

## Ethnobotany. Lecture 24

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March 25, 2013

# Outline

- 1 Natural product chemistry
  - Polyketides and other small molecules
  - Glycosides
  - Alkaloids



# Natural product chemistry

## Polyketides and other small molecules

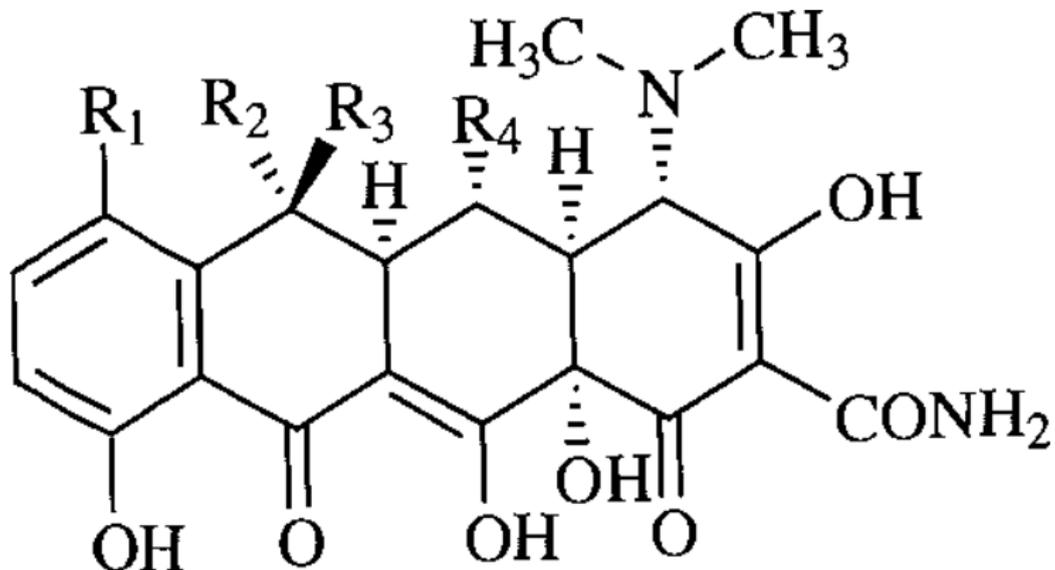


# Polyketides and derived products

- Short molecules with interleaving ketogroups
- Many antibiotics (e.g., tetracycline, erythromycin)



