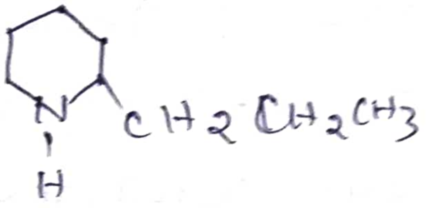
Conine

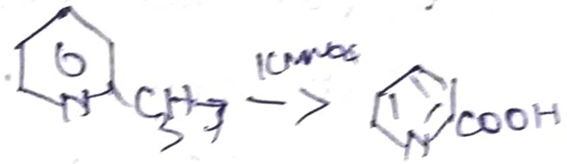
$C_8H_{17}N$ - B.P : 166-167°c - $[\alpha]_D$ +15.7°

i) Occurs in oil of hamlock

ii) When distilled with Zn dust; conine is converted into conyrine $C_8H_{11}N$



$C_8H_{19}N$ (conifne)

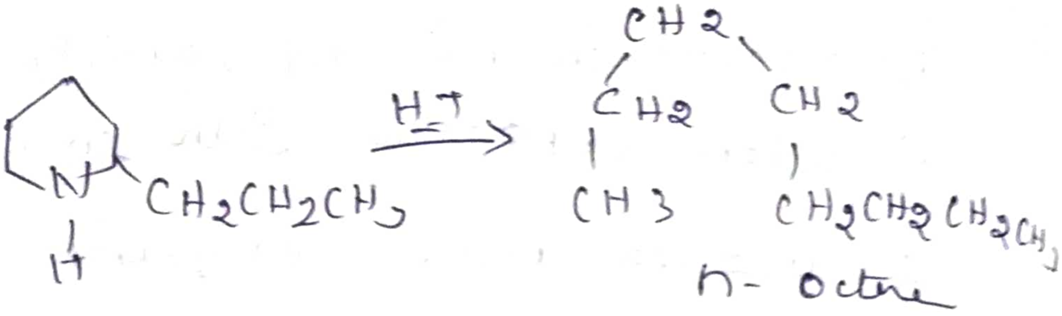


pyridine-2-carboxylic aci

give oxidation of conyrine T persorgate gives pyidine -2- carbonyl acid (α-picolinic acid it follows that a pyridine nucleus is present with a side chain in the 2-position

iii) This side chain must catain 3 corban atoms, since e are lost Conyrine 11 oxidysd This side-Chain is therefore either n-penyl or ysotopyl and it was defuialy shown to be n-propyl by the thef that when heated ε hydriodic acid at 300°C undero Pressure, coniine Forms n-actane

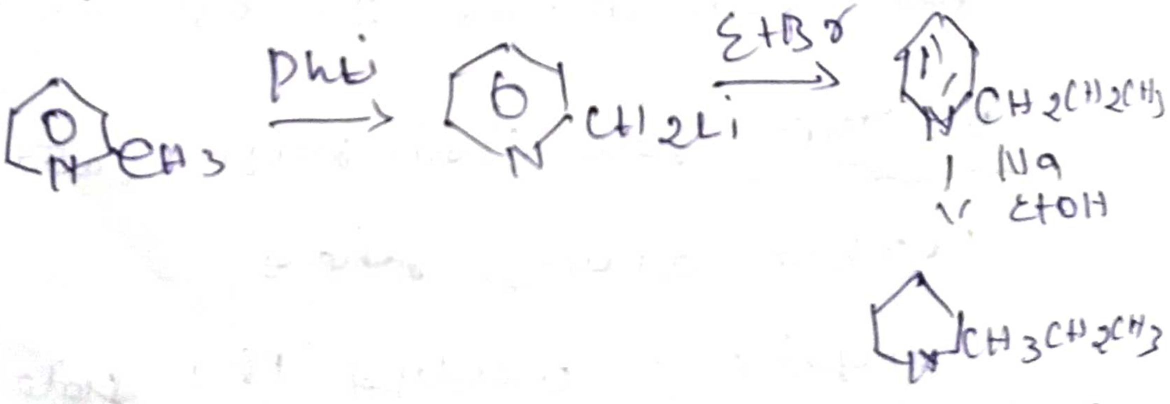
iv) had the size Chain been Isophopyl, them the expected



v) For this evidence it therefore Follow that conine is - 2 - n - propylppiridine and this has been confirmed by syntly

