Thus 3 molecules of ATP and two of NADPH are consumed in converting CO_2 into a hexose such as glucose or fructose.

Photorespiration

The C_4 PATH Way. [C_4 plants prevent photorespiration]

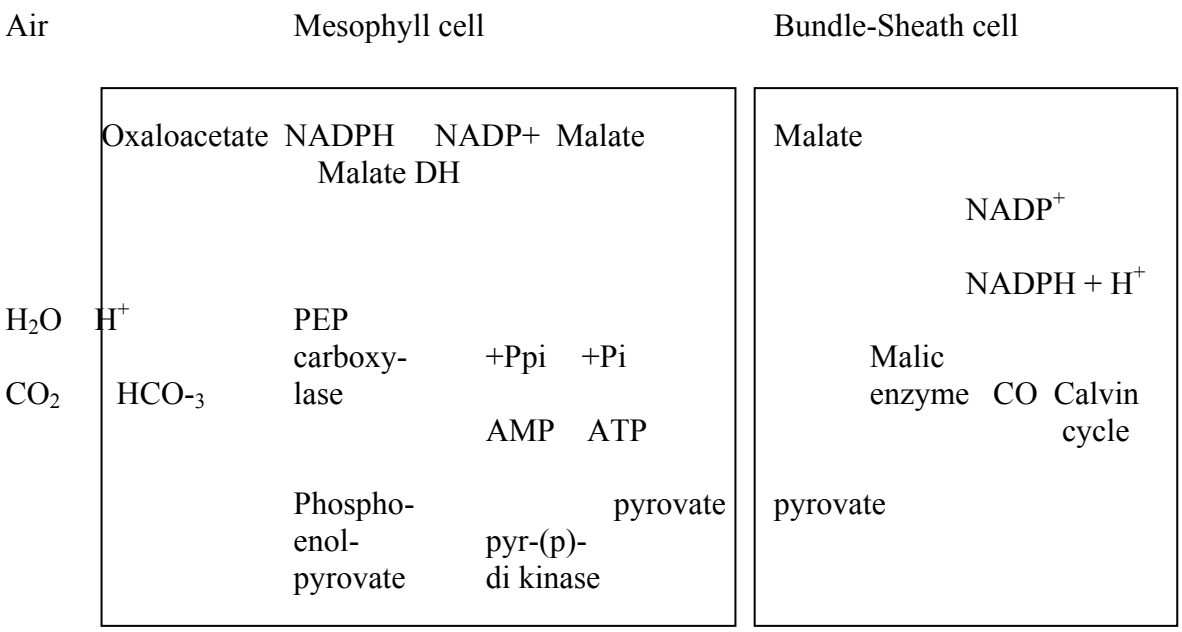
The enzyme [rubisco] has an oxygenase activity, which increases more rapidly with temperature than does. Its carboxylase activity. Tropical plants avoid very high rates of wasteful photorespiration by achieving a high local conc. of CO_2 at the site of Calvin cycle in their photosynthetic cells. The C_4 path way is used to transport CO_2. The oxygenase activity converts Ribulose 1,5 bis(p) to phosphoglycolate and 3-phosphoglycerate, its carried out at one same active site of the carboxylation so both reactions compete with each other. However, under normal conditions the rate of the carboxylase activity is 4 times higher than the oxygenase activity.

Photorespiration

[Rubiso] ribulose-1,5-bisphosphate carboxylase, is not specific for CO_2 as a substrate, O_2 competes with CO_2 at the active site, and rubisco catalyzes the condensation of O2 with ribulose-1,5-bisphosphate to form one molecule of 3-phosphoglycerate and one of phosphoglycolate. This is the 1^{st} step in photorespiration in which 2 molecules of phosphoglycerate is converted to one molecule of serine. [which has 3 carbons] and a molecule of CO_2.

This consumes O_2, and unlike mitochondrial respiration. It doesn't conserve energy.

C_4 pathway starts in the mesophyll cell to transport CO_2 via C_4 compounds to Bundle-Sheath cell.