# Tetracycline



# Glycerides

- Saturated fats
- Unsaturated fats, especially omega-n-unsaturated

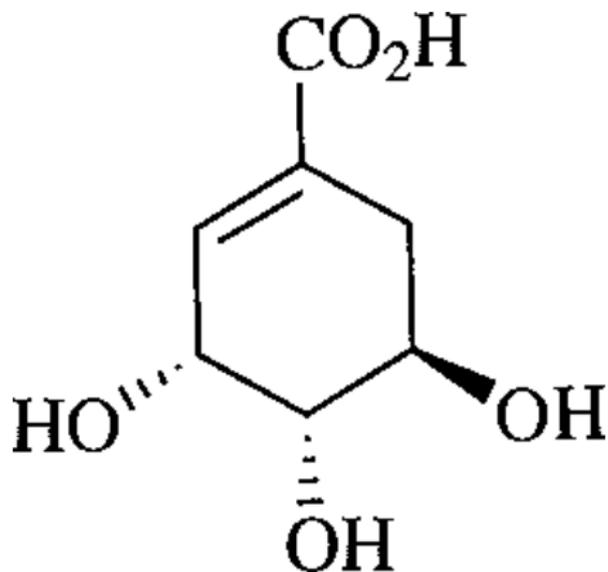


# Shikimic acid and derived products

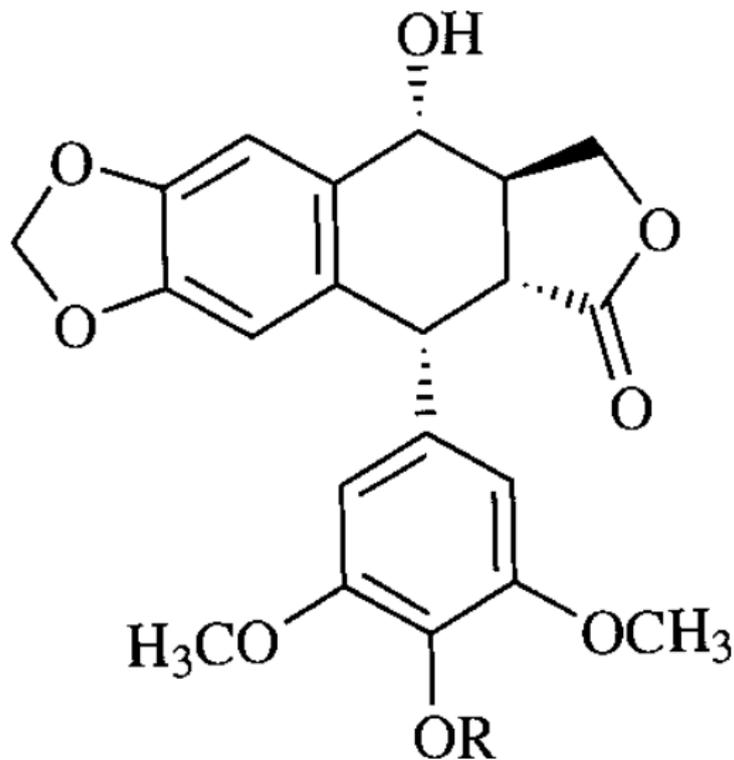
- Phenylpropenes, like eugenol
- Lignans like podophyllotoxin



# Shikimic acid



# Podophyllotoxin

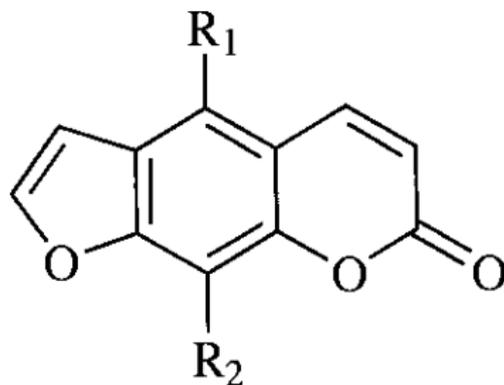


# Coumarins

- Phytoalexins with anti-bacterial properties
- Some (psoralens from umbel family plants and bergapten from citrus family) are phototoxic



# Psoralen

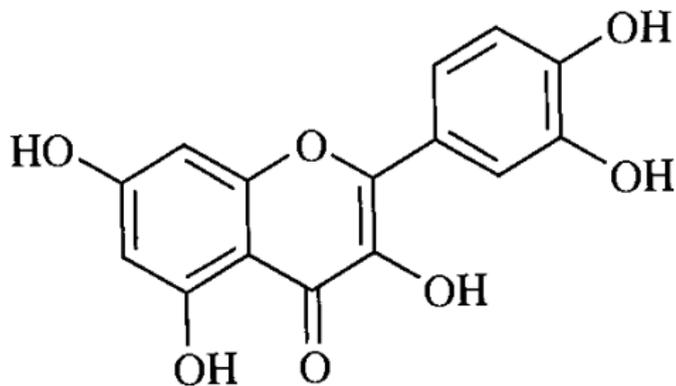


# Flavonoids

- Derivatives of phenylpropane ( $C_6-C_3$ )
- Strong antioxidants
- Examples: naringin from grapefruit, quercetin from oak and other plants, resveratrol from grapes



# Quercetin (flavonoid)



# Tannins

- Similar to flavonoids, but much heavier
- Bind to proteins and provide astringent taste

