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Introduction to Ergot Alkaloids and a Detailed View on Its Pharmacological Application in Medicine

Iqraa Salim Shaikh
Third year student of b. Pharmacy, aiktc, panvel, india

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ABSTRACT: Ergot Is an Indole Class of Alkaloid. It is A Dried Sclerotium Of Fungus Claviceps Purpurea, Which Belong to The Family of Clavicipitaceae. Ergot Has Many Pharmacological Activity Which Includes Anti- Migraine, Vasoconstrictor, Anti-Hypertensive Etc. In This Review Article, We Will Briefly Talk About the Introduction to Alkaloids and Reflect A Light on Ergot as An Alkaloid. We Will Understand How Ergot Is Important for Its Pharmacological Activity. Natural and Semi-Synthetic Ergot Alkaloids Possess Valuable Pharmacological Activities and They Are Widely Used in The Therapy of Human CNS Disorders. Ergotamine Is an Important Chemical Constituent or Ergot Which Shows Important Pharmacological Activity. In Herbal Medicine Ergot Alkaloid Has Shown Promising Results. We Will Discuss About How Ergot Function's as An Important Alkaloid.

I. INTRODUCTION

The Term Alkaloid Was First Proposed by German Pharmacist Carl Friedrich WilhelmMeissnerin 1819 Which Means Alkali-Like. In 1804, German Chemist Friedrich Serturner Isolated Alkaloid (Called Morphium) From Opium Plant from There Study of Alkaloid Began. German Chemist Albert LadenburgHad Done First Complete Synthesis of Alkaloid In 1886.He Worked on Drug Coniine, Which Was the First Important Class of Alkaloids in History of Organic Chemistry. The Term Alkaloid Came Into Lime Light In 1880 Only After A Review Article Which Was Published by Oscar Jacobsen In the Chemical Dictionary of Albert Ladenburg. Also, French Researchers Pierre Joseph Pelletier And Joseph Bienaime Had an Immense Contribution Towards Development of Chemistry of Alkaloid. With the Help of Spectroscopy and Chromatography Technique More Than 12000 Alkaloids Had Been Identified By 2008. By Utilization Of These Techniques' Development Reached Higher in The Study of Chemistry of Alkaloids.

According to LadenburgAlkaloids Defined As "They Are Naturally Occurring Plant Substance, Contain At Least One Nitrogen Atom in A Heterocyclic Ring. They Are Basic in Nature."

Their Basic Properties Are Due to The Presence Of N-Atom Embedded in Heterocyclic Ring. TheirCharacter Resembles with Complex Amines at Some Extent. In the Recent Study of Alkaloid's Chemistry Two More Characteristics Features Were Added in The Definition of Alkaloid i.e., Complex Molecular Structure and Significant Pharmacological Activities.

Now, Definition of Alkaloids Is "Physiologically Active Basic Compounds of Plant Origin, In Which At Least One Nitrogen Atom Forms Part of The System".

About 1000 Alkaloids (Known), Which Belong To 100 Families, 500 Genera, Cover Almost 1200 Species. Scientists Observed That Alkaloids Are Not Evenly Distributed Among the Plant Kingdom. They Have Been Found to Be Absent in Algae and Lower Plants with The Exception of Some Families of Fungi. The Noticeable Example of Fungal Alkaloids Include Ergot Alkaloids.

Except AmaryllidaceaeAnd LiliaceaeFamily, Class of Monocotyledons Plants Does Not Produce Alkaloids. Generally, Dicotyledons Contain Alkaloids Except Some Families Like LabiateaAnd Rosaceae. Almost15% Of Vascular Plants Having Alkaloids Content. There Has Been Observed Fluctuations in The Content of Alkaloid in Different Stages of Various Organ of Plant, Amid Different Seasons as Well as Between Day and Night. Alkaloids That Are Found in Specific Organ of Plants, It Does Not Necessary They Are Synthesized from Those Organs Only. We Can Take an Example Here of Datura And Nicotiana Species, They Are Formed in Roots but Later Translocated to The Leaves. Researchers Invented Various Experimental Techniques Namely Grafting Techniques, Labelling with Radio-Isotopes to Demonstrate This Fact.