When the C4 pathway and Calvin cycle operate together, then the next reaction is:

$$6CO_2 + 30\ ATP + 12\ NADPH + 12\ H_2O \longrightarrow C_6H_{12}O_6 + 30\ ADP + 30\ Pi +$$

$$12\ NADP+ + 18\ H+$$

e.g. for C_4 plants corn, sugar can,

C_4 plants which grow in high light intensity and temp, have several important characteristics: high photosynthetic rate, high growth rates, low photorespiration rate, low rates of water loss, and an unusual leaf structure.

Plant Respiration

- Cellular respiration refers to the molecular processes involved in O_2 consumption and CO_2 formation by cells.

- It occurs in 3 major stages, in the 1st stage: organic fuel molecules – glucose, F.A, and some a.a. are oxidized to yield two-carbon fragments in the form of acetyl CoA.

- In the 2nd stage, the acetyl CoA is fed into TCA cycle, which enzymatically oxidizes them to CO_2, the energy released by oxidation is conserved in the reduced electron carriers NADH and $FADH_2$.

- In the 3rd stage of respiration, these reduced cofactors are themselves oxidized, giving up proton (H^+) and electrons. The e- are transferred along a chain of e-carrying molecules, known as the respiratory chain to O_2, which they reduce to form H_2O. During this process energy is formed as ATP, in the process called oxidative phosphorelation.

- Oxidative phosphorelation occurs equally well in light or darkness.

- It occurs at the mitochondira.

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Oxidative Phorphorylation

- The NADH and $FADH_2$ formed in glycolysis. FA oxidation and TCA cycle are energy rich molecules because each contains a pair of e- having a high transfer potential. When these e- are donated to molecular oxygen a large amount of free energy is liberated, which can be used to generate ATP.

- Oxidative phosphorelation is the process in which ATP is formed as electrons are transferred from NADH or $FADH_2$ to O_2 by a series of electron carriers.

- Oxidation of NADH yields 3 ATP. Oxidation of $FADH_2$ yields 2 ATP.

- Respiratory assemblies contain numerous e- carriers, such as cytochromes. The step-by-step transfer of electrons from NADH or $FADH_2$ to O_2 through those carriers leads to the pumping of protons out of the mitochondrial matrix, ATP is synthesized when protons flow back to the mitochondrial matrix through an enzyme complex. Thus, oxidation and phosphorelation are coupled by a proton gradient across the inner mitochondrial membrane.

- The mitochondrial respiratory chain consists of a series of e- carriers.

- Most of these carriers are integral membrane proteins, with prosthetic groups capable of accepting or donating either one or two e-.

- Each componant of the chain can accept e- from the preceding carrier and transfer them to the following one, in a specific sequence.

- In the respiratory chain, there are 3 types of e- transfer systems:

  1. Direct transfer of e- as in the reduction of Fe^{3+} - Fe^{2+}.

  2. Transfer as a hydrogen atom [H^+ + e-]

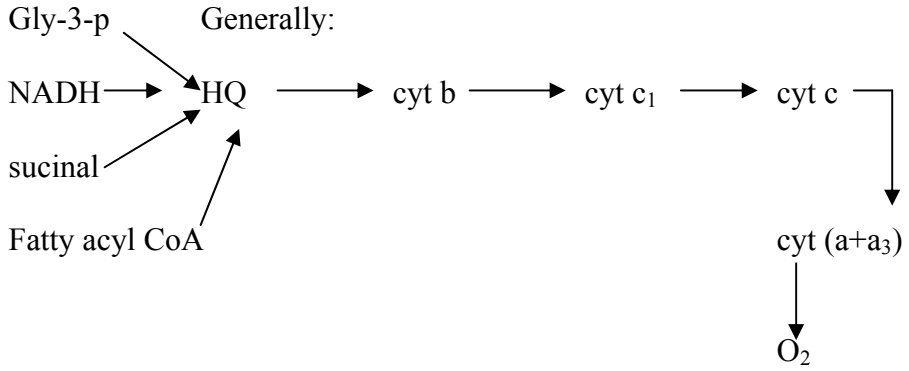
  3. Transfer as a hydride ion [H^-], which bears 2 e-.

