

ALKALOIDS AND TERPENES

⊙ Alkaloids are defined as a class of organic nitrogenous bases, generally of plant origin, which have structure containing one or more nitrogen heterocyclic rings & have marked physiological action.

Above definition not perfect and does not cover all alkaloids.

i (i) ~~eg~~ ephedrine → N is not present as a part of heterocyclic ring

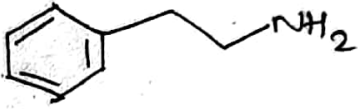
(ii) Pepsine → Neither basic nor possess any toxic physiological action
(from black pepper)


(iii) Purines → Conforms above definition but not considered in alkaloids


(iv) Alkaloids, not only plant origin but also of animal origin & from synthesis are known.

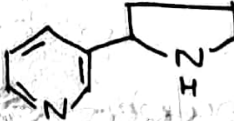
Classification of alkaloids

- ① According to genus in which they occur
Eg: Ephedra alkaloid, Cinchona alkaloid etc
- ② According to their use/physiological activity
Eg: Analgesic alkaloid, Cardioactive alkaloid etc
- ③ Based on prominent heterocyclic ring system present in them.

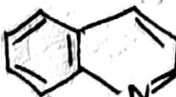
(a) Phenylethylamine alkaloid 


(b) Pyridine alkaloid 

(c) Pyrrolidine alkaloid 

(d) Pyridine - pyrrolidine alkaloid 

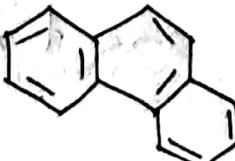
(e) Piperidine alkaloid

(f) Quinoline alkaloid 

(g) Isoquinoline alkaloid 

(h) Indole alkaloid 

(i) Tropane alkaloid 

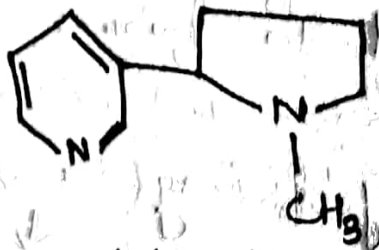
(j) Phenanthrene alkaloid 

General Properties

- (1) → Majority alkaloids are colourless crystalline solids except (liquid) cocaine, nicotine etc.
- (2) → Liquid alkaloids — Insoluble or sparingly soluble in water
Soluble in organic solvent ethanol, ether, chloroform etc.
- (3) → Basic in nature
(so react with acid to form salt)
↓
soluble in H_2O
- (4) → Optically active, majority being dextrorotatory
↓
rotate plane polarised light to left
- (5) → Possess significant physiological activity
- (6) → Alkaloids in mineral acid react with certain reagent to form compound with characteristic colour & M.P.
These are used for identification of alkaloids & hence known as alkaloid reagent

NICOTINE (N-Methyl-2- β -pyridylpyrrolidine)

- chief source — Tobacco plant
(highest in leaves, depending on plant variety, it may vary from 0.6% to 8%)



Nicotine

physiological activity:

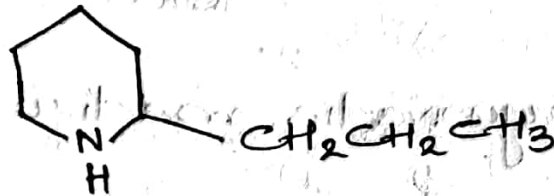
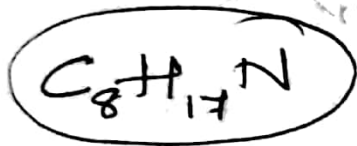
- Extremely poisonous
- In small dose — temporarily stimulate central nervous system, afterwards cause depression.
- Increase heart beat — cause constriction of blood vessel, thereby B.P.
- Highest dose (30-50 mg) — lethal & cause respiratory paralysis and death.
- Long term inhalation through tobacco smoking produce lung cancer & bronchial asthma

uses

- In dilute solution - used as insecticide
- Destroy lice and mite on animals like sheep.

CONIINE (α -n-propylpiperidine)

- Source - Hemlock herb
(occurs in seed & other part of herb as its malic acid & caffeic acid)



Physiological activity

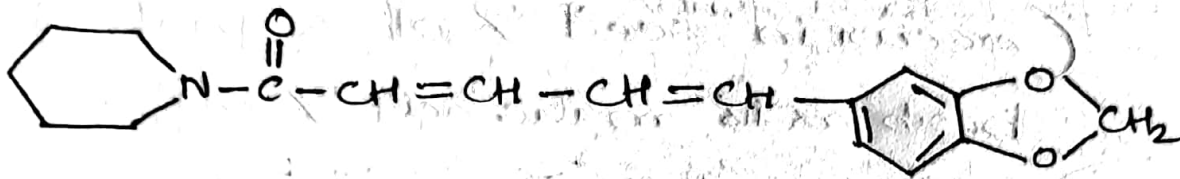
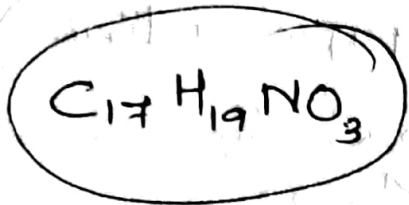
- Highly poisonous
- Affect Nervous system (causing paralysis followed by convulsions & finally death)

→ uses :

Oil of hemlock - contains ~~hemlock~~ coniine as a deadly poison - (Early times to kill criminals and traitors condemned to death) Only in early period.