The racemic conine was resolved by menes of (+) - tort aric acid and the (+). Obtuned

conine has also been sythesized From 2 - methyl pyridine and Phenyllithium as Follows



piperine ($C_{17}H_{19}NO_3$) M.P 128 - 129.5°C

-> occurs in pepper (black)

hydrolysis of pipperine with alkali gives piperic acid and piperidine Thus the alkaloid is the piperidine amide of piperic acid

$$C_{17}H_{19}NO_3 + H_2O \xrightarrow{KOH} C_{12}H_{10}O_4 + C_5H_{11}N$$

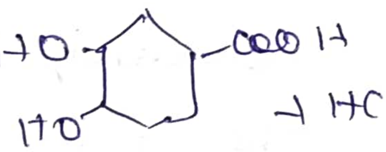
Piperidine

since piperidine is hydropyridine, the structure of piperine rest on the elucidation of that of piperic acid

the volume test show that piperic acid contain one carboxyl grp and 2 double bonds.

When oxidised T permanganate piperic acid gives first piperonal and then piperonylic acid at 200°c under pressure piperonylic acid forms protocatechuic acid (3,4-di hydroxybenzoic acid

$C_8H_6O_4 + H_2O \xrightarrow{HCl}$



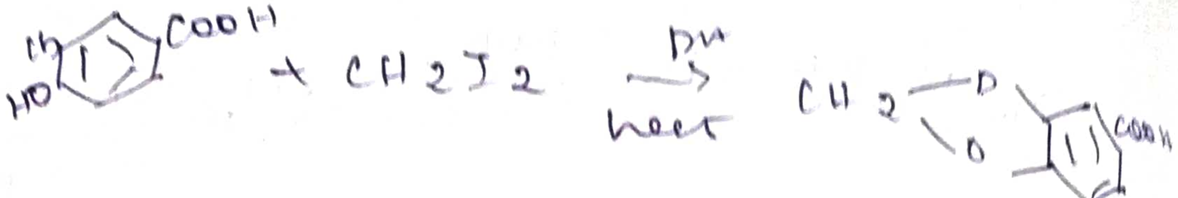
$+ HCHO$

piperonylic acid

Protocatechuic acid

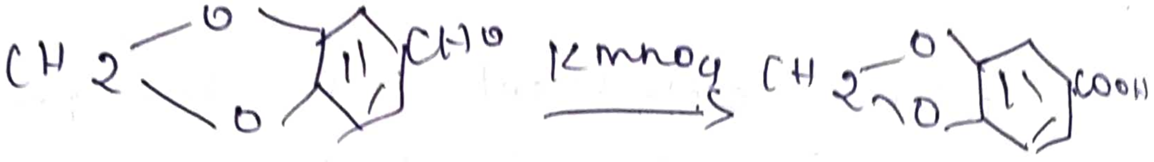
Since one atom of carbon is elimination and there are no free hydroxyl grps in piperonylic acid the structure of the acid is probably the methylene ether of protocatechuic acid

Piperonylic acid is 3,4-methylene dioxy benzoic acid) this has been



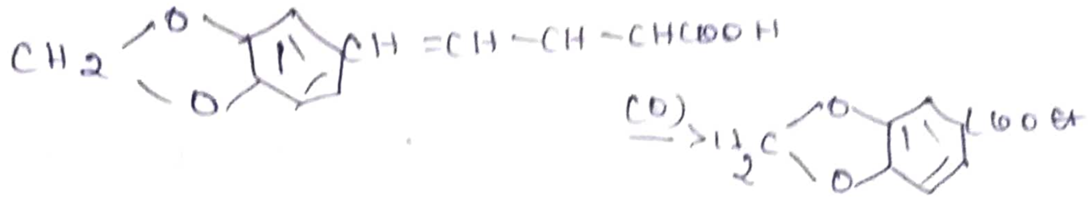
Piperonyli acid

Further we since Reperonal (analogy) gives piperyle acid on oxidation piperonal is therefore 3,4, methylenedioxy-benzehldyele



From thie resuts of Oxydative deeyradation it therefore follows that piperic acid is benzene derivative contaniy any one side chain It is the side chain that contains the 2 double bonds (the ready addition of bromine shows the presence and since the careful oxidation of piperic and gives tartaric acid in addition to piperonal and piperonylic acid the side chain is a straight chain