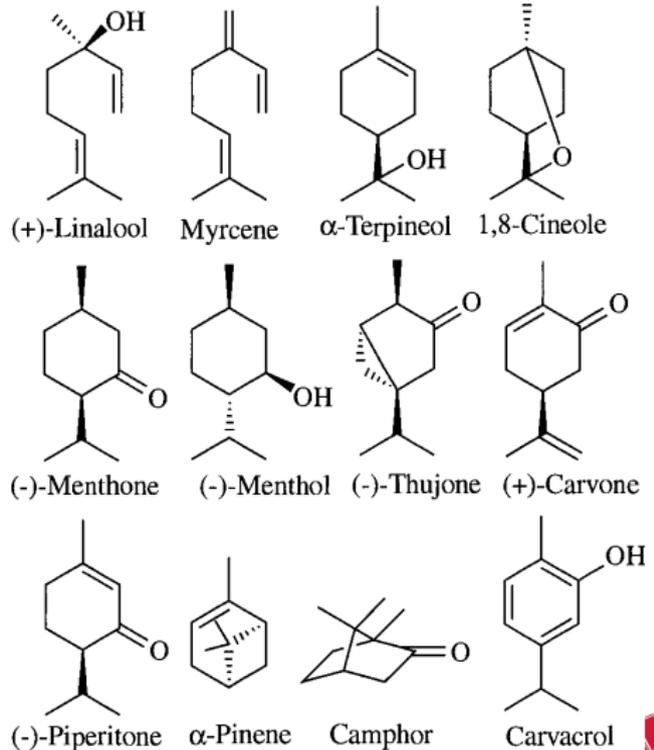
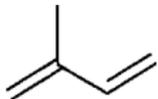


# Terpenes and monoterpenes

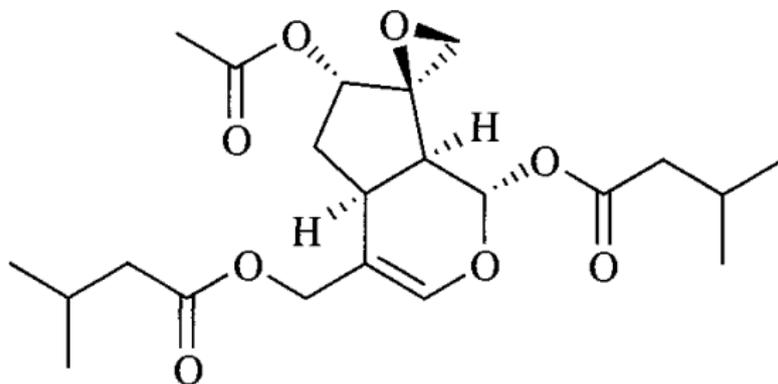
- Terpenes = isoprenoids, derivatives of isoprene ( $C_5$  unit)
- Monoterpenes are simplest, they are constituents of volatile (essential) oils
- Examples: menthol from mint, myrcene from *Eucalyptus*, camphor, iridoids like valepotriates from valerian