Alkaloids Exhibit Optical Activity as They Contain One Or More Asymmetric Carbon Atoms in The Molecule. Isomerization Is the Process Where Compounds Having Same

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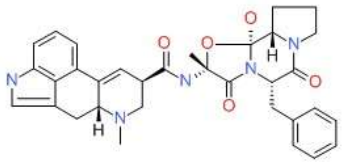
Empirical Formula but Having Different Structure and Properties.

Example:

Antimigraine Activity Of (--)-Ergotamine Was Found to Be 3-4 Times More Than (+)-Ergotamine Isomer.

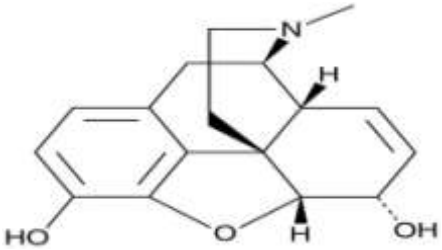
(--)-Ergotamine



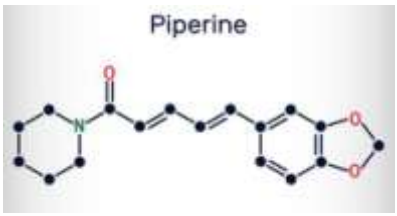
Features:

1. More Acidic Medium Required to Form Their Respective Salt with The Corresponding Acid of Those Alkaloids Who Having Low Pka Values i.e., Weaker Bases.
2. For Strongly Basic Alkaloid (High Pka Values), Comparatively Low Acidic Medium Required to Form Their Respective Salt with Acid.
3. As the Alkaloid Contain Basic Properties, They Are Neutralize by Acids to Form Salts Which in Turn Converted into Free Bases by The Addition of Weak Bases Such as Ammonia, Sodium Carbonate or Calcium Hydroxide.
4. Some Alkaloids Are Neither Acidic nor Basic, They Are Called Amphoteric Alkaloids. This Because Presence of Phenolic Group in Morphine or Presence of Carboxylic Functional Group in Narceine.

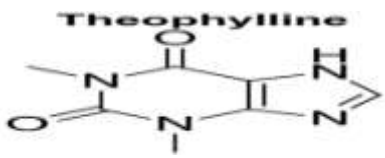
Morphine



5. Piperine, Papaverine, Narceine, Narcotine And Caffeine Are Some of The Alkaloids That Posses Weak Basic Properties and Their Salts Are Unstable.



6. Few Naturally Occurring Alkaloids Act as Neutral or Slightly Acidic Namely, Ricinine And Theophylline.



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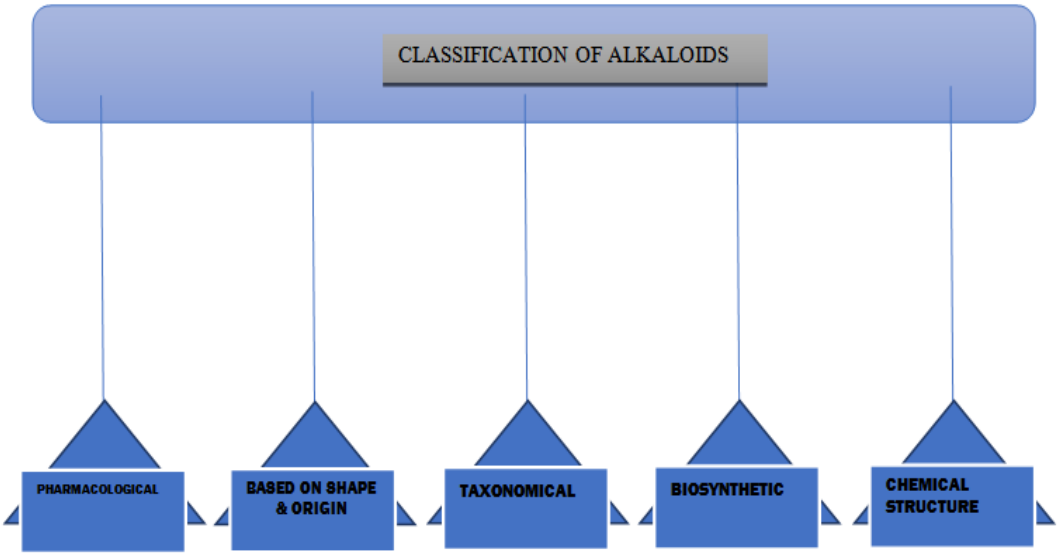

