BCH 413- PLANT BIOCHEMISTRY (2 UNITS)

- ORGANIZATION OF PLANT CELLS
- PHOTOSYNTHESIS
- ALKALOID
- PLANT HORMONES
- BIOSYNTHESIS OF PLANT CAROTENOID
- BIOCHEMISTRY OF PLANT DEVELOPMENT
- STRUCTURES, FUNCTIONS AND RELATIONSHIP OF PLANT GROWTH REGULATORS
- HERBICIDES

ORGANIZATION OF PLANT CELLS -: refer to Bio 101. Taking notes of organelles such as cell wall, chloroplast, mitochondria, ribosome e.t.c and their respective functions.
PHOTOSYNTHESIS -: This is the process by which photosynthetic organism harness radiant energy and convert it to useful forms of chemical energy basically to sustain not only their own existence but also the existence all aerobic non-photosynthetic organism. The net equation involving the chemistry of photosynthesis is summarized thus:

$$6CO_2 + 6H_2O + \text{SOLAR ENERGY} \longrightarrow C_6H_{12}O_6 + 6O_2$$

This process is also often referred to as carbon cycle and is responsible for the continuous existence of life. The specialized organelle where photosynthetic chemical reactions occur is called the chloroplast. The chemical event that occur in photosynthesis is in two distinctive phases namely

I. Light reaction
II. Dark reaction

Note that light reaction is dependent on an input of radiant energy and involves four processes/stages.

I. Photochemical excitation of chlorophyll
II. Oxidative cleavage of water (photooxidation)
III. Formation of NADPH (photoreduction)
IV. Formation of ATP (photophosphorylation)

The dark reaction involves the enzymatic assimilation and conversion of CO_2 to CHO. Note that the NADPH and ATP formed in the light reaction as sources of reducing power and energy respectively i.e

$$\xrightarrow[\text{ATP}]{\text{NADPH}} \; CO_2$$

$$(CH_2O)_n$$

LIGHT REACTION OF PHOTOSYNTHESIS.

Not all wavelengths of light are absorbed during photosynthesis. Green, the color of most plants, is actually the color that is reflected. The light that is absorbed splits water into hydrogen and oxygen:

H_2O + light energy ---> ½ $O_2 + 2H^+$ + 2 electrons

1. Excited electrons from Photosystem I can use an electron transport chain to reduce oxidized P_{700}. This sets up a proton gradient, which can generate ATP. The end result of this looping electron flow, called cyclic phosphorylation, is the generation of ATP and P_{700}.
2. Excited electrons from Photosystem I could flow down a different electron transport chain to produce NADPH, which is used to synthesize carbohydratyes. This is a noncyclic pathway in which P_{700} is reduced by an exicted electron from Photosystem II.
3. An excited electron from Photosystem II flows down an electron transport chain from excited P_{680} to the oxidized form of P_{700}, creating a proton gradient between the stroma and thylakoids that generates ATP. The net result of this reaction is called noncyclic photophosphorylation.
4. Water contributes the electron that is needed to regenerate the reduced P_{680}. The reduction of each molecule of $NADP^+$ to NADPH uses two electrons and requires four photons. Two molecules of ATP are formed.

The primary photochemical event that happens is the absorption of photons of light by chlorophyll molecule which results in their excitation to higher energy levels. Thereafter, electrons from the excited chlorophyll molecules are transferred to specialized acceptor molecule and ultimately to $NADP^+$ which is accompanied by ATP formation. Water serves as e^- donor (reducing agent) purposely to return the electron deficient (oxidized chlorophyll) molecule back to the ground state in a process accompanied by the release of oxygen molecules.

The net reaction is given is given thus:

Note -: light dependent phase of photosynthesis include two separate photosystems both of which must be activated for maximum efficiency. These photosystems are photosystem 1 or PS 1 or P_{700} (which contain largely chlorophyll a and photosystem 11 or PS 11 or P_{680} which contain both chlorophyll a and chlorophyll b.