# Isoprene and monoterpenes



# Didrovaltrate (iridoid)

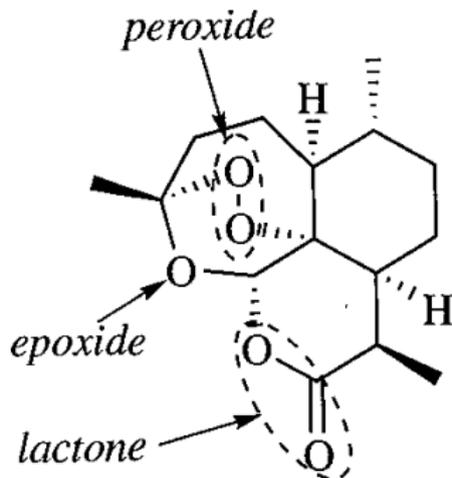


# Sesquiterpenes

- Have C<sub>15</sub> skeleton
- Example: artemisinin from sage



# Artemisinin (sesquiterpene)

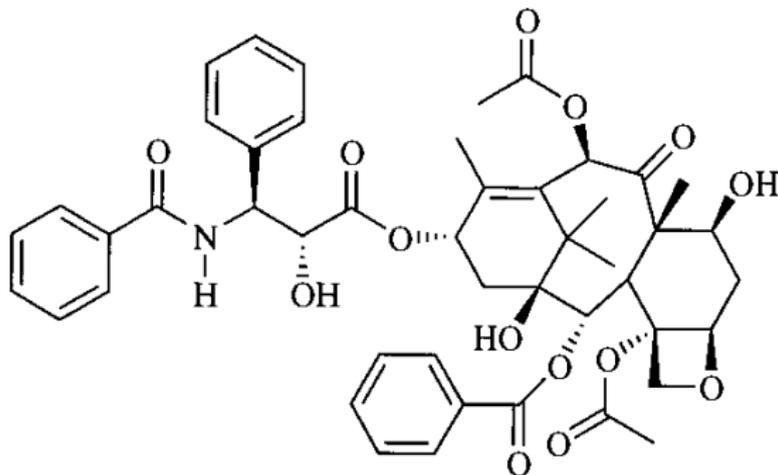


# Diterpenes

- Have C<sub>20</sub> skeleton
- Example: taxol from yew tree (actually, mostly from its endophyte *Taxomyces*)



# Taxol (diterpene)

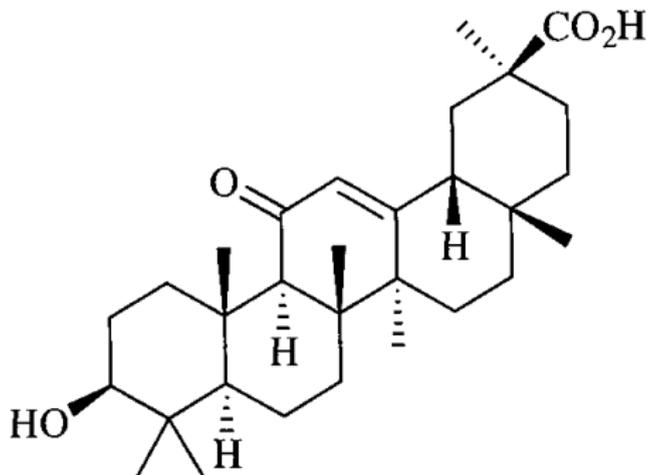


# Triterpenes

- Have  $C_{30}$  skeleton and (often) four condensed rings
- Examples: steroids, glycyrrhetic acid from liquorice and resins



# Glycyrrhetic acid (triterpene)

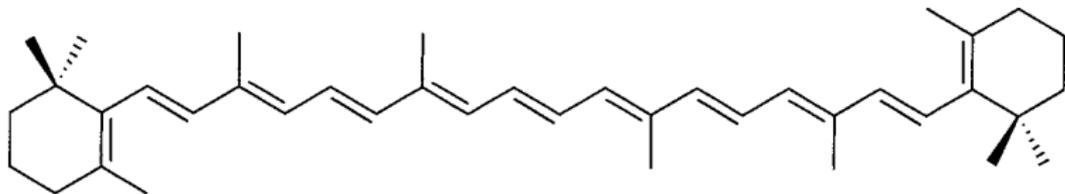


# Tetraterpenes

- Have C<sub>40</sub> skeleton and four condensed rings
- Carotenes, like  $\beta$ -carotene from carrot and lycopene from tomato



# $\beta$ -carotene (tetraterpene)



# Natural product chemistry

## Glycosides

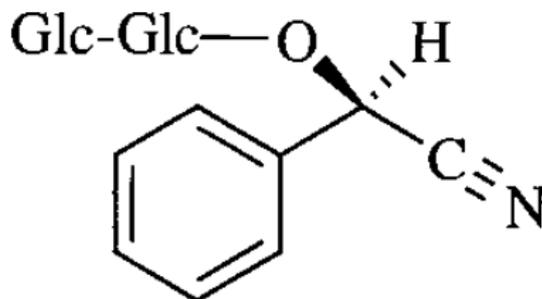


# Glycosides I

- Glycosides are any radicals binded to monosaccharides
- Cyanide glycosides have HCN (cyanide group)
- Example: amygdalin from almond
- Glucosinolates contain allyl isothiocyanate group
- Example: mustard oils of cabbage family plants