1. Pharmacological Classification

- Alkaloids Show Broad Range of Pharmacological Activities.
- However,This Classification Is Not Commonly Known.
- Examples:

Morphine asNarcotic Analgesic
Quinine Used asAntimalarial
Ergonovine Has Oxytocic Effect.

2. Based on Shape and Origin

- FurtherClassified Into:
- True Alkaloids:

TheyPossess Heterocyclic N-Atom Which Is Derived from Amino Acid.
They Are Basic and Toxic in Nature.
All Are Solid White Except Nicotine-Brown Liquid
Examples: Quinine, Morphine, Cocaine

- PseudoAlkaloids:

TheyGive the Standard Qualitative Test for Alkaloids but They Does Not Contain Many of The Characteristics of Alkaloid.
Examples: Caffeine andConessine.
Exception: Thiamine(Vitamin B1) -They Have All the Properties of Alkaloid but They Are Not Regarded as Alkaloids Because They Are Distributed Almost in Living Matter.

- Proto Alkaloids:

In This Nitrogen Atom Is Derived from Amino Acid but Not A of Heterocyclic Ring.
Examples: Hordenine, Ephedrine, Colchicine, Mescaline, Bascia Angustifolia.

3. Taxonomical Classification

- Based on Taxon (Taxonomic Category) We Can Talk About This Classification.
- Taxonomic Classification Enclosed Variety of Alkaloid Which Based on Their Respective Distribution in A Variety of Plant Families.
- Phyto chemistTook Further Step to Classify Alkaloids Based on Their Chemotaxonomic Classification.
- Families:

Cannabinaceous Alkaloids; E.g., Cannabis Sativa Linn
Solanaceous Alkaloids; E.g., Atropa Belladonna L, Datura Candida

4. Biosynthetic Classification

- ThisClassification Simply Lies on Precursor from Which Alkaloid Synthesized.
- Examples:

Indole Alkaloids -Tryptophan
Phenylethylamine Alkaloids- Tyrosine
Imidazole Alkaloids- Histidine
Piperidine- Lysine
Pyrrolidine Alkaloids- Ornithine

5. Chemical Classification

- This Is the Most Accept Way of Classify Alkaloids Based on Presence of Basic Heterocyclic Ring.
- Examples

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Indole Alkaloids. E.g., Ergometrine, Ergotamine
Pyrrolidine andPyrrole Alkaloids. E.g., Hygrine
Tropane Alkaloids. E.g., Atropine
Pyridine and Piperidine Alkaloid. E.g., Coniine
Pyrrolizidine Alkaloid. E.g., Echimidine
Quinoline Alkaloid. E.g., Quinine, Cinchonine
Imidazole Alkaloid. E.g., Pilocarpine
Isoquinoline alkaloids. E.g., D-tubocurarine
Phenanthrene alkaloids. E.g.,Morphine, Codeine
Purine alkaloids. E.g., Caffeine
Aporphine alkaloids. E.g., Boldine
Steroidal alkaloids. E.g., Conessine
Diterpene alkaloids. E.g.,Aconitine
Alkylamine alkaloids. E.g., Ephedrine