- Most of the e- entering the mitochondrial respiratory chain arise from the oxidative action of dehydrogenases that collect e- from the oxidative reactions of the pyrovate dehydrogenase complex, TAC cycles. β-oxidation pathway, and the oxidative steps of amino a catabolism and funnel them on e- pairs into the respiratory chain. The DM use either NADH, NADPH or $FMNH_2$, $FADH_2$, flavin nucleatides, as e- acceptors.

  1. NADH/NADPH are water soluble e- carriers that associate reversibly with DH. NADH acts as a diffusible carrier transporting e- derived from catabolic reactions to their point of entry into respiratory chain. NADPH is a diffusible carrier that supplies e- to anabolic reactions.

  2. Flavoproteins: contain a very rightly, sometimes covalently, bound flavin nucleotides, either FMN or FAD. The standard reduction of flavin nucleatides depends on the protein with which it is associated.

Sequence of the e- transport chain:



- UQ: `ubiquinon' is located on the innermitochondrial membrane. It is also called coenzyme Q; it is a fat soluble benzoquinon, it is very small hydrophobic molecule

that can freely diffuse with the lipid bilayer of the inner mitochondrial membrane, and can shuttle reducing equivalents between other, less mobile, electgron carriers in the membrane.

- Cytochromes; are iron-containing electron transfer proteins, that has a characteristic strong color due to the presence of the heme prosthetic group.

- 3 classes of cytochromes/a, b, and c, each has a different light absorption spectra.

- The heme groups of a and b are tightly, but not covalently, bound to their associated proteins; heme groups of c-type cytochromes are covalently attached.

- The cytochromes a, b and some of type c are integral proteins.

- Cyt c of mitochondria, is a soluble proteins that associate through electrostatic interactions with the outer surface of the mitochondrial inner membrane.

- The electron transport chain carriers, could be separated into four complexes; I, II which catalyze e- transfase to UQ from 2 different e- donors; NADH/complex I and succinate/complex II.

  Complex III carries e- from UQ to cyt c, and complex IV completes the sequence by transferring e- from cyt c to O_2.

- Complex I: NADH dehydrogenase complex; flavoprotein complex, contains FMN – and Fe-S centers.
  It transfers e- as hydride ions from NADH to UQ.

- Complex II: Succinate DH, flavoprotein complex. It contains FAD. e- flow from succinate to FAD to Fe-s centers of the complex enzyme to UQ.

Complex III: called cytochrom bc, complex or ubiquinon-cytochrome c oxidoreductor; contains cyb. b_{562}, cyt b_{566}, cyt c, Fe-S protein and 6 other proteins subunits. Complex III cyt is an integral protein. cyt c_1 and Fe-s are on the outer surface. While cyt b spans the memb – there is a switch between the two e- carrier "UQ" to one e-carrier "cytochromes b, c, c_1"

- This switch is accomplished in a series of reactions called the Q cycle.

- Complex III functions as a proton pump; this is important to ATP synthesis.

- Complex III e.g. transfere e- from UQ to cyt c.

- UQH_2 is oxidized to UQ and cyt c is reduced.

Figure

Complex IV called cytochrome oxidase, contains cyt a, cyt a_3, integral protein. It contains two copper ions Cu_A and Cu_B that are important to transfer e- to O_2. It carrier 4e- for the reduction of O_2 3, without generating hydrogen peroxide or hydroxyl free radicals.

- It causes net movement of protons from the matrix to the intermembrane space. It functions as a proton pump.

Figure

Coupling of ATP synthesis and electron flow.