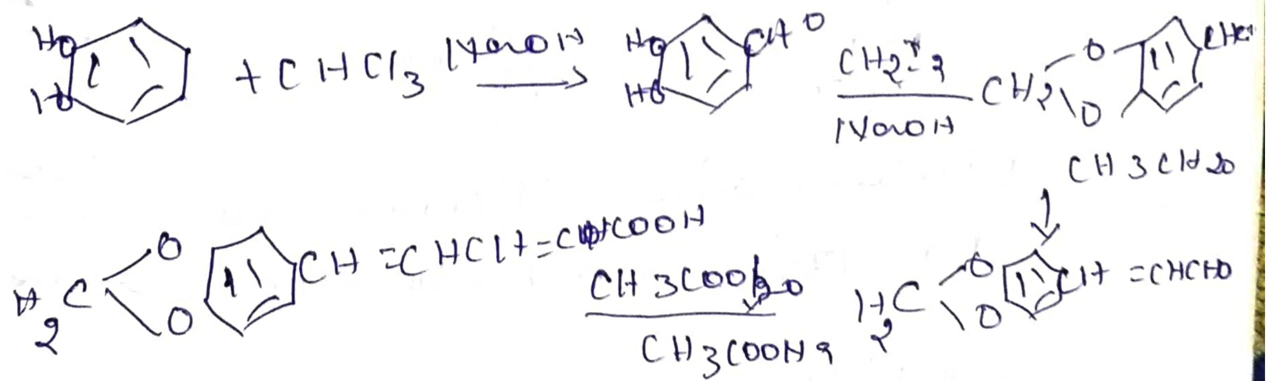
If we assume (7) as the structure of piperic acid then all of the foregoing paths of oxidation may be accounted for



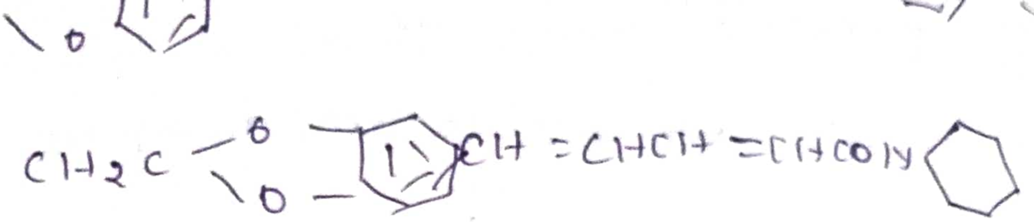
+ HOOC CHOHCHOHCOOH

This has been confirmed by synthesis Claolenburg et al' 1894)

Piperonal (prepared the Reimer Tiemann rxn) is condensed with acetaldehyde in the presence of sodium hydroxide and the salt of them heated with acetic anhydride in the presence of sodium acetate.



When the acid chloride of piperic acid is heated with piperidine in benzene solution piperine is formed; thus piperine is the piperidine amide of piperic acid.



Piperine

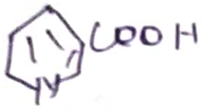
The Stare Chemestry of piperine has been show to be trans across the double bonds the cis, cis Steroisomer is Chavicine;

It also occurs in pepper.

Nicotine: $C_{10}H_{14}N_2$ - B.P 247°C

Tobacco alkaloid

$C_{10}H_{14}N_2 \xrightarrow[\text{[O]}]{KMnO_4}$



Nicotine

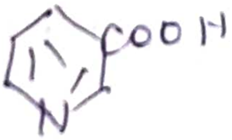
Dimethyl sulphuric acid (or) nitric acid

Nicotinic acid

occurs naturally Of $[\alpha]_D - 169$

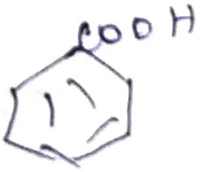
Picolinic acid

mp 137°C



Nicotinic acid

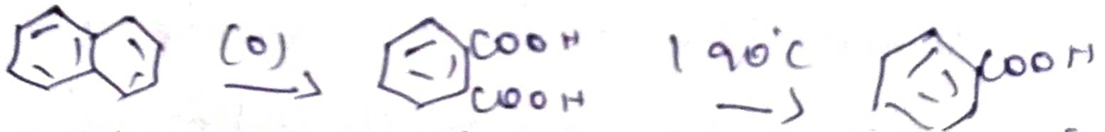
m.p 234-237°C



isonicotinic acid

mp 317°C

isoniconitc acid



quinoline quinolinic acid nicotinic acid