ERGOT ALKALOIDS

Ergot Is an Indole Class of Alkaloid. They Contain 3,4-Substituted Indole Derivatives Having a Tetracyclic Ergoline Ring Structure. Ergot Belong to The French Word "Spur" Which Named Given After the Similarity Between Sclerotia Of Fungus and Spur on Rooster Legs.It Is Known As "Annaamaya" Or "Sraavikaa" In Ayurveda And in Unnani Called "Agrat". ItIs A Dried Sclerotium Of FungusClaviceps Purpurea, Which Belong to The Family of Clavicipitaceae. Usually Claviceps Refers to Club-Like Nature of Sclerotium (Formation of Hardened Mass While Growing of Certain Fungi), Whereas Purpurea Signifies Its Purple Color. ProduceNaturally on Rye Plant. Rye Plant Is the Host and Ergot Are the Parasite. For Good Quality and Quantity of Ergot, Rye Plant Is Best Among All the Host. Commonly Ergot Called Fungal Disease Because in Place of Normal Seeds, Hard Seedlike Structure Formed Termed As 'Sclerotia' Which Indicates Resting Stage of The Fungi. Ergot Alkaloids Are a Diverse Category Of Secondary Metabolites That Have Been Mainly Classified Into 2 Groups I.e Lysergic Acid And Clavine. D-Lysergic AcidDerivatives, aminoalcohol or a short Peptide Chain Is Attached To The Ergoline Nucleus In Amide Linkage Via Carboxy Group In The 8-Position. In Clavine Alkaloid, Methyl or Hydroxymethyl Are Added In Place of Carboxy Group. Lysergic Acid Dimethylamide Or LSD Is The Synthetic Derivative Of Lysergic Acid, Which Is The Key Intermediate In The Biosynthesis of Ergot Alkaloids. During Beginning of Farming, Itself Ergot Infected Grasses, And It Was First Registered Around 600 BC. Due to The Consumption of Bread Which Was Made from Contaminated Rye, The Diseased Widespread in Europe Named Chronic Ergot Poisoning (Ergotism). Also Referred As "Ignis Sacer" Meaning HolyFire Or "St. Anthony's Fire". Symptoms Include for This Disease Such as Hallucinations, Severe Gastrointestinal Upset with Painful Feelings of Intense Heat in The Limbs Due to Severe Restrictions of Blood Flow with Concomitant Loss of Limb. Ergot Alkaloids are Biosynthesized From L-tryptophan and Isoprene 3R-Mevalonic Acid Derivatives Of Dimethylallyl Diphosphate.

Geographical Source

Ergot Are Found Most Part of The Germany, France, Switzerland, Hungry, Czechoslovakia, Russia, India. In India They Are Cultivated inKodaikanal.

Description

We Will Learn About Description of Ergot in Two Ways:

I. Macroscopic Study

- **Size of Sclerotium**—1-4cm Long, 2-7mm Broad
- **Shape**—Fusiform, Sub-Cylindrical, Slightly Curved, Tapering at Both Ends
- **Outer Surface**—Dark or Violet-Black inColor, Longitudinal Furrows, Occasionally Found Small Transverse Cracks.
- **Fractured Surface**—Thin, Dark Outer Layer, Whitish or Pinkish-White Central Zone Pseudo Parenchyma in Which Darker Lines Radiate from The Centre.
- **Odor**—Characteristic
- **Taste**—Unpleasant

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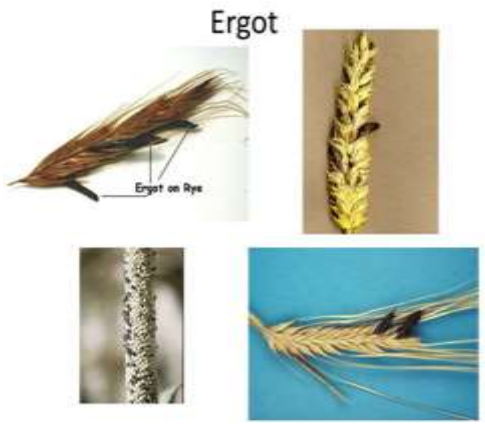
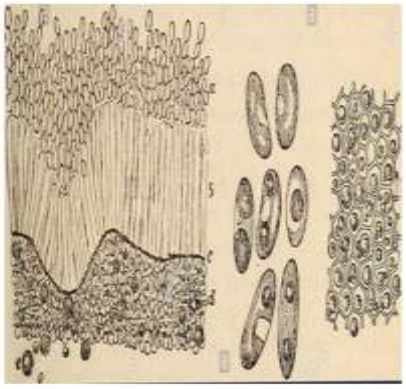