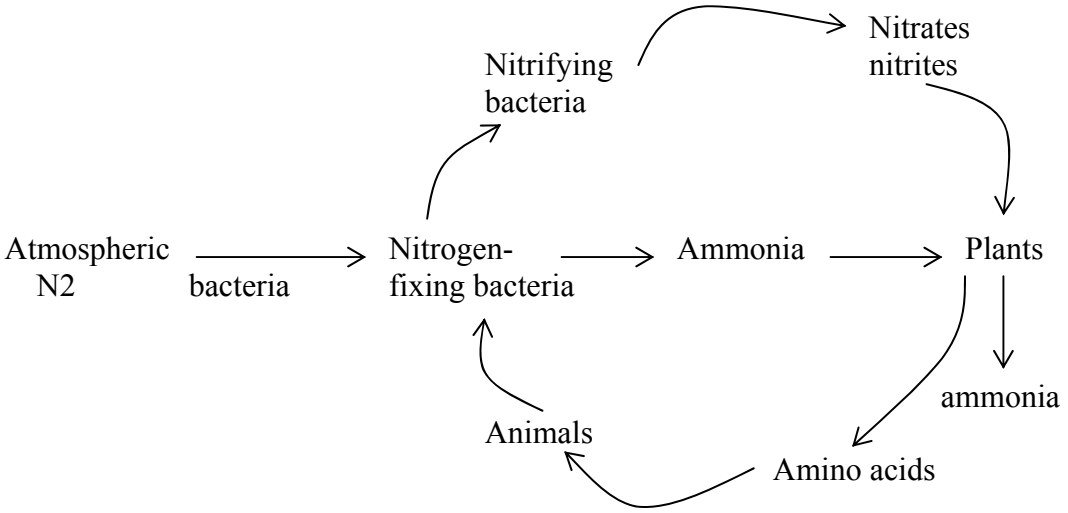
- ATP synthase, is an E complex present in the inner-mitochondrial memb. It is made of 2 major components [F_1, Fe].

- The transfer of e- along the respiratory chain is accompanied by outwork pumping of protons across the inner mitochondrial membrane, which results in a transmembrane difference in proton concentration Ca proton gradient) and thus in pH; the matrix becomes alkaline relative to the cytosolic side of the memb.

NITROGEN FIXATION

- Some bacteria can capture molecular nitrogen (N_2) from the atmosphere and unit to form biologically useful nitrogenous compounds. This is called nitrogen-fixation. Because animals and most plants can't do this, bacteria form the starting point of many food chains in the biosphere.

  - The cycling of nitrogen in the biosphere



Nitrogen fixation; is the 1st step of nitrogen cycle. This is a reduction of atmospheric nitrogen by nitrogen fixing bacteria to form ammonia NH_3 or NH_4^+.

- Soil bacteria that derive their energy by oxidizing ammonia to nitrite (NO_2) and ultimately to nitrate (NO_3^-) are so abundant and active that nearly all ammonia reaching the soil ultimately becomes oxidized to nitrate. [The process is known as, nitrification].

- Plants and many bacteria can readily reduce nitrate to ammonia by the action of nitrate reductase. Ammonia so formed can be built into amino acids by plants, which are then used by animals as a source of both non-essential and essential amino acids to build animals proteins.

- When organisms die, the microbial degradation of their proteins returns ammonia to the soil, where nitrifying bacteria convert it into nitrite and nitrate again.

- A balance is maintained between fixed nitrogen and atmospheric nitrogen by bacteria that convert nitrate to N_2 under anaerobic condition. This process is called denitrification. [These soil bacterias are NO_3^- rather than O_2 as the ulternate e-acceptor in a reactions similar to oxidative phosphorelation].

Nitrogen fixation is carried by a highly conserved complex of protein called nitrogenase complex. It is made of two key components:

- Dinitrogenase reductase
- Dinitrogenase

Nitrogen fixation is carried out by a highly reduced form of dinitrogenase; and it requires 8e-; 6 for the reduction of N_2 and $_2$ to produce 6 molecules of H_2.

Dinitrogenase is reduced by the transfer of e- from dinitrogenase reductase. The required 8e- are transferred to dinitrogenase one at a time. with the reduced reductase binding and the reduced reductase dissociating from dinitrogenase in a cycle.

This cycle requires the hydrolysis of ATP by the reductase.

The immediate source of e- to reduce dinitrogenase reductase varies, with reduced ferrodoxin, reduced flavodoxin.

The rate of ATP is not thermodynamic; in the reaction carried out by dinitrogenase reductase both ATP binding and ATP hydrolysis bring about important protein conformational changes required to bring about the reaction.