# Amygdalin (cyanide glycoside)



**Amygdalin (Glc = glucose)**

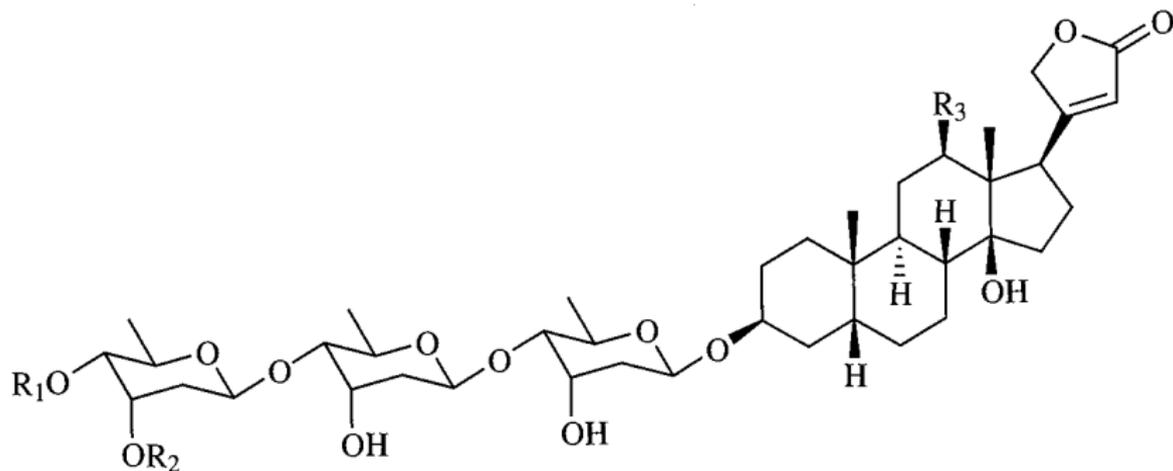


# Glycosides II

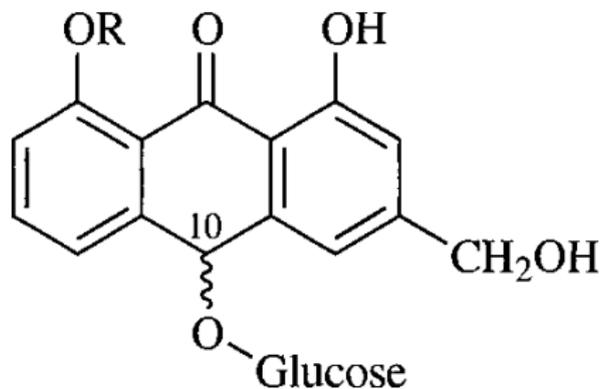
- Cardiac glycosides are “steroid-like”
- Example: digotoxin from foxglove (*Digitalis*)
- Anthraquinone glycosides contain anthraquinone nucleus (3-ring system)
- Examples: aloin from *Aloë*, cascarioside from cascara (*Rhamnus purchiana*); often laxative



# Digitoxin (cardiac glycoside)



# Aloin (anthraquinone glycoside)



# Natural product chemistry

## Alkaloids

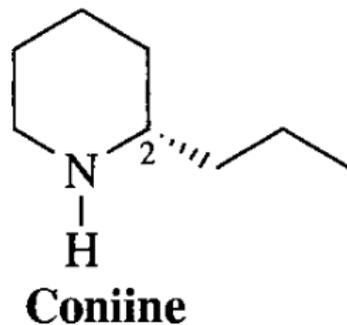
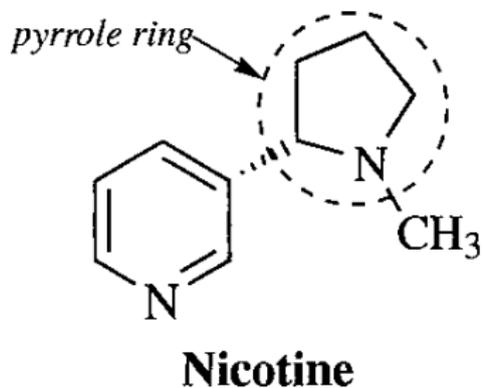