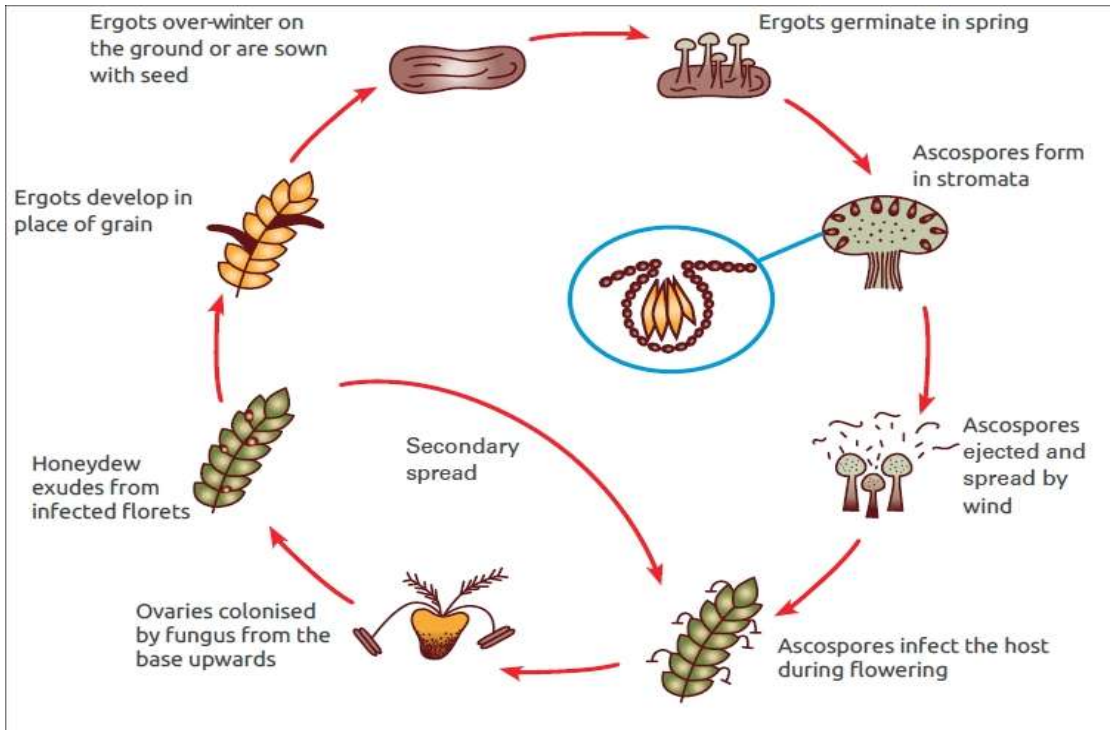
II. Microscopic study

- The Outermost Layer of The Sclerotium Is Made of Thin, Flattened, Polygonal Cells of Purple to Dark Brown in Color.
- Inner Part Is Made Up of Dense Pseudo Parenchymatous Cells Composed of Chitin.
- They Also Contain Cells with Fixed Oil.
- The Mycelial Cells Are Round and Oval and Thick.
- Sclerotium Does Not Contain Starch, Calcium Oxalate, Cellulose or Any of The Lignified Tissue.

LifeCycle of Ergot Alkaloids

The Life Cycle of Fungus Go Through 3 Important Stages of Its Life.

1. Sphacelia Or Honeydew or Asexual Stage
2. Sclerotium Or Ascigerous Or Sexual Stage
3. Ascospore Stage.



1. Sphacelia Or Honeydew or Asexual Stage

- In Spring Season, First Rye Plant Got Infected by Spores of Fungus.
- When Flower Blooms for About One Week, The Spores Are Travel to The Flower Through Wind or Insect from Their They Are Collected at The Base Where Moisture Is Present.

