

## *The Alkaloids*

*Alkaloids* (alkali-like) are defined as organic nitrogenous compounds of plant origin that are physiologically active, ending in the suffix "*ine*".

Plants have been a rich source of alkaloids but some are found in animals, fungi, and bacteria. Among the plants, the *angiosperms* are rich in alkaloids.

The following families represent good examples of plants which contain alkaloids:

- Leguminosae.
- Papaveraceae.
- Ranunculaceae.
- Rubiaceae.
- Solanaceae.
- Berberidaceae.

The Labiatae and Rosaceae are almost free of alkaloids; the *gymnosperms* only rarely contain alkaloids.

The names of alkaloids are obtained in various ways:

- ✓ From the *generic* name of the plant yielding them as *atropine*.
- ✓ From the *specific* name of the plant yielding them as *cocaine*.
- ✓ From the *common* name of the drug yielding them as *ergotamine*.
- ✓ From their *physiologic activity* as *emetine*.
- ✓ From the *discoverer* as *pelletrine*.

Alkaloids usually contain one nitrogen atom, but some may contain up to 5.

The nitrogen may exist as a primary amine ( $\text{RNH}_2$ ), as secondary amine ( $\text{R}_2\text{NH}$ ), or as a tertiary amine ( $\text{R}_3\text{N}$ ).

As the nitrogen atom bears an unshared pair of electrons, such compounds are basic and resemble ammonia's chemical properties. The degree of basicity varies greatly, depending on the structure of the molecule and the presence and location of

Like ammonia, the alkaloids are converted into their salts by aqueous mineral acids, and when the salt of an alkaloid is treated with hydroxide ion, nitrogen

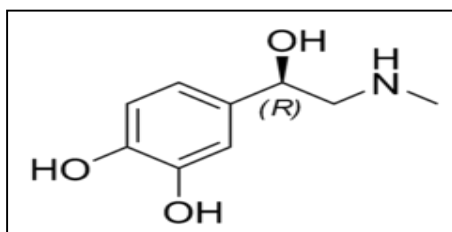
gives up a hydrogen ion and the free amine is liberated. The quaternary ammonium compound have no proton to give up thus is not affected.

The alkaloids, like other amines, form double salts with the heavy metals appear as precipitates, and are used in their identification. These reagents include:

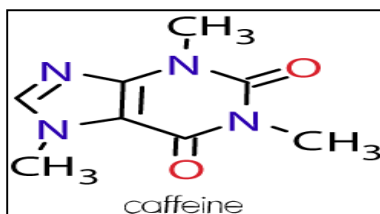
- 1) Wagner's reagent (iodine in potassium iodine).
- 2) Mayer's reagent (potassium mercuric iodide).
- 3) Dragendroff's reagent (potassium bismuth iodide).
- 4) Hagger's reagent (saturated solution of picric acid).

### Types of alkaloids:

1. **True alkaloids:** these characterized by contain nitrogen atom in the heterocyclic ring and derived from amino acids. Example is *Atropine*.
2. **Proto alkaloids:** which contain nitrogen atom without a heterocyclic ring and also derived from amino acids. Examples include *Adrenaline* and *Ephedrine*.



3. **Pseudo alkaloids:** These characterized by heterocyclic ring with a nitrogen atom, but are not derived from amino acids. Example Caffeine.



*In General the Alkaloids are Classified According to Chemical Structure in to two Broad Divisions:*

- A. Non-heterocyclic or atypical alkaloids or biological amines.
- B. Heterocyclic or typical alkaloids, divided in to 14 groups according to their ring structure ,as follows:
  - 1. Pyrrol and pyrrolidine.
  - 2. Pyrrolizidine.
  - 3. Pyridine and piperidine.
  - 4. Tropine.
  - 5. Quinolone.
  - 6. Isoquinolone.
  - 7. Aporphine.
  - 8. Norlupinane.
  - 9. Indole.
  - 10. Indolizidine.
  - 11. Imidazole.
  - 12. Purine.
  - 13. Steroids.
  - 14. Terpenoids.