ELECTRON TRANSPORT CHAIN IN PHOTOSYNTHESIS

The electron flow in the dual photosystem model of the light reaction could be by:

I. Non-cyclic phosphorylation
II. Cyclic phosphorylation

In non-cyclic phosphorylation, the electron flow from one photosystem is associated with ATP production while the electron flow from the other is associated with NADPH production. However, the conventional and normal mode of operation is non-cyclic flow, though the chlorophyll can shift to cyclic mechanism under certain conditions. The processes of non-cyclic phosphorylation are considered in three segments thus:

a) PS 11 -: It involves the production of oxygen. No intermediate is involved. It is assumed that photooxidation of water occur to give O_2 and H^+.
b) PS 11 to P_{700}-: Electrons from photosystem 11 enters the pathway reminiscent of that in mitochondria. At least one molecule of plastoquinone and oxidized P_{700}, there exist at least three different electron carriers namely cytochrome b, which

is an iron-sulphur (Fe-S) protein, cyt-f and plastocyanin with one atom of copper (Cu).

c) REDUCTION OF NADP$^+$ -: The intermediate electron acceptor from P_{700} is chlorophyll a, which passes the electron to membrane bound (FeS) protein, then to $(FeS)_2$ ferredoxins. Finally, electron flow via flavoprotein to NADP$^+$.

There exist some similarities between the processes of oxidative phosphorylation and photophosphorylation and these are;

1. Oligomycin anf phlorhizin are inhibitor of both electron and phosphorylation
2. Antimycin A blocks the oxidation of b-type cytochrome
3. The same lipophylic phenols (e.g 2,4-dinitrophenol) acts as an uncoupler.
4. All inhibitors of electron transport prevents phosphorylation.
5. Both processes depend upon the integrity of the membrane

The flow of electrons in the photosystem model of light reaction is shown below

DARK REACTION (FIXATION OF CO_2)

The dark reaction is summarized by this equation

The conversion of CO_2 to simple sugar is through Calvin Cycle. The first reaction of this cycle is the conversion of ribulose-1,5-bisphosphate to two molecules of 3-phosphoglyrate molecules and it is catalyzed by the enzyme ribulose-1,5-phosphocarboxylase (RUBISCO)

The synthesis of hexose sugar from 3PG is achieved by the concerted actions of enzymes of glycolysis and those of pentose phosphate pathway as summarized by Calvin-Benson_Bassham Scheme shown below.

NET REACTION:

The reaction is regulated by the action of RUBISCO whose activity is inhibited by fructose-1,6-bisphosphate and activated by fructose-6-phosphate.

After the formation of fructose-6-phosphate, it is converted to starch follow the re action sequence below:

fructose-6-phosphate
↓
glucose-6-phosphate
↓
ADP-glucose
↓
Starch/sucrose

Here is a summary of the steps used by plants and other organisms to use solar energy to make chemical energy:

1. In plants, photosynthesis usually occurs in the leaves. This is where plants can get the raw materials for photosynthesis all in one convenient location. Carbon dioxide and oxygen enter/exit the leaves through pores called stomata. Water is delivered to the leaves from the roots through a vascular system. The chlorophyll in the chloroplasts inside leaf cells absorbs sunlight.
2. The process of photosynthesis is divided into two main parts: light dependent reactions and light independent or dark reactions. The light dependent reaction happens when solar energy is captured to make a molecule called ATP (adenosine triphosphate). The dark reaction happens when the ATP is used to make glucose (the Calvin Cycle).
3. Chlorophyll and other carotenoids form what are called antenna complexes. Antenna complexes transfer light energy to one of two types of photochemical reaction centers: P_{700}, which is part of Photosystem I, or P_{680}, which is part of Photosystem II. The photochemical reaction centers are located on the thylakoid membrane of the chloroplast. Excited electrons are transferred to electron acceptors, leaving the reaction center in an oxidized state.
4. The light-independent reactions produce carbohydrates by using ATP and NADPH that was formed from the light-dependent reactions.

FLAVONOID AND ALKALOID

Flavonoids and their derivatives are examples of natural pigments which are examples of natural pigments which are responsile for the colour of a number of foods and food products/materials. They have the basic structure shown below

Among the pigment derived from these structures are

I. Anthocyanins
II. Flavonones
III. Flavanol
IV. Flavones

It is the extent of delocalization of the electrons of central heterocyclic ring that is responsible for the different colours of anthocyanins (red or violet).

In food biochemistry, about six forms of anthocyanins are important and these has OH group on the 3,5,7 carbon while of the OH or methoxyl on 3^I, 4^I and 5^I carbons of the ring confers the difference.