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- There Germination Occur and Formed Filamentous Hyphae and By Enzymatic Action It Enters into The Wall of The Ovary.
- Then Sphacelia Formed Which Is Soft, White Mass on The Surface of The Ovary. A Sweet Viscous Yellowish Liquid Is Secreted During This Stage, Known as Honeydew Contain Reducing Sugars.
- Small Oval Conidiophores Are Abstracted from End of Some Hyphae.
- Because Of The Sweet Taste of Honeydew Insects Like Ants and Weevil Sucks the Sweet Liquid and Carry the Conidiophores to The Other Parts of The Plant and Fungal Infection Spreadin The Rye Plant.

2. Sclerotium Or Ascigerous Or Sexual Stage

- In This Stage Hyphae Go Down into Deeper Parts of The Ovarian Tissue and Replace It by Pseudo Parenchyma Tissue Which Are Compact, Hard, Dark Purple in Color.
- It Forms Sclerotium And This State Called Resting or Dormant Stage of Fungus.
- As the Time Passes Sclerotium Or Ergot Increases in Size and Show Sphacelia Present at Its Apex.
- During Summer, It Collected by Manually or By Machine Then Dried to Remove Moisture Content.

3. Ascospore Stage

- Mature Ergot Falls on The Ground as It Not Collected and They Produce Stalked Like Projection in Spring Season Which Is Known as Stromata.
- Stromata Have Globular Head and Inner Part of These Head There Are Many Flask-Shape Pocket Called Perithecia. These Perithecia Possess Ascospores.
- Inspects or Wind Transport Ascospores To the Other of The Plant as We Discussed in The First Stage.

Ergot Can Also Be Cultivated by Saprophytic Production:

- In This Conidiophores Used for Inoculum. Mature Sclerotia Are Harvested After 6 Weeks of Inoculation. It Can Also Be Picked Up by Hand or Using Machine.
- It Is More Convenient Than Natural Production as It Can Be Produced Throughout the Year and Gives Higher Yield of Alkaloids.

Chemical Constituents

- Ergot Contain Alkaloids as Chemical Constituents
- Alkaloids of Ergot Are Classified into Two Groups: Water-Soluble Group

And Water-Insoluble Groups

- Water-Soluble Groups Also Known as Ergometrine Groups and It Should Contain NLT 15% Of the Total Alkaloid of Ergot.
- Remaining Amount of Ergot Contain Water-Insoluble Group (Ether Soluble)

	Group	Alkaloids
Water-soluble group		
I.	Ergometrine group	Ergometrine, Ergometrinine
Water-insoluble group		
II.	Ergotamine group	Ergotamine, Ergotaminine, Ergosine, Ergosinine
III.	Ergotoxine group	Ergocristine, Ergocristinine, Ergocryptine, Ergocryptinine, Ergocornine, Ertgocorninine

- DextrorotatoryAlkaloids Are Therapeutically Inactive and Levorotatory Alkaloid Are Active.
- They Are Also Contain Histamine, Tyramine and Other Amino Acid as Chemical Constituents.

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- They Are Composed of Ergosterol, Fungi sterol, Mannitol, Lactic Acid, Succinic Acid, Ergonovine, Sclerythrin.
- Putriscine, Cadaverine, Agmatine, And Amino Acid Contribute Color to the Ergot.
- Physiologically Active Alkaloids Obtained from Lysergic Acid.

Let us discuss briefly about main constituents of ergot

i. Ergometrine (Ergovine)

- Nomenclature: [8beta (S)]-9,10-Diadehydro-N-(2-Hydroxy-1-Methylethyl)-6-Methylergoline-8-Carboxamide.
- In 1935 Ergometrine Was First Isolated by C Moir And HW Dudley For Treating Bleeding After Childbirth.
- It Sold Under the Brand Name of Ergotrate, Ergostat, Syntometrine And Many Other.
- It Shows Its Effect Within 15 Minutes After Taken by Mouth and Through I.V Or I.M Its Onset of Action Is Faster.
- In Human, Ergometrine Acts at Alpha-Adrenergic, Dopaminergic, And Serotonin Receptors and Exerts Its Effect on Uterus as It Has Oxytocic Property.
- Ergometrine Gives Blue Fluorescence in Water.