Nitrogen fixation is an anaerobic reaction, the enzyme dinitrogenase reductase is inactivated by oxygen.

The energy required for nitrogen fixation was probably the evolutionary driving force for this association of plants with bacteria. [Such as leguminous plants].

The bacteria in root nodules have access to a large reservoir of energy in the form of the abundant CHO made available by the plant. Because of this energy the bacteria may fix hundreds of times more nitrogen than free bacteria.

NH_3/NH_4^- is used in the transamination reactions.

N_2 is inorganic form of nitrogen. It is converted to organic compounds [urea, pro, N cpds]. Then other organic compounds are converted to inorganic form.

In some agricultural countries, micro-organisms are used to generate nitrogen.

[Microorganisms are found normally in the soil].

Nitrate Reduction (Nitrification)

$NO_3' \rightarrow NH_3$ Nitrifying bacteria in soil.

(1) $NO_3' + 2H+ + 2e- \longrightarrow NO_2' + H_2O$

(Nitrate reductase several fat NADH and FADH)

$(NO_3 + NADH + H^+ \longrightarrow NO_2 + NAD + H_2O)$

(2) $NO_2^- + 6\ e- + FH+ \longrightarrow NH_2+ + 2H_2O$

Nitrite reducate
(complex; though several agents)

$3NADPH+ + NO_2^- + 5H^+ \longrightarrow NH_4^+ + 3\ NADP + 2H_2O$

a.a. and proteins in plants:

The constituents of pro are all α a.a. exept proline, having a side chain, neutral bsic, or acidic.

Only L-a.a. forms are encountered in proteins. Some a.a. present in cell-wall material of higher plants have D-a.a. (Table 1)

Non-Protein Amino Acids

Plants synthesis all the a.a. required for the synthesis of their protein. In addition they synthesis at least 100 a.a. which are not incorporated into proteins. Some of these a.a. occur only in a single species or small number of species. Many have unusual structures.

Some of the non-pro a.a. are intermediates in pathways of synthesis of the pro. a.a.

Some of them are homologues or simple substituted derivates of pro a.a. Some of them arise from the corresponding k.a. by transamination. Some of the non-pro a.a. are very toxic in which they do not occur naturally.

Proteins in seeds:

This is a bulk of reserve proteins in some seeds; such as in pea cotyledons. The protein consists of two globulins vicilin and legumin.

Protein bodies occur widely in the cy cotyledons and endosperm of both starch-bearing and oil-bearing seeds.

Table 1

The Structures of Amino Acids predsent in Most Plant Proteins

Monoamino monocarboxylic acids:

Glycine	$CH_2(NH_2).CO_2H$
Alanine	$CH_3.CH(NH_2).CO_2H$
Valine	$CH_3.CH(CH_3).CH(CH_2).CO_2H$
Leucine	$CH_3.CH(CH_3)CH_2.CH(NH_2).CO_2H$
Isoleucine	$CH_3.CH_2.CH(CH_3).CH(NH_2).CO_2H$

Hydroxy aliphatic acids:

Serine	$CH_2(OH).CH(NH_2).CO_2H$
Threonine	$CH_3.CH(OH).CH(NH_2).CO_2H$

Dicarboxylic amino acids

Aspartic acid	$HO_2C.CH_2.CH(NH_2).CO_2H$
Glutamic acid	$HO_2C.CH_2.CH_2.CH(NH_2).CO_2H$

Amides

Asparagine	$H_2NOC.CH_2.CH(NH_2).CO_2H$
Glutamine	$H_2NOC.CH_2.CH_2.CH(NH_2).CO_2H$

Basic amino acids

Lysine	$CH_2(CH_2).CH_2.CH_2.CH_2.CH(NH_2).CO_2H$
Arginine	HN C.NH.$CH_2.CH_2.CH_2.CH(NH_2).CO_2H$ H
Histidine	N CH HC C.$CH_2.CH(NH_2).CO_2H$ N H

Sulfur-containing acids:

Cysteine $HS.CH_2.CH(NH_2)CO_2H$

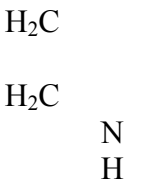
Cystine $S.CH_2.CH(NH_2).CO_2H$

$S.CH_2.CH(NH_2).CO_2H$

Methionine $CH_2.S.CH_2.CH.CH(NH_2).CO_2H$

Imine acid:

Proline

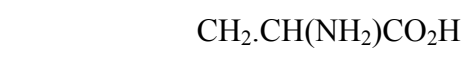


Aromatic amino acids:

Phenylalanine $CH_2.CH(NH_2).CO_2H$

Tyrosine

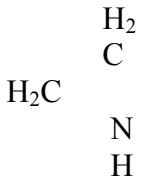
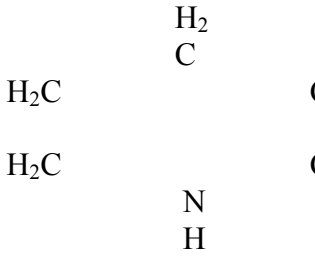
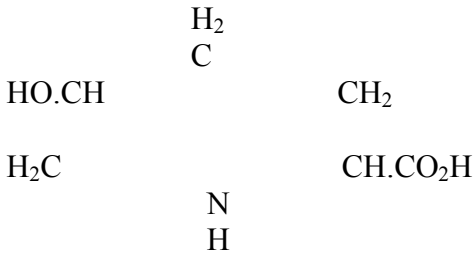
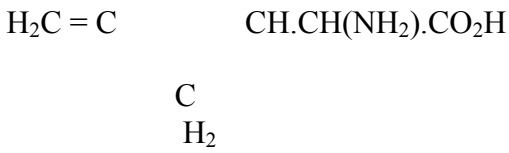
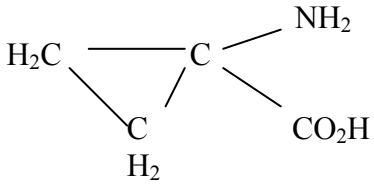
Tryptophan



Table

Structural Relationships and Distribution of Some Nonprotein Amino Acids

Nonprotein amino acid (corresponding; protein amino acid and relation-ship in parentheses)	Structural	Distribution
Acid		
α-Aminoadipic acid (H)	$HO_2C.(CH_2).CH(NH_2).CO_2H$	Many plants
γ-Hydroxyglutamic acid (S) (glutamic acid)	$HO_2C.CH(OH)CH_2.CH(NH_2).CO_2H$	Some Liliaceae and ferns
γ-Methyleneglutamic acid (S) (glutamic acid)	$HO_2C.C(=CH_2).CH_2.CH(NH_2).CO_2H$	Random, e.g. tulip and peanuts
Amides		Some
N-Ethylasparagine(S) (asparagine)	$(C_2H_2)HN.OC.CH_2.CH(NH_2).CO_2H$	Cucurbitaeae
Basic		
α,γ-Diaminobutyric acid (H) (lysine)	$H_2N.CH_2.CH_2.CH(NH_2).CO_2H$	Sporadic, some legume seemds and antibiotics
Homoarginine (H) (arginine)	HN C.NH.$(CH_2)_4$.$CH(NH_2).CO_2H$ H_2N	Some Lathyrus species
Hydroxy Homoserine (H.I) (serine, threonine)	$HO.CH_2.CH_2.CH(NH_2).CO_2H$	Many plants
Aromatic		
m-Carboxyphenylalanine (S) (phenylalanine)	$CH_2.CH(NH_2).CO_2H$ CO_2H	*Iris, Reseda*
Heterocyclic:		
β-Pyrazol-1-yalalanine (i) (histidine)	HC = CH HC N.CH_2.$CH(NH_2).CO_2H$ N	Some cucurbi-taceae; also as γ-glutamyl peptide
Sulfur-containing		
S-Methylcysteine (S) (cysteine)	$CH_3.S.CH_2.CH(NH_2).CO_2H$	Legumes, Cruxi-ferae; also as γ-glutmyl peptide