The anthocyanins are often linked to one or several sugars and this often confer pigment changes as well as different function on them.

Certain flavonoids, such as leucocyanidins are colourless, however during oxidation processes, these colourless compounds undergo transformation into anthocyanidins (red or pink). This exemplifies what happen in certain varieties of apples, pears or bean. Moreso, the bitter taste of some grape fruits, lemon or oranges are due to the presence of flavonones such as naringin and hesperidin.

IMPORTANCE OF FLAVONOIDS IN FOOD TECHNOLOGY

1) Flavonol glycosides representing about 30% of the dry extract in tea contributes to astringent quality.
2) A non-bitter compound,naringenin may be obtained from naringin (bitter) by treating it with α -L-rhamnosidase and β -glucosidase in a process known as debitterization of narigin.
3) α-L-rhamnosidase is also known to react with hesperidin to yield dehydrochalonehesperidin glucoside, which is a sweet tasting substance often used as sweetner.

It should be noted that it is important to control the Ph, temperature and conditions supporting oxidation during storage so as to minimize or prevent reaction(s) which may give rise to colorless compound, because this is undesirable for the fruits and vegetable industries.

BIOLOGICAL AND PHARMACOLOGICAL PROPERTIES OF FLAVONOID

One of the functions of flavonoid in plant is to protect them against disease caused by microorganism and also to act as feeding deterrent to insects and other herbivores animals by providing toxic substances, thereby inhibiting the growth of microorganism or give unpleasant sensation to the taste buds of animals. Some isonvertin from the uvana roots (*Annonaceae*) have been reported to possess antimicrobial and cytotoxic property.

- Also, taxifolin, derivative of dihydroflavonol exhibits significant anti-inflammatory activity similar to that of hydrocortisome
- Furthermore, dihydroquarcetin (flavonol) has been shown to possess antiviral activities
- Naphtoquinone which are found in flowers and mushrooms are used as colouring or purgative
- Dicoumarol is known to be used in prevention of blood clotting.

OTHER IMPORTANT DRUGS/CHEMICALS THAT COULD BE DERIVED FROM PLANTS ARE LISTED BELOW

Drugs from Plants

- There are over a hundred chemical substances that have been derived from plants for use as drugs and medicines. This is by no means a comprehensive list of all of the plants, names of chemicals, or uses for those chemicals, but it should serve as a useful starting point for further research. For your convenience, I have listed the common name of a plant next to its scientific name. Be advised that common names are very imprecise and often assigned to completely different plants, so use the scientific name when looking for additional information concerning a plant.

Drug/Chemical	**Action**	**Plant Source**
Acetyldigoxin	Cardiotonic	Digitalis lanata (Grecian foxglove, woolly foxglove)
Adoniside	Cardiotonic	Adonis vernalis (pheasant's eye, red chamomile)
Aescin	Antiinflammatory	Aesculus hippocastanum (horse chestnut)

Aesculetin	Antidysentery	Frazinus rhychophylla
Agrimophol	Anthelmintic	Agrimonia supatoria
Ajmalicine	Treatment for circulatory disorders	Rauvolfia sepentina
Allantoin	Vulnerary	Several plants
Allyl isothiocyanate	Rubefacient	Brassica nigra (black mustard)
Anabesine	Skeletal muscle relaxant	Anabasis sphylla
Andrographolide	Treatment for baccillary dysentery	Andrographis paniculata
Anisodamine	Anticholinergic	Anisodus tanguticus
Anisodine	Anticholinergic	Anisodus tanguticus
Arecoline	Anthelmintic	Areca catechu (betel nut palm)
Asiaticoside	Vulnerary	Centella asiatica (gotu cola)
Atropine	Anticholinergic	Atropa belladonna (deadly nightshade)
Benzyl benzoate	Scabicide	Several plants
Berberine	Treatment for bacillary dysentery	Berberis vulgaris (common barberry)
Bergenin	Antitussive	Ardisia japonica (marlberry)
Betulinic acid	Anticancerous	Betula alba (common birch)
Borneol	Antipyretic, analgesic, antiinflammatory	Several plants