# Alkaloids I

- Alkaloids are most important pharmaceutical components from plants
- They are based on heterocyclic rings and related to nucleic bases
- Pyridine-like alkaloids are based on pyridine ring
- Examples: nicotine, coniin from hemlock



# Pyridine alkaloids

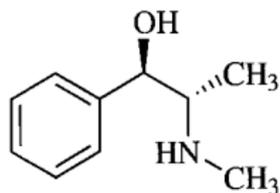


# Alkaloids II

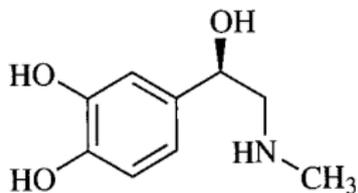
- Phenylalkamine alkaloids are amines, not heterocycles
- Ephedrine which is similar to adrenaline; hallucinogenic mescaline from peyote cactus (*Lophophora williamsii*); dangerous colchicine from autumn crocus (*Colchicum*)
- Quinoline and isoquinoline alkaloids contain more than two rings
- Famous group: quinine from *Cinchona* tree; morphines from opium poppy; tubocurarine, main component of curare poison from *Chondrodendron*; emetine from ipecac (*Caephaelis*)



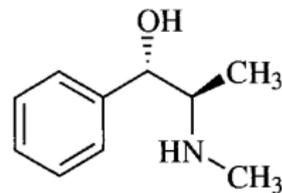
# Phenylalkamine alkaloids



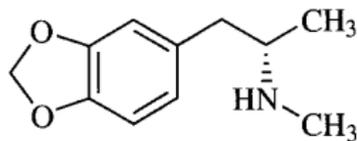
**(-)-Ephedrine**



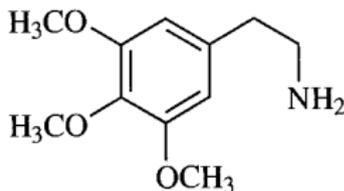
