B. Sc. III Year

Alkaloids

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Alkaloids

- Alkaloids are physiologically active basic nitrogenous compound containing at least one nitrogen atom.
- Alkaloids are plant originated and most of the alkaloids contain nitrogen atom is a part of heterocyclic ring but some alkaloid like ephedrine and adrenaline it is a part of side chain.
- The name alkaloid is due to alkali like substance.
- General properties of alkaloids :
- i) Most of the alkaloids are colourless, crystalline and non volatile solids.
- ii) Alkaloids are insoluble in water and soluble in organic solvent.
- iii) They have bitter taste and optically active leavo rotatory compounds.
- iv) Alkaloids are basic in nature.
- v) They contain at least one nitrogen atom.

Classification of Alkaloids

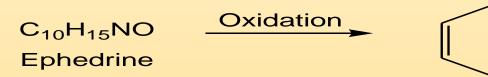
 Alkaloids are classified on the basis of nature of ring system present in the alkaloid structure as follows.

S.No.	Name of the alkaloid group	Ring system present	Examples
1	Phenyl-ethylamine group	CH ₂ -CH ₂ -NH ₂	Ephedrine, adrenaline.
2	Pyrrolidine group		Hygrine, gramine,
3	Pyridine-piperidine group		Piperine

S.No.	Name of the alkaloid group	Ring system present	Examples
4	Pyridine-pyrrolidine group		Nicotine
5	Quinoline group		Quinine, chinchonine
6	Isoquinoline group	N	Papaverine
7	Phenanthrene group		Morphine, codeine
8	Indole group		Reserpine

Constitution of Ephedrine

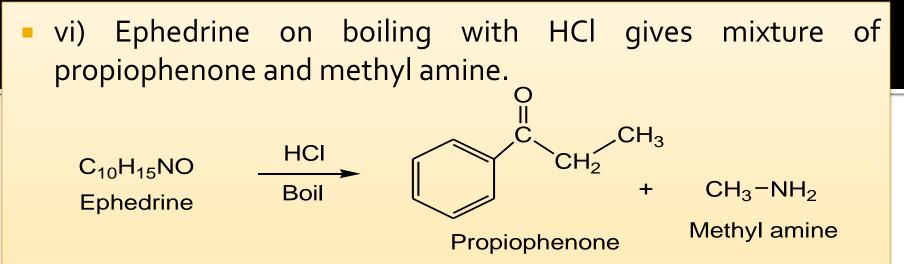
- i) Qualitative analysis shows ephedrine contains C, H, N and O elements.
- ii) Quantitative analysis shows molecular formula of ephedrine is C₁₀H₁₅NO
- iii) Ephedrine on oxidation with oxidizing agent gives benzoic acid.



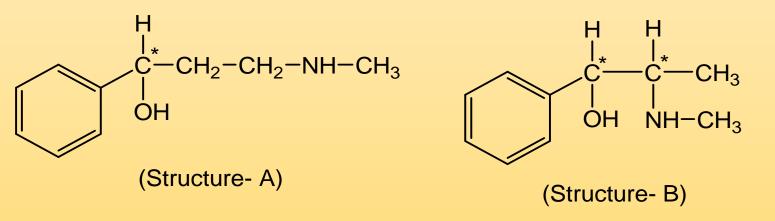


 It indicates that, ephedrine contains at least one benzene ring with one side chain C₄H₁₀NO C₄H₁₀NO

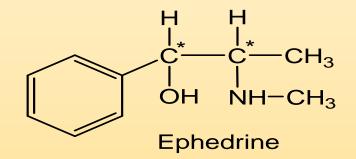
- iv) Ephedrine on treatment with nitrous acid gives nitroso compound.
 - $C_{10}H_{15}NO + HNO_2 \longrightarrow Nitroso compound$ Ephedrine
- It indicates that, ephedrine is a secondary amine.
- v) Ephedrine on benzoylation with benzoyl chloride gives dibenzoyl derivative.
 C₁₀H₁₅NO + C₆H₅COCI → Dibenzoyl derivative of ephedrine Ephedrine
- It indicates that, one molecule of benzoyl chloride is utilized for benzoylation of one –NH group and second molecule of benzoyl chloride must be utilized for benzoylation of one –OH group.
- Therefore, ephedrine contains one –NH and one –OH group.



 It indicates that, formation of propiophenone and methyl amine is possible only when the ephedrine possesses one of the following structures.