PLANT HORMONES

plant hormone are specific organic substances produced naturally in higher plants, controlling growth and other physiological functions at the site remote from its place of production.they are known to be active in minute amount.they could be natural (endogenous) or synthetic. The initial biological reactions and changes chemical composition within the plant, thereby influencing developmental processes such as changes in growth pattern which leads to the formation of roots, shoots, leaves, flowers and other structural entities characteristics of plant. About six groups of endogenous plant hormones are known namely

1. Indole-3-acetic acid (IAA) (an auxin)
2. Gibberellic acid (a gibberellins)
3. Zeatin (a cytokinin)
4. Absciscic acid
5. Caffeine acid (a phenolic)
6. Ethylene

Indole-3-acetic acid could be synthesized from the tryptophan follow the processes of deamination followed by decarboxylation or vice-versa.

The compound could be destroyed by the enzyme IAA oxidase. Other synthetic auxins are

- Indole-3-propionic acid
- Indole-3-butyric acid

The biological activities and physiological relevance or importance of this hormones includes:

I. Inhibition of lateral buds
II. Control of leaves abscission

III. Moderate cell enlargement
IV. Promotes cell enlargement
V. Promotes cell division in cambium
VI. Promotes germination at moderate concentration
VII. Induces a highly increased number of vascular strands in roots
VIII. Accelerates flowering
IX. It promotes parthenocarpy
X. Prevents premature dropping of fruits and leaves
XI. Enhances improved fruit settings

GIBBERELLINS: there exist about 40 diferent types of gibberellin which are named as GB_1 to $GB_{40.}$ They contain lactone ring on cyclohexene ring with substituted OH and carboxyl functional groups. The early part of biosynthesis of GB is similar to that of carotenoids and terpenoid: in that, it begins from acetyl coA down to geranylgeranyl phosphate and involves intermediates such as mevalonate and mevalonate-5-phosphatepyrophosphate. However the other steps from geranylgeranyl pyrophosphate to gibberellin biosynthesis differ from those of carotenoids. The summary of gibberellins synthesis is given below

Importance of gibberellins in plant physiology includes:

i. Regulation of sub-apical meristem activities such as stem cell enlargement
ii. Control of fruit growth
iii. Initiation of flowering
iv. Leaf expansion
v. Hyponasty of leaves
vi. Parthenocarphy
vii. Increase the length of hypocotyls and cotyledon

CYTOKININS OR PHYTOKININ OR KINETIN

These hormones contain group of high specificity (purine nuclei) and one lipophilic group without specificity (the furan ring). They have been known to be extracted from tomato juice, coconut milk, immature fruits of Zea mays. They are known to be translocated in the xylem stream as well as basipetal movement in petiole. Their physiological effects include:

i. Delays the breakdown of chlorophyll in detached leaves.
ii. Participates in orderly development of embryo during seed development
iii. It promotes cell division.
iv. Increases the rate of protein synthesis
v. Enhances the breakdown of dormancy of seeds

ABSCISSIC ACID (ABA)

This plant hormones affects plant growth at a relatively low concentration. It posess an asymmetric carbon, hence can exist at (+) or (-) enantiomers. Naturally occurring ABA are usually in (+) form (2-cis-ABA). It can be transformed into 2-trans form in the presence of UV-light ABA is usually manufactured in matured leaves and then move up to the shoot apex through the phloem. Physiological effects of ABA includes:

i. It controls bud dormancy
ii. It initiates flowering
iii. Controls leaves abscission
iv. Regulates opening and closing of stomata
v. Inhibits gibberellins induced enzyme synthesis

PHENOLICS

These are derivatives of phenol molecules and include compounds like cathechol, caffeine/caffeic acid and anthocyanidin. Some of them are powerful fungicidal and bacteriocidal agents. They are known to be able to protect plants from invasion by fungi and bacterial. If a plant is “wounded”, phenolic compounds become concentrated around the damaged tissue(s) andf tend to “seal off” the area from the rest of plant. Large complex of phenolic molecules are frequently found in plant vacuoles or lumen of dead cells. Some insoluble phenolics are waste products of metabolic reactions. The phenolics are known to mediate physiological effects by way of:

i. Inhibiting cell division and cell enlargement
ii. In some cases, they prevent germination of many seeds

