

**MSc Botany SEM IV**

**Paper VI**

**NITROGEN CONTAINING COMPOUNDS**

**ALKALOIDS**

**GLUCOSINOLATES**

**CYANOGENIC GLYCOSIDES**

**NON-PROTEIN AMINO ACIDS**

**Professor Nalini Pandey**

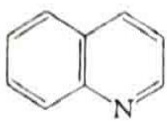
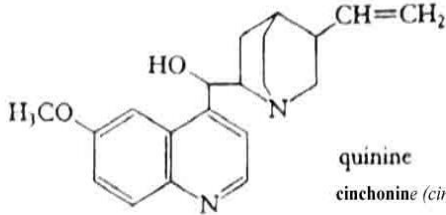
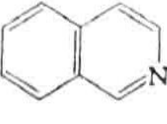
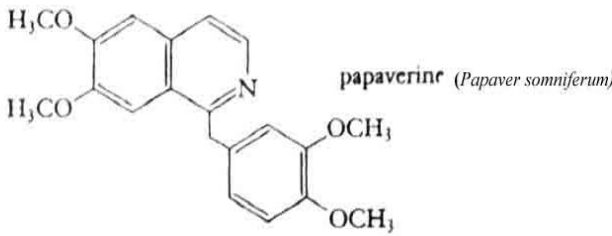
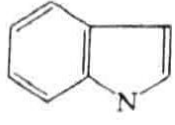
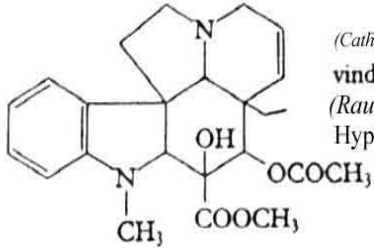
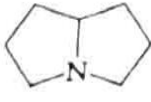
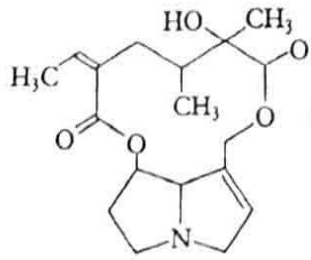
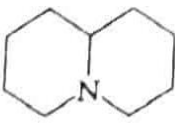
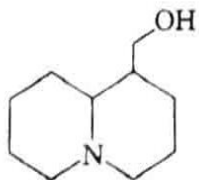
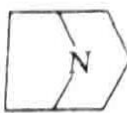
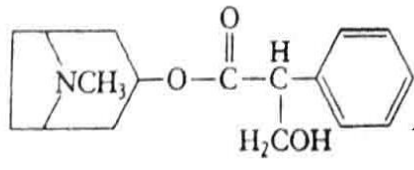

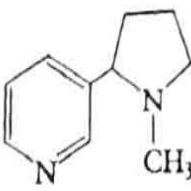
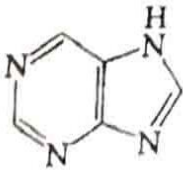
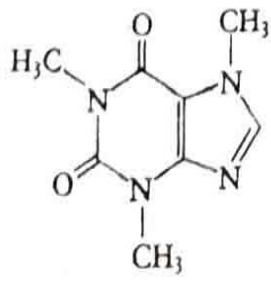
## Alkaloids

Alkaloids are compounds which are basic in nature and contain at least one tertiary nitrogen in a heterocyclic ring as well as oxygen. They have complex molecular structure and significant pharmacological activity. They are produced in plants but their functions in plants are unknown and 85-95% of plants manage without producing alkaloids. They are byproducts of plant metabolism and they are stored in vacuole. The nitrogen atom is protonated, hence they are positively charged and generally water soluble. They are generally synthesized from amino acids particularly lysine, tyrosine, tryptophan. However, the carbon skeleton of some alkaloids contains a component derived from the terpene pathway. Several different types, including nicotine and its relative, are derived from ornithine, an intermediate in arginine biosynthesis.

Alkaloids were classified according to the plants genera in which they occurred. More than 2000 alkaloids are known of which 10-15% are produced in plants of nearly 40 plant families. They may occur in leaves (nicotine), bark (quinine) and roots (reserpine). Earlier they were named after the plant that they were obtained from eg. Papaverine (*Papaver somniferum*), Ephedrine (*Ephedra*), Cinchonine (*Cinchona*), Atropine (*Atropa*), Senecionine (*Senecio*), Strychnine (*Strychoa*), Ergotine (*Ergot*), Piperine (*Piper*) but now they are classified according to the main ring system: Caffeine is a purine-typed alkaloid similar to nucleic acids bases adenine and guanine. The pyrrolidine (five-membered) ring of nicotine arises from ornithine; the pyridine (six-membered) ring is derived from nicotinic acid.

The role of alkaloids in plants is in defense against predators (insect, animal attack) like alkaloid from plants such as Lupines is poisonous for grazing livestock and may become fatal in large amounts. However one group of alkaloids pyrrolizidine is tolerated by herbivores and may also be used in their own defence. Two forms of pyrrolizidine alkaloids are the non-toxic N-oxide found in plants which is reduced to toxic tertiary form in the digestive tract of herbivores. However some adapted herbivores can convert the toxic form back to non-toxic N-oxide eg. senecionine (*Senecio*). These herbivores store these N-oxide in the bodies against own predators. Alkaloids may also act like hormones and function as plant stimulants or regulators of growth, metabolism and reproduction.