PIPERINE (α -n-propylpiperidine)

→ Source — Pepper



physiological activity

→ Not toxic

→ Ingredient in ayurvedic medicine

→ In recent decades — it enhanced digestive capacity
used as analgesic, antipyretic
anti-inflammatory, CNS-depressant

Use:

→ Used in human food, medicine, preservative
in perfumery etc.

TERPENOIDS

- Occur in parts of plants such as flowers, leaves, fruits, stems, seed etc. And are responsible for the ^{fragrance,} ~~fragments~~ associated with these parts.

→ Terpenoids consist of a group of hydrocarbon most of which have molecular formula $(C_5H_8)_n$, or their oxygen derivatives (alcohol, aldehyde, ketone) which possess characteristic pleasant odours.

Essential oils

→ Volatile oils that can be obtained from the sap and tissues of the various parts of plants by steam distillation are called essential oils.

→ chief constituent — Volatile terpenoid hydrocarbons called terpenes, $C_{10}H_{16}$ Sesquiterpenoids & their oxygenated derivative

→ Used ~~as~~ in perfume due to pleasant odour.

* Isolation of essential oil & terpenoids

(a) Isolation of essential oil from plants

Plant parts are macerated & then steam distilled. The steam volatile essential oil distill over along with water. They form a layer separate from the aqueous layer. Oily layer is separated & collected

(Plant Parts \rightarrow Macerated (softened in water)
 \rightarrow Steam distilled \rightarrow essential oil distill along
with water \rightarrow oily layer \rightarrow Separated and
collected)

(b) Separation of the component terpenoids of
the essential oils.

- \rightarrow Separated by fractional distillations.
- \rightarrow Terpenoid hydrocarbons distil first, followed
by oxygenated derivatives.
- \rightarrow Chromatography can be used for the isolation
and separation of terpenoids.

Eg: citral \rightarrow from oil of lemon grass, lemon,
oranges etc

linalool \rightarrow from oils of lavender, rose,
coriander

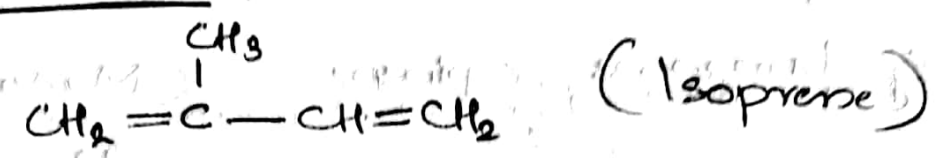
α -pinene \rightarrow from oil of turpentine, ~~eucalyptus~~
eucalyptus etc

Properties

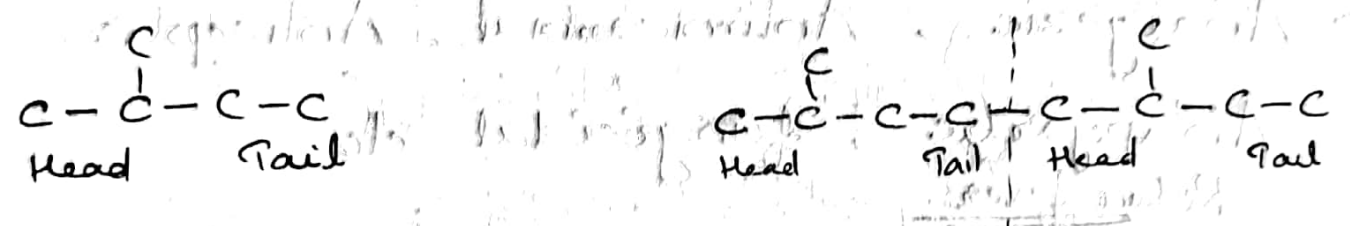
- \rightarrow colourless fragrant liquid, lighter than water
- \rightarrow few are solid terpenoids - in they are insoluble
in water, soluble in organic solvent, steam volatile
and optically active.

* Structural unit of terpenoids — "Isoprene Rule"

→ The skeleton structure of all natural terpenoids are built up of isoprene units. This is known as isoprene rule



"Molecules of all natural terpenoids are built up of isoprene units and these isoprene units are joined head to tail" — Special isoprene rule



Classification

(1) → On the basis of no. of isoprene units

<u>No. of atoms</u>	<u>No. of isoprene unit</u>	<u>Class</u>
10	2	Monoterpenoids
15	3	Sesquiterpenoids
20	4	Diterpenoids
25	5	Sesterterpenoids
30	6	Triterpenoids
40	8	Tetraaterpenoids (Carotenoids)
>40	>8	Polyterpenoids

(2) → further classification.