ETHYLENE

This is a volatile gas formed by ripening of fruits produce/synthesize high concentration of this compound in the intracellular spaces of the fruit tissue. It can also be produced in other tissue and organs such as leaf, stem, and roots (though at low concentration). Glucose and linoleic acid functions as precursors for the ethylene biosynthesis thus:

Physiological effects of ethylene includes among others:

i. It triggers the ripening of many fruits.
ii. It accelerates the abscission of leaves, stem and flowers
iii. It inhibits stem elongation
iv. It bring about stem swelling
v. Involves in epinasty
vi. It is also involved in flower petal discolouration
vii. It reduces the incidence of pests and diseases

BIOSYNTHESIS OF CAROTENOID

The carotenoids are highly unsaturated hydrocarbon formed from the isoprene units linked end-to-end or their oxygenated derivatives. They are of two main groups namely

(I) Carotenes
(II) Xanthophylls

Both types are water insoluble pigment. The carotenes are purely hydrocarbon in nature whereas the xanthophylls are oxygen-containing derivatives.

They have common biochemical origin which is acetyl coA. They are always/mostly of plant origin but can also be found in animals, since the oxygenated half molecule of α,β and ɣ-carotene_ is vitamin A commonly found in milk, egg and liver. The most common carotene is β -carotene, which is a C-40 hydrocarbon consisting of a highly branched unsaturated chain containing identical substituted ring structure at each end. Other carotenoids are variance of β -carotene. Enzymatic symmetrical cleavage of _β -carotene by carotenase will yield two molecules of vitamin A. in animal, for instance, this conversion represents a chief natural source of vitamin A.

It should be noted that the alcoholic form of vitamin A (i.e retinol) is essential for the chemical phenomenon of vision. It can be enzymatically converted to the oxidized aldehyde form (retinal) which become complexed with opsin to form active protein which functions as primary photoreceptor of incident light that ultimately transmits information to the nervous system. Biosynthetic pathway for carotenoids and its relationship with the steroids is given below:

Acetyl coA → dimethylallyl → geranylPPO$_4$ → farnesylPO$_4$ geranylgeranylPPI
→ Phytoene → lycopene → carotenes (α, β, ɣ-carotenes)

HERBICIDES

Pesticides are pest killing agents. They are described as substances intended for preventing, destroying, repelling, mitigating or controlling any pest, including unwanted species of plants or animals or animals during the production, storage, transport, distribution and processing of foods, agriculture products or animal feeds which may be administered to animals for the control of ectoparasites and vector of diseases dangerous to man and animals. They are classified broadly according to their:

(I) Intended use or target organism
(II) Chemical nature
(III) Mode of action

Herbicides are therefore pesticides intended for killing plants or control weeds by interrupting their normal growth. They may either have certain selectivity by chemical property by the way of application in the control of weeds, grasses, or bushes in crop land, rangeland or forest or be a “total herbicide” for use on industrial sites and right-off way locations. They could be systemic or contact in action.

Over 100 types of herbicides are known to exist. All of these falls into a particular class or group which are broadly classified as:

i. Dinitrophenol herbicide
ii. Carboxylic acid herbicide
iii. Bipyridilium herbicide

Examples of dinitrophenol herbicide is 2,4-dinitro-o-cresol otherwise known as Sinox while 2,4-dichlorophenoxy-acetic acid (2,4-D) is an example of carboxylic acid herbicides. The two most important examples of bipyridilium herbicides are diquat and paraquat.

Paraquat (1,1^{I}-dimethyl-4,4^{I}-bipyridinium dichloride) is otherwise known as methyl viologen is a non-selective herbicide. It is a quartenary herbicide, fast acting, widely used for broadleaf weed control. It is one of the world's worst poisons on earth, thus it has been banned or restricted in some countries.

It is synthesized from pyridine from the reaction of two sodium molecules in anhydrous ammonia and quartenizing a $4,4^{I}$-bipyridyl product with methyl chloride under pressure. It has the chemical structure shown below:

It is non-explosive and non-inflammable in aqueous formulation. It is relatively stable under normal temperature, pressure and pH. Paraquat is corrosive to metals and reacts with strong oxidizers. It is stable in acid or neutral solutions but readily hydrolysed by alkali to its simpler constituents. The most frequently route of exposure to paraquat is either accidentally or intentionally. Its residues have been reported to be found in plants, soil, water and in foods.