Nearly all alkaloids are also toxic to humans when taken in large quantity eg. Strychnine, atropine, coniine (poison hemlock) are poisoning agents. At lower doses they are pharmacologically useful eg. morphine, codeine, scopolamine are used in medicine. Other alkaloids cocaine, nicotine and caffeine are used non medically as stimulants. On a cellular level their mode of action is variable. They may interfere with components of nervous system especially the transmitters or they affect membrane transport, protein synthesis or the enzyme activities.

Alkaloid Class	Example	Other Representatives and functions
Quinolizine	  quinine cinchonine ( <i>cinchona</i> )	Anti malaria
Isoquinoline	  papaverine ( <i>Papaver somniferum</i> )	morphine codeine berberine Analgesic, cough treatment
Indole	  vindoline ( <i>Catharanthus roseus</i> ) (Rauwolfia serpentina) Hypertension	vinblastine reserpine strychnine Strychnos, Eye disorder, rat poison Ergotamine Ergot
Pyrrrolizidine	  senecionine	retrorsine
Quinolizidine	  lupinine <i>Lupinus</i>	Heart function cytisine
Tropane	  atropine <i>Atropa belladonna</i>	scopolamine cocaine Antidote to poison, dilation
Piperidine	  nicotine <i>Nicotina tabaccum</i>	coniine <i>Conium sp</i> Stimulant, tranquilizer Poison
Purine	  caffeine <i>Theobroma coca</i>	<i>Ricinus sp</i> Ricinine Stimulant

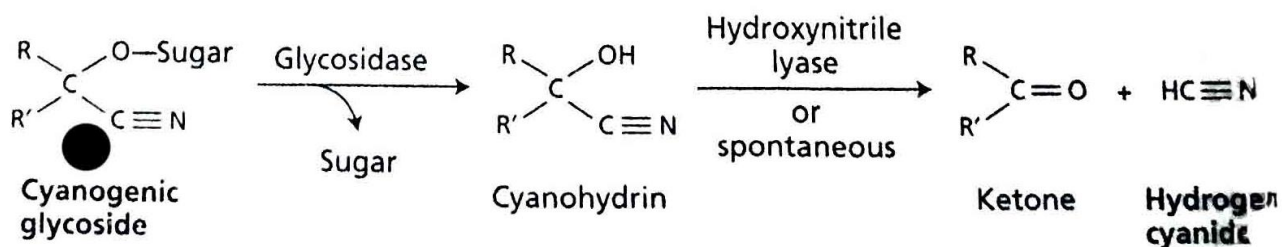
## CYNOGENIC GLYCOSIDE AND GLUCOSINOLATES

Various nitrogenous protective compounds other than alkaloids are found in plants. Two groups of these substances- Cyanogenic glycoside and glucosinolate, are in themselves non-toxic but are readily broken down to give volatile poisons when the plant is crushed. Cyanogenic glycoside release the well-known poisonous gas hydrogen cyanide (HCN).

### Cyanogenic glycosides

As the name suggests the Cyanogenic glycosides are glycosides containing a cyanide group. Cyanogenic glycosides are not normally broken down in the intact plant because the glycoside and the degradative enzymes are spatially separated, in different cellular compartments or in different tissues. In sorghum, for example, the cyanogenic glycoside *dhurrin* is present in the vacuoles of the epidermal cells, while the hydrolytic and lytic enzymes are found in the mesophyll. The breakdown in plants is a two-step-enzyme process. Species which produce the cyanogenic glycosides also make the enzymes required for their breakdown into sugar and HCN:

1. In the first step sugar is cleaved by glycosidase an enzyme which separates sugar from the molecule to which it is linked.
2. In the second step the resulting hydrolyzed product  $\alpha$ -hydroxynitrile or cyanohydrins can decompose spontaneously at a low speed to liberate HCN or this step can be accelerated by hydroxynitrile lyase.



Under ordinary conditions this compartmentation prevents decomposition of glycoside. When the leaf is damaged, however, as during herbivore feeding, the cell content of different tissues mix and HCN forms. Cyanogenic glycosides are widely distributed in the plants kingdom and are frequently encountered in legumes, grasses, and species of the rose family.

These cyanogenic glycosides also have a protective function in certain plants. HCN is a fast-acting toxin that inhibit metalloproteins, such as the iron-containing cytochrome oxidase, a key enzymes of mitochondrial respiration. The presence of cyanogenic glycosides deters feeding by insects and other herbivores, such as snail and slugs.