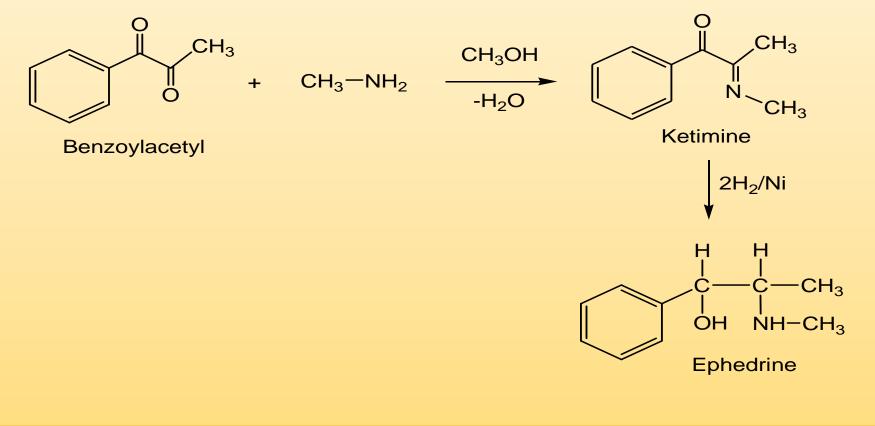


 Out of these two structures, only Structure-B undergo hydramine fission on boiling with HCl to produce propiophenone and methyl amine. Hence Structure-B is more possible structure of ephedrine as follows.



Synthesis of Ephedrine from 1-phenyl propane-1,2-dione (Benzoylacetyl)

 Benzoylacetyl on condensation with methyl amine in methanol to give ketimine, which on reduction with H₂/Ni gives ephedrine.

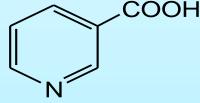


Constitution of Nocotine

- i) Qualitative analysis shows nicotine contains C, H and N elements.
- ii) Quantitative analysis shows molecular formula of ephedrine is C₁₀H₁₄N₂
- iii) Nicotine on oxidation with chromic acid gives nicotinic acid.

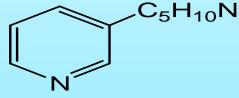


C₁₀H₁₄N₂ Nicotine

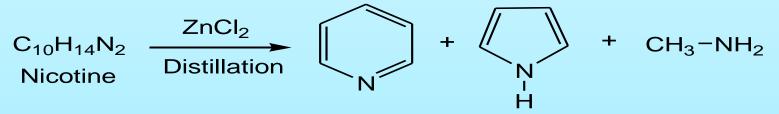


Nicotinic acid

It indicates that, nicotine is a pyridine ring with one side chain at 3-position.



- iv) Nicotine on treatment with methyl iodide gives dimethiodide.
 - $C_{10}H_{14}N_2 + 2 CH_3I \longrightarrow$ Dimethiodide Nicotine
- It indicates that, two nitrogen atoms in nicotine are tertiary.
 One nitrogen atom is present in the pyridine ring and other nitrogen atom may be present in side chain.
- v) Nicotine is distilled with zinc chloride gives pyridine, pyrrole and methyl amine.

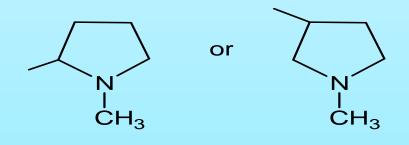


 It indicates that, nicotine contain pyridine ring with side chain pyrrole containing nitrogen atom may be tertiary.

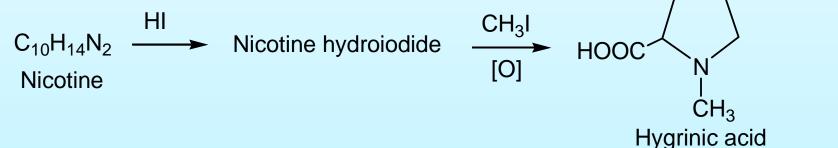
- vi) Nicotine on reduction, it utilize three H₂ molecule for reduction.
- It indicates that, nicotine contain pyridine ring with side chain is saturated.
- vii) Nicotine on heating with HI gives compound A and methyl iodide.

 $C_{10}H_{14}N_2 + HI \longrightarrow Compound A + CH_3I$ Nicotine

 It indicates that, side chain contain pyrrolidine ring with –NCH₃ group and the attachment of this side chain may be either at 2 or 3 position.



 viii) Nicotine on treatment with HI gives nicotine hydroiodide. Which on again methylation and then oxidation gives hygrinic acid.



- It indicates that, attachment of –N methyl pyrrolidine ring (side chain) at 2-position to pyridine ring at 3-position in nicotine structure.
- Therefore possible structure of nicotine is as follows.



Synthesis of Nocotine from Nicotinonitrile

Synthesis of nicotine from nicotinonitrile as follows.