First aid measures and managements principle in case of paraquat poisoning includes:

i. Induction of vomiting
ii. Washing of contaminated skin thoroughly with water and soap
iii. Aspiration of gastric content and perform gastric lavage followed by administration of mineral absorbent such as fuller's earth (kaolin), bentonite or activated charcoal in order to remove any unabsorbed PQ remaining in the GIT.
iv. Purgatives such as $MgSO_4$, Mg Citrate, Sorbitol or mannitol may be given.

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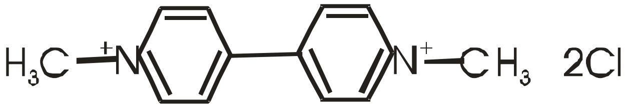
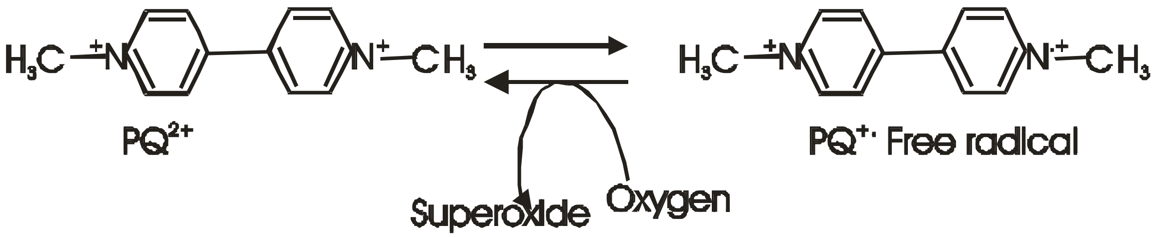
The importance of oxidative stress as a mechanism of PQ toxicity has been demonstrated in ic outcomes of the redox cycling reactions were identified and these includes:

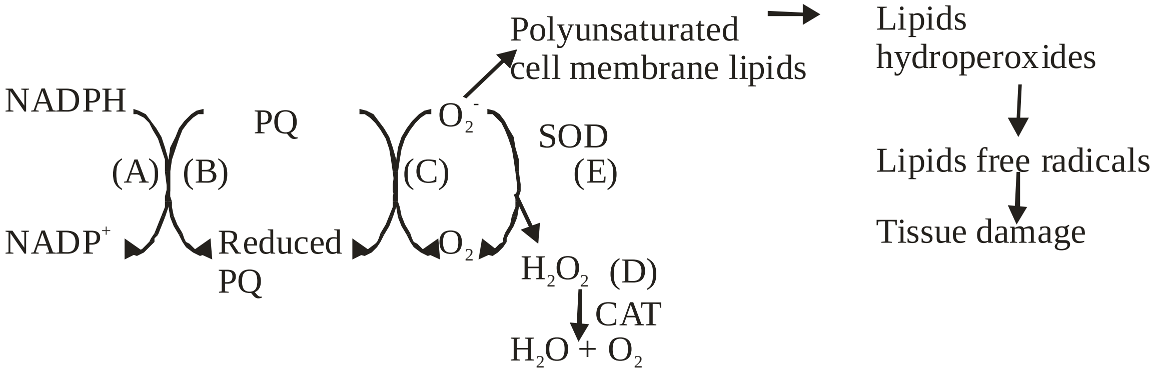
1. Generation of superoxide anion which can lead to the formation of more toxic reactive oxygen such as hydrogen peroxides and hydroxyl radicals.
2. Oxidation of the cellular NADPH, the major source of reducing equivalents for the intracellular reduction PQ, which results in the disruption of important NADPH-requiring biochemical processes.
3. Lipid peroxidation which results in the oxidative degeneration of cellular polyunsaturated fatty acids.



The redox cycle reaction of PQ that causes superoxide production is shown below:



The mechanism of action for the *in vivo* toxicity of paraquat is shown below:



STUDY QUESTIONS

Explain the molecular organization of plant cell.

1. Define photosynthesis.
2. What materials are required for photosynthesis? What is produced?
3. Write the overall reaction for photosynthesis.
4. Describe what happens during the cyclic phosphorylation of photosystem I. How does the transfer of electrons lead to the synthesis of ATP?
5. Describe the reactions of carbon fixation or the Calvin cycle. What enzyme catalyzes the reaction? What are the products of the reaction?