## *Exp. No.1*

### *[Lab.1]                      Black Pepper*

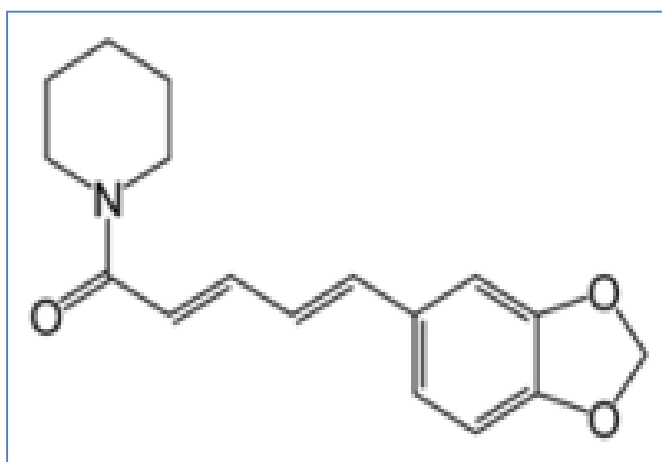
*The* botanical name: **Pipper nigrum** of the family **Piperaceae**. It belongs to the third group of the typical alkaloid, which is the *pyridine* and *piperidine* group.

This plant is a perennial plant producing berry –like and aromatic pungent fruits, that are green when unripe and become red at mature, then the dried berries become **black** and wrinkled producing **black pepper**.

The pepper yields both, black and white pepper according to the method of drying .In that when the ripe and unripe fruit are dried directly under the sun, **black pepper** is the result. While if the fruit is first soaked, and then removed the outer skin, before drying, and then the result is **white pepper**.

The alkaloid extracted from the black pepper is ***piperine***.

Piperine alkaloid is a solid substance essentially insoluble in water. It is a weak base that is tasteless at first, but leaves a burning aftertaste. The molecular formula is  $C_{17}H_{19}NO_3$  ,and the chemical Chemical structure of piperine is:



Piperine

## The Pharmacological Activity of Piperine :

- 1) Piperine aid in the digestion of food due to its stimulation to the digestive enzymes.
- 2) There is some evidence that it has an anticonvulsant activity in the treatment of epilepsy.
- 3) There is some evidence that it has an anticancer and anti-inflammatory activity due to its antioxidant property.

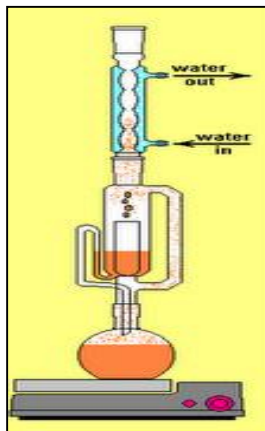
## The Isolation and Identification of Piperine from Black Pepper:

### **1. Extraction:**

**Aim:** to isolate the piperine alkaloid from black pepper. .

### **Equipments:**

- ❖ Large beaker & medium size beakers.
- ❖ Soxhlet instrument.
- ❖ Funnel & filter paper.
- ❖ Water bath.



**Soxhlet**

**Reagents:**

- ❖ 90% ethanol.
- ❖ 10% alcoholic potassium hydroxide.

**Procedure:**

**Method of extraction:** Decoction.

**Plant used:** Piper nigrum.

**Part used:** Seeds.

**10 gm** fine powdered of black pepper in **150 ml** of 90% ethanol for **2 hrs.** In Soxhlet extractor

↓  
Hot filtration

**30 ml** of extract solution concentrated on water bath at **60<sup>0</sup>C**

↓  
Add

**2 ml** of 10% Alcoholic KOH

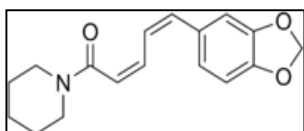
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Filtrate & alcoholic extract is left over night

## Results:

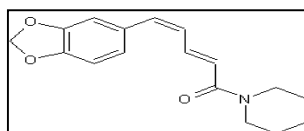
Yellow needles with melting point of  $125^{\circ}\text{C}$  are deposited. Yielding **0.3 gm** of piperine alkaloids.

## Discussion:

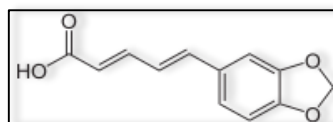
1. The plant is affected by heat; therefore Soxhlet apparatus is used in its extraction.
2. The use of **90% ethanol** is to extract both, the alkaloid and the alkaloidal salt that might be present. (This is true for the extraction of most alkaloids).
3. The use of **alcoholic KOH** is to precipitate the isomers of piperine that are **chuvacine, isochuvacine** and **piperic acid**.