**Adrenaline**



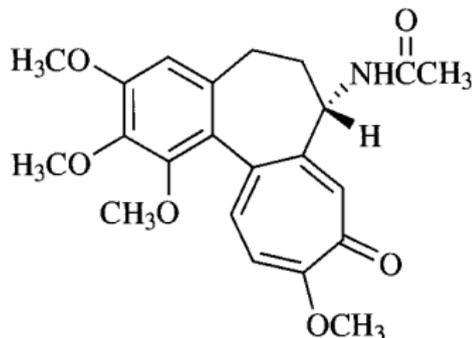
**(+)-Pseudoephedrine**



**MDMA (ecstasy)**



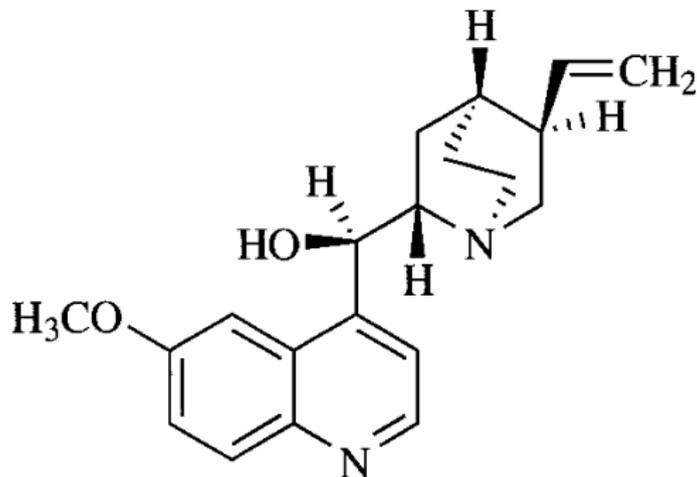
**Mescaline**



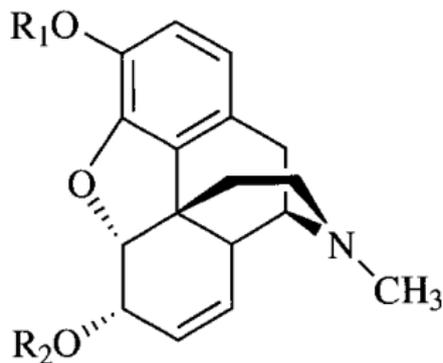
**Colchicine**



# Quinine (quinoline alkaloid)



# Morphine (isoquinoline alkaloid)



**Morphine,  $R_1 = R_2 = H$**

**Heroin,  $R_1 = R_2 = \text{acetyl}$**

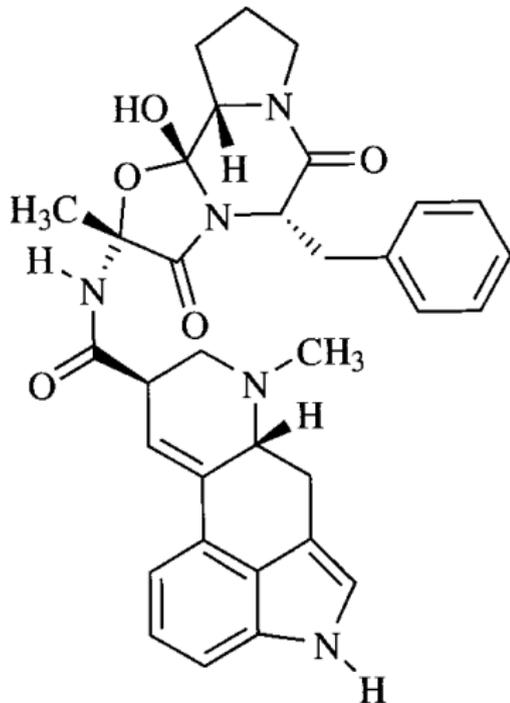


# Alkaloids III

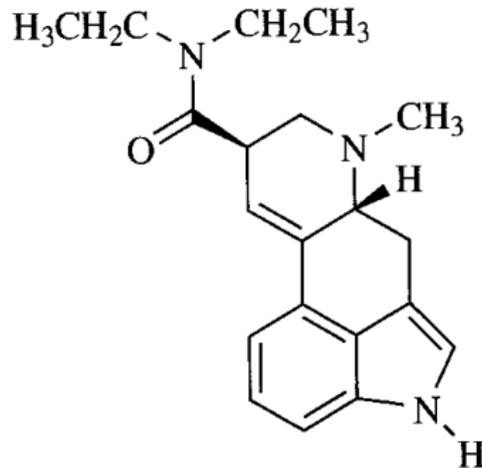
- Indole alkaloids contain connecting nitrogen atom
- Examples: reserpine from snake root (*Rauvolfia*), LSD which is a chemical analog of ergotamine from ergot fungus which is a rye parasite; brucine which is a powerful poison from nux-vomica (*Strychnos*).
- Tropane alkaloids contain tropane “chair”
- Examples: hyosciamine from deadly nightshade (*Atropa*) and cocaine from *Erythroxylon*
- Xanthine alkaloids are derivatives of xanthine (with two ketone groups)
- Examples: caffeine, theophylline, theobromine from coffee, tea and cocoa, respectively