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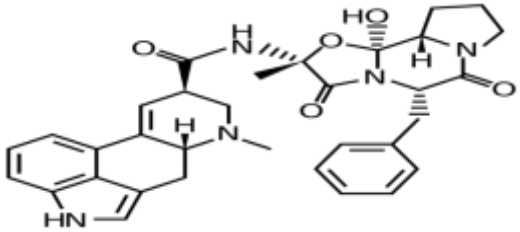
ii. Ergotamine

❖ Nomenclature: (6ar,9R)-N-((2R,5S,10as,10bs)-5



-Benzyl-10b-Hydroxy-2-Methyl-3,6-Dioxooctahydro-2H-Oxazolo[3,2-A] Pyrrolo[2,1-C] Pyrazin-2-Yl)-7-Methyl-4,6,6a,7,8,9-Hexahydroindolo[4,3-Fg]Quinoline-9-Carboxamide.

❖ First Isolated byArthur Stoll At Sandoz in 1918 And In 1921 It Marketed asGynergen.
❖ Ergotamine Is an Alpha-1 Selective Adrenergic Agonist Vasoconstrictor Used to Treat Migraine, Migraine Variants or Histaminic Cephalalgia And Cluster Headache.
❖ It Act as Agonist of Serotonin Receptors Including 5-HT1 and 5-HT2 Subtypes.
❖ Trade Name: Cafergot When It Given with Caffeine andErgomer.
❖ It Can Be Administered by Mouth Or I.V orI.M.
❖ It Metabolized in Hepatic System with Half-Life Of 2 Hours.
❖ It Cannot Be Given Patients with Atherosclerosis, Coronary Artery Disease, Hepatic Disease and Patient Who Taken HIV Protease Inhibitors, Macrolide Antibiotics and Certain Azole Antifungals.

PharmacologicalActivity

Ergot (Ergoline) Derived Compounds Has Broad Spectrum of Pharmacological Activities Among All the Other Natural Compounds. Their Diverse Action Entirely Depends on The Affinities of The Ergoline Ring Towards Different Receptors of The Body Such as Noradrenaline, Dopamine, Serotonin Receptors. They Can Act as Agonist or Antagonist or Sometimes They Show Dual Nature as Partial- Agonist and Antagonist.

Some of Commercially Ergot Derived Compounds and Their Pharmacological Therapy Are Illustrated Below:

Compounds	Pharmacological Therapy
Ergotamine	Anti-migraine, Vasoconstrictor, Can Be Used as Uterotonic
Ergometrine	Uterotonic
Dihydroergotamine	Antihypertensive
Dihydroergopeptine Mixture	Vasodilator
Dihydro-Alpha-Ergocryptine	Anti-Parkinson, Anti-hyperprolactinemic
Bromocriptine	Anti-Parkinson, Anti-hyperprolactinemic
Cabergoline	Anti-ParkinsonAnti-

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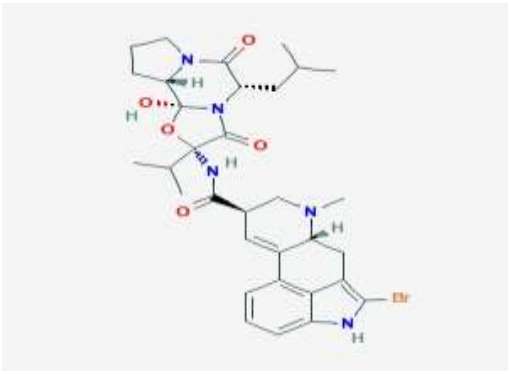
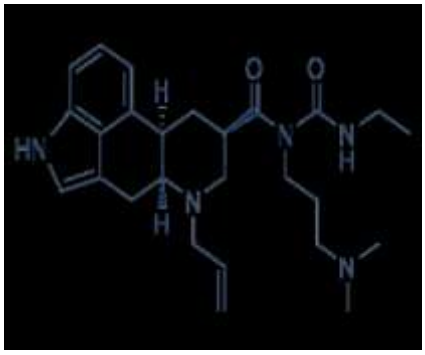
	hyperprolactinemic
Nicergoline	Antihypertensive, Vasodilator
Lisuride	Anti-Parkinson, Anti-hyperprolactinemic, Antimigraine