**Chuvacine**

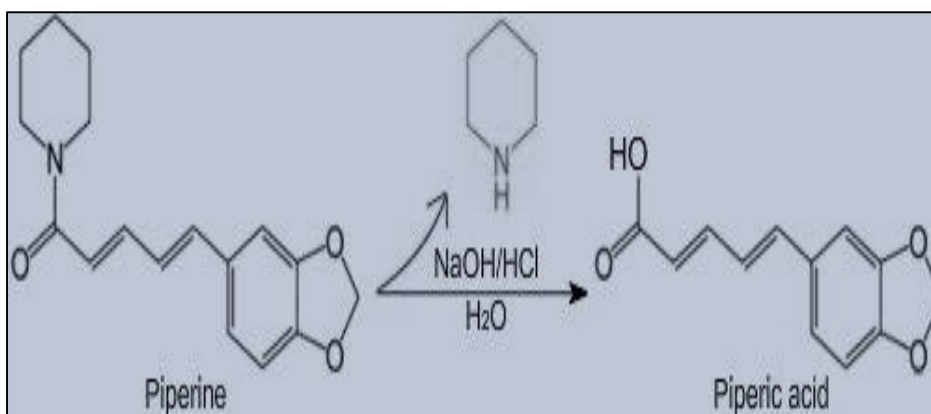


**isochuvacin**



**Piperic acid**

4. Alcohol was used in the preparation of KOH instead of water, since water will hydrolyze piperidine and piperic acid as shown below:



## Quantitative and Qualitative Analysis of Piperine Alkaloid:

### Quantitative Analysis:

This is done by weighing the crystals of piperine alkaloid.

### Qualitative Analysis:

#### The General Chemical Tests :

##### *1. Mayer 's Test:*

**Aim:** to indicate in *general* the alkaloid as other alkaloids.

##### **Equipments and Reagents:**

- ✓ Petri dish.
- ✓ Ethanol.
- ✓ HCl.
- ✓ Mayer's reagent.



### ***Procedure:***

Take few crystals of *piperine alkaloid* and dissolve in few ml<sub>s</sub> of *ethanol*, in Petri dish then add **2 drops** of *HCl*. Then add **2 drops** of *Mayer's reagent*.

### ***Result:***

*White* precipitate will occur.

## ***2. Wagner 's Test:***

***Aim:*** to indicate in *general* the alkaloid as other alkaloids.

### ***Equipments and Reagents:***

- ✓ Petri dish.
- ✓ Ethanol.
- ✓ HCl.
- ✓ Wagner's reagent.

### ***Procedure:***

Take few crystals of *piperine alkaloid* and dissolve in few ml<sub>s</sub> of *ethanol*, in Petri dish then add **2 drops** of *HCl*. Then add **2 drops** of *Wagner's reagent*.

### ***Result:***

***Brown*** precipitate will occur.

## ***3. Dragendorff's Test:***

***Aim:*** to indicate in *general* the alkaloid as other alkaloids.

### ***Equipments and Reagents:***

- ✓ Petri dish.
- ✓ Ethanol.
- ✓ HCl.
- ✓ Dragendorff's reagent.

### ***Procedure:***

Take few crystals of *piperine alkaloid* and dissolve in few ml<sub>s</sub> of *ethanol*, in Petri dish then add **2 drops** of *HCl*. Then add **2 drops** of *Dragendorff's reagent*.

### ***Result:***

**Orange** precipitate will occur.



**Black pepper**

## *The Identification of Piperine Alkaloid By Chromatography (TLC) :*

- ❖ By the use of thin layer chromatography (T.L.C)
- ❖ The stationary phase = *Silica gel G*.
- ❖ The mobile phase = *Toluene: Diethylether: Diaxon (62.5:21.5:16)*.
- ❖ The standard compound =
- ❖ The spray reagent = *Dragendorff's reagent*.
- ❖ Mechanism of separation = *Adsorption*.
- ❖ Developing = *Ascending*.
- ❖ ***Other mobile phases :***  
*Toluene: Ethyl acetate (70:30), Acetone Water: Ammonia (90:7:3)*.

### ***Procedure:***

- 1) Prepare **100ml** of mobile phase, and place it in the glass tank.
- 2) Cover the tank with glass lid and allow standing for **45 minutes** before use.

- 3) Apply the sample spots, and the standard spot on the silica gel plates, on the base line.
- 4) Put the silica gel plate in the glass tank and allow the mobile phase to rise to about *two-third* the plate.
- 5) Remove the plate from the tank, and allow drying, and then detecting the spots by the use of the spray reagent.

**Result:**

Orange spot will appear.

**Study problems:**

- Q1. Give the botanical name of black pepper and mention its alkaloids?
- Q2. What is the pharmacological activity of piperine alkaloids?
- Q3. Give the reasons off the use of alcoholic KOH in the extraction procedure of black pepper?
- Q4. How can you identify an extract containing piperine alkaloids?