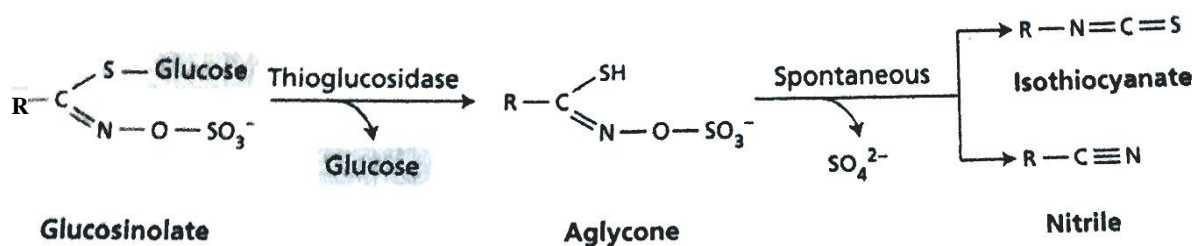
The tubers of cassava (*Manihot esculenta*), a high-carbohydrate, staple food in many tropical countries, contain high levels of cyanogenic glycosides. Traditional processing methods, such as

grating, grinding, soaking and drying, leads to the removal or degradation of a large fraction of the cyanogenic glycosides present in cassava tubers. However, chronic cyanide poisoning leading to the partial paralysis of the limbs is still widespread in regions where cassava is a major food source because the traditional detoxification method employed to remove cyanogenic glycosides from cassava are not completely effective. In addition, many population that consume cassava have poor nutrition, which aggravates the effects of the cyanogenic glycosides. Efforts are currently under way to reduce the cyanogenic glycosides content of cassava through both conventional breeding and genetic engineering approaches.

### Glucosinolates

Glucosinolates or mustard oil glycosides, break down to release volatile defensive substances. In brassicaceae and related plant families, glucosinolates gives off the compounds responsible for the smell and taste of vegetables such as cabbage, broccoli, and radishes.

The release of these mustard-smelling volatiles from glucosinolates is catalyzed by a hydrolytic enzyme, called a thioglucosidase or myrosinase, that cleaves glucose from its bond with the sulfur atom. The resulting aglycone, the non-sugar portion of the molecule, rearranges with loss of the sulfate to give pungent and chemically reactive products, including isothiocyanates and nitriles, depending on the condition of hydrolysis. These products function in defense as herbivore toxin and feeding repellents. Like cyanogenic glycosides, glucosinolates are stored in the intact plant separately from the enzymes that hydrolyze them, and they are brought into contact with these enzymes only when the plant is crushed.



As with other secondary metabolites, certain animals are adapted to feed on glucosinolate-containing plants without ill effects. For adapted herbivores, such as the cabbage butterfly, glucosinolates often serve as stimulants for feeding and egg laying, and the isothiocyanates produced after glucosinolates hydrolysis act as volatile attractants.

Most of the recent research on glucosinolates in plant defense has concentrated on rape seed or canola (*Brassica napus*), a major oil crop in both North America and Europe. Plant breeders have tried to lower the glucosinolates levels of rapeseed so that the high-protein seed meal remaining after oil extraction can be used as animal food. The developed varieties with low glucosinolates

levels in seeds but high glucosinolates levels in leaves are able to hold their own against pests and still provide a protein-rich seed residue for animal feeding.

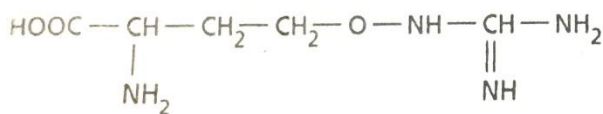
### NON-PROTEIN AMINO ACIDS

Many plants contain unusual amino acids called non-protein amino acids, that are not incorporated into protein but are present instead in the free form and are biochemically important act as protective substances. Non-protein amino acids are often very similar to common protein amino acids. Canavanine, for example, is a close analog of arginine, and azetidine-2-carboxylic acid has a structure very much like that of proline.

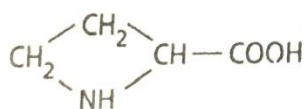
Non-protein amino acids exert their toxicity in various ways. Some block the synthesis or uptake of protein amino acids; others, such as canavanine, can be mistakenly incorporated into proteins. After ingestion, canavanine is recognized by the herbivores enzyme that normally binds arginine to the arginine transfer RNA molecule, so it becomes incorporated into protein in place of arginine. The usual result is a nonfunctional protein because either its tertiary structure or its catalytic site is disrupted.

Plants that synthesized non-protein amino acids are not susceptible to the toxicity of these compounds. The jack bean (*Canavalia ensiformis*), which synthesizes large amounts of canavanine in its seeds, has protein-synthesizing machinery that can discriminate between canavanine and arginine and it does not incorporate canavanine into its own proteins.

#### Nonprotein amino acid

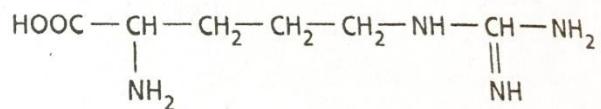


Canavanine

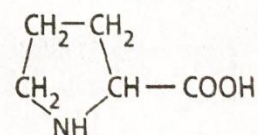


Azetidine-2-carboxylic acid

#### Protein amino acid analog



Arginine



Proline