Imino acids: Azetidine-2-carboxylic acid (H)(proline)		Many Liliaceae
Pipecolic acid (H) (proline)		Many plants, especially legume seeds
5-Hydrohypipecolic acid(H) (4-hydroxyproline)		Dates, ferns, legumes
Cyclopropyl acids: α-(Methylenecyclopropyl) glycine (A) (leucine)		Litchi seed
1-Aminocyclopropyl-1-acarboxylic acid		

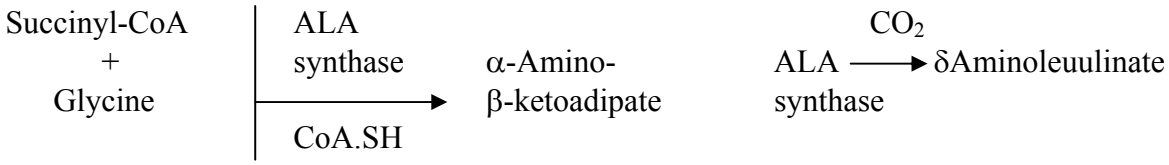
Chlorophyll Synthesis

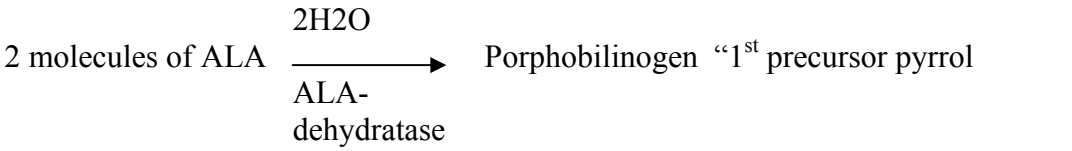
- Poophin ring + alcohol – phytole

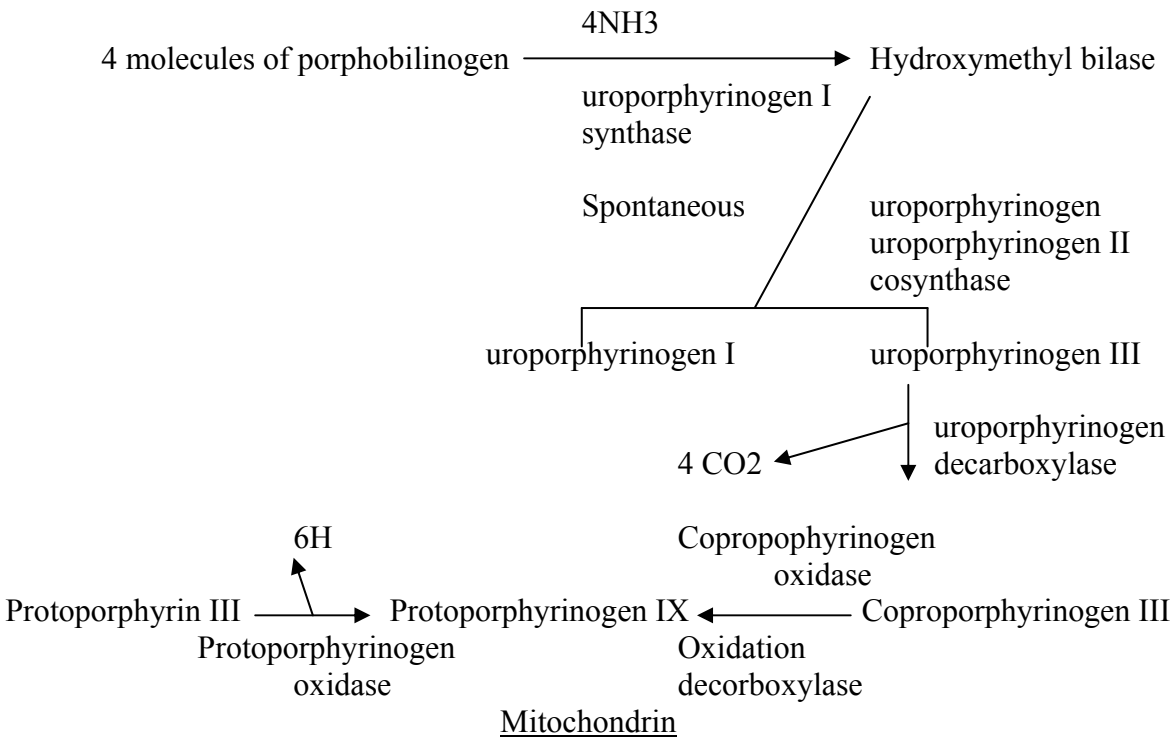
- Porphyrins: are cyclic compounds formed by the linkage of 4 pyrrole rings through methyl bridges. A characteristic property of porphyrins is the formation of complexes with metal ions bind to the nitrogen atom of the pyroole rings [e.g. iron-porphyrin, `heme', Mg- porphyrin, chlorophyll.