Due to The Affinity of Adrenergic Receptors, Classical (Natural) Ergot Alkaloids Has Vasoconstrictive and Sympatholytic Adrenolytic Effects. Ergopeptine, Clavines, And Simple D-Lysergic Acid Amides Such as Ergometrine Has Affinity Towards 5-HT Receptors Because Of This, They Show Much Less Adrenolytic Effects and Strong Anti-serotoninergic Action. ErgometrineUsed In Prevention and Treatment of Postpartum Hemorrhage. Sometimes It CausesSide Effects Include Nausea, Vomiting, Precordial Distress and Angina like Pain(Coronary Spasm). Spectrumof Pharmacological Activities Can Be Widened by Changing in Ergoline Ring as Well as Introducing Unnatural Side Chains at the C-8 Substituent. Hydrogenated Derivatives of Ergotamine Has Dominant Adrenolytic Effects with Association of Vasoconstrictive Effect. ErgotamineIs A Partial Agonist of Alpha-Adrenoreceptor and 5-HT Receptors and Used in The Treatment of Migraine by Constrict the Cranial Blood Vessels. Dihydroergotamine A Semi-synthetic Compund, Which Used in The Migraine and Has an Application asAntihypertensive Agent and In Cerebral Dysfunction in The Elderly. The Compound Containing Dihydroergoline Ring Such asNicergoline. It Acts by Blocking Alpha-1-Adrenoceptor, Which Induces Vasodilation and Increases Artial Blood Flow (Antihypertensive). It Has Several Other Functions Such As (A) It Enhances Cholinergic and Catecholaminergic Neurotransmitter (B)Inhibit Platelet Aggregation (C) Increased Utilization of Oxygen and Glucose by Promoting Metabolic Activity. (D) Has Neurotrophic and Antioxidant Properties. BesidesAdrenolytic Effects, Ergotoxine Also Has Inhibitory Effect on Prolactin Which Is the Peptide Hormone Released from The Pituitary Gland. 2-Bromo-Ergocriptine Was First Clinically Important Prolactin Inhibitors Which Is Used to Treat Prolactin-Related Disorders Such as Prolactin-Dependent Mammary Carcinoma, Galactorrhea, Amenorrhea. In 1979 Keller And Da Prada Found That Bromocriptine Also Used To Treat Parkinson's Disease As It Has Dopamine Like Activity Due To Its Interaction With Dopaminergic Receptor Sites. Lisuride, It's Dihydroanalogue Terguride And Pergolide Are Also Came into Picture as Anti- Prolactine And Anti-Parkinson Agents. Cabergoline Is the More Active for Dopamine Receptor (D2) Agonist Than the Bromocriptine and Has Fewer Side Effects. Zifa And Fillion (1992) Revealed in Their Study That, Inspite of Non-Selectivity of Ergoline Towards Heterogenous Family of Serotonin Receptors (5-HT Receptors), They Possess Activity as Agonist and Antagonist Against 5-HT1A and 5-HTA2 Receptors Which Likely to Involved in Psychiatric Disorders Such as Schizophrenia and Depression. By Rearrangement Of Rings C andD of Tetracyclic Ergoline Ring Another Group of Ergoline Synthesize Called Abeo-Ergoline Which Also HasSerotoninergic Effects with Higher Affinity and Selectivity For 5-HT1A Receptors.

2-Bromo-ergocryptine.



Cabergoline



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II. CONCLUSION

From This Review Article We Got toKnow AboutIntroduction of Alkaloids and The Wide Range of Pharmacological Features of Ergot Alkaloids. Ergot Alkaloids Have Remarkable Medicinal Importance Varying from Used in Migraine to Use as Uterotonic. They Are Potent Alpha-Blocker That Caused Contraction of Smooth Muscles. It Can Control Postpartum Bleeding, Used to Treat Some Disorders and Diseases. It Help to Reduce Hypertension by Acting as Vasodilator. They Have Structural Resemblance with Various Neurotransmitter Which Help Them to Interact with The Receptors and Show Their Effects on Different Targets. By Different Modification Of Ergoline Ring, Will Resolve the Problem of Side Effects Which Associated with Classic Drugs.

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