(a) Acyclic terpenoids — Terpenoids having open-chain structures
Eg: Citral, Geraniol

(b) Cyclic terpenoids — Terpenoids having rings

Eg: Limonene, α -pinene (Monocyclic, Bicyclic etc)

Uses of Some Essential Oils

(a) Lemongrass oil

→ ^{Pain killer} Analgesic, ^{To kill microbes} Antimicrobial, Antiseptic, Antipyretic, fungicidal etc
Reduce fever

① Skin care and cosmetic products (Soap, lotion

shampoo, tonics)

② Ingredient in air freshener & deodorant

③ Insect repellent (to kill mosquito, ant etc)

④ As aromatherapeutic oil (relieve stress, anxiety etc)

⑤ As analgesic and anti-inflammatory

⑥ To treat bacterial and fungal infection

(ringworm & athlete's foot etc)

and

(b) Eucalyptus oil

→ ~~AD~~ Have analgesic, antimicrobial & antiseptic properties

- ① Antiseptic for wound, burn & ulcers
- ② In perfumes & cosmetics
- ③ Insect repellent
- ④ Liniments and ointment to relieve pain
- ⑤ In mouthwash, toothpaste, cough drops
- ⑥ Inhalant to remove nasal congestion
- ⑦ to treat bacterial infections of the tooth.

(c) Sandalwood oil

→ Have antiseptic, anti-inflammatory, antispasmodic, disinfectant, emollient, sedative properties etc

- ① Ingredient in skin care products.
- ② Inhalant in vapour therapy (Cough, asthma, chest infection etc)
- ③ As a massage oil
- ④ Internal & external antiseptic (wound, ulcers etc)
- ⑤ In perfume, cosmetics
- ⑥ Insect repellent, Mouth freshness.
- ⑦ Ingredient in incense stick, spray, fumigant etc

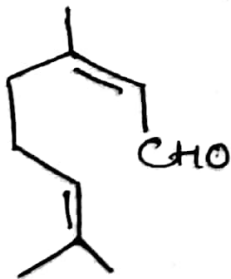
Individual Terpenoids

* Monoterpenoids

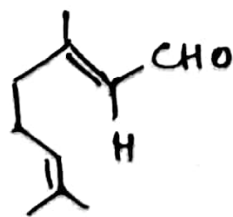
(1) Citral $C_{10}H_{16}O$

→ source - 60-80% in lemon grass oil
- oil of lemon, oranges etc

→ Isolated by fractional distillation of lemongrass oil under reduced pressure - treated with saturated sodium bisulphite solⁿ - to get its crystalline bisulphite addition product - then decomposed by Na_2CO_3 solution to get back citral in pure form

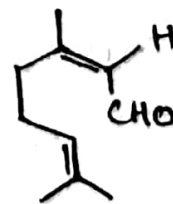


Exhibits geometrical isomerism & exist in two forms



Citral-a or Geraniol

Trans form



Citral-b or Neral

Cis form

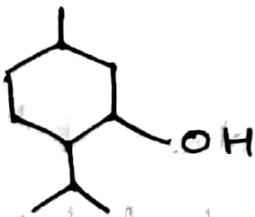
Uses

- ① Preparation of synthetic lemon flavour
- ② Manufacture soap, perfumes, other cosmetics
- ③ Starting material for synthesis of vitamin A
- ④ Preparation of geraniol in rose perfumes

Menthol $C_{10}H_{20}O$

→ Cyclic terpenoid alcohol

→ Source — Peppermint oil upto 80%.



menthol

Uses

→ has antiseptic, analgesic & mild anaesthetic properties

→ Cooling sensation when comes into contact

① In throat lozenges, chewing gum, inhaler

② In gargles, mouthwash, toothpaste

③ In liniments, ointments for pain-relieving

④ face creams, shaving cream.

⑤ Certain brand of cigarettes & candles.

Vulcanisation

- Natural rubber become soft at high temp & brittle at low temp
- shows high water absorption capacity
- Soluble in non-polar solvents
- It is non-resistant to attack by oxidising agent

Improving these properties, a process called vulcanisation is carried out.

"The process by which a network of crosslink is introduced into an elastomer with a view to improve its properties is called vulcanisation"

Eg: Natural rubber vulcanised by heating with small amount of sulphur at $110^{\circ}\text{C} - 140^{\circ}\text{C}$ — In the presence of certain substance like butyraldehyde-~~aniline~~ aniline, di-*o*-tolylguanidine or zinc dimethyl dithiocarbonate — Such substance called 'accelerators'

Advantages

- Introduction of short chains of sulphur atoms as cross links between polymer chain
- ↓
- This introduce stiffness, strength, resilience

- Thus greater tensile strength, extendability, resistance to wear and tear, mouldability.

→ stiffness depend on amount of S added

Eg: For tyre, belts etc - 3-5% S added

For battery case - 30% S added

Ebonite or hard rubber - 32% of S