- Biosynthesis of porphyrins.

  Precursories, ALA I δ-Aminoleuulinate]:







- After that the magnesium is added to it. Mg-protoporphyrin is the substitute for the 1st of a series of reactions which terminates in chlorophyll formation. these reactions involve additional changes in side chains and finally the partial reduction of one of the pyrrole rings.

- Chlorophyll a contain two esterified groups. The carboxyl of the propionic is at position 7 is esterified with phytol alcohol. Esterification with phyrol [chlorophyllide and + pytol chlorophyll a + H_2O]

Mg – protoporphyrin IX + 5-adenayl methionine

↓

Mg – protoporphyrin monometry ester

↓

Mg – 2,4 dirinyl protoporphyrin as

↓

Mg-2-vinyl pheoporphyrin as I protochlorphyllide a3

↓ reduction I light is required – reduction of ring D

Chlorophyllide a + phytol (chlorophyllase) Chlorophyll a

- Chlorophyll synthesis in the dark. Most higher plants require light for chlorophyll synthesis, some can synthesize chlorophyll in the dark. [Many algea].

- Control of chlorophyll synthesis:
  1st ATP source in plants chlorophast is different from mitochondria, and the mechanisms available for the formation of succinate and succinyl CoA are different. There differences could markedly affect the means of controlling ALA synthase.

- Some kind of RNA synthesis is required for the large scale production of chlorophyll. An inhibitor of DNA metabolism. [Fluorodeoxyuridine] – actinomycin D, an inhibitor of DNA-dependent RNA synthesis, block greening of illuminated dark-grown leaves of maize and red kidney bean.

<u>Cellulose:</u>

- Is the most abundant compound in plants.

- Of the yearly 30 billion tons of carbon transformed into organic compounds by higher plants, about one-third is made into cellulose.

- 50% of paper is cellulose. 50% of wood is cellulose, 50% of cotton in the clothes is cellulose.

- Cellulose serves as a structural function.

- Cellulose is an unbranched polymer of glucose residues joined by β-1,4-linkage. The B-configuration allows cellulose to form very long straight chains. [Each glucose residue is related to the next by a rotation of 180 degrees, and the ring oxygen atom of one is hydrogen bonded to the 3-OH gr of the next. Fibrils are formed by parallel chains.]

- Mammals don't have cellulose.

- Synthesis: UDPG [uridine-5- α-D-glucopyranosyl-pyrophosphate].

Hemicellulose:

- hemicellulose A, hemicellulose B.

- Cellulose is synthesized in by "cellulose synthase". It is synthesized in some plants from GDP-glucose and in other from UDP-glucose.

$$\text{Activated glucose} + (\text{gje})_n \xrightarrow[\text{Pre-existing cellulose chain}]{} \text{UDP or GDP} + (\text{gln})_{n+1}$$

- Cellulose is hydrolyzed by an enzyme "cellulase" present in some bacteria [cellulose E D-glu].

- Hemicellulose; are not related structurally to cellulose but are polymers of pentose [particularly D-xylans], polymers of D-xylose in B (1-4) linkage with side chains of arabinose and other sugars.

- Pectin: polymer of methyl D-galacturonate.

- Fructans: (called levans) are homo-polysaccharides composed of D-fructose units.

- Inulin: D-fructose units B (2-1) linkage.