# Ergotamine and LSD (indole alkaloids)



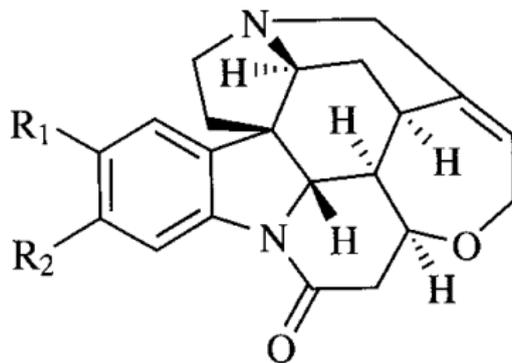
**Ergotamine**



**LSD (Lysergic acid diethylamide)**



# Brucine (indole alkaloid)

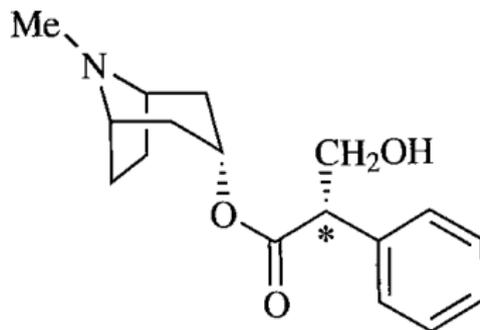


**Strychnine,  $R_1 = R_2 = H$**

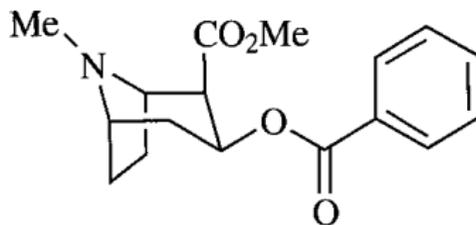
**Brucine,  $R_1 = R_2 = CH_3O$**



# Tropane alkaloids



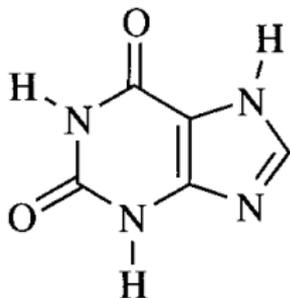
**(-)-Hyoscyamine**



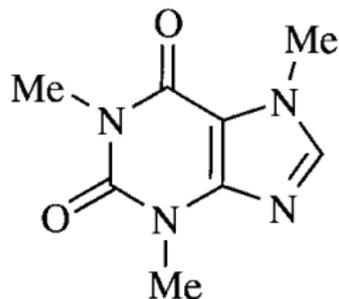
**Cocaine**



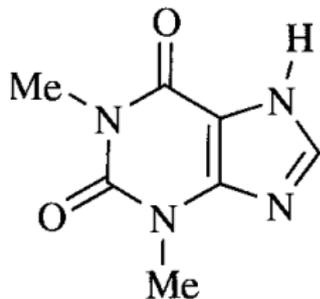
# Xanthine alkaloids



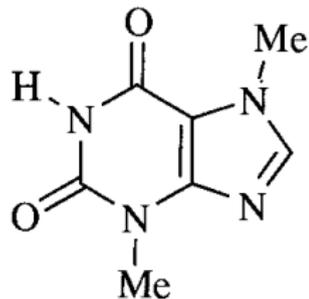
**Xanthine**



**Caffeine**



**Theophylline**



**Theobromine**



# Summary

- Polyketides are source chemicals to many antibiotics
- Derivatives of shikimic acid are phenylpropenes, lignans, coumarins, flavonoids and tannins
- All terpenes (including carotenes, steroids and resins) are derivatives of isoprene
- Glycosides is an artificial group
- Alkaloids are relatives of nucleic bases; they are most important plant chemicals



# For Further Reading



A. Shipunov.

*Ethnobotany* [Electronic resource].

2011—onwards.

Mode of access:

[http://ashipunov.info/shipunov/school/biol\\_310](http://ashipunov.info/shipunov/school/biol_310)



M. Heinrich and others.

*Fundamentals of pharmacognosy amd phytotherapy* (selected chapters). [Electronic resource].

Churchill Livingstone, 2004.

Mode of access: [http://ashipunov.info/shipunov/school/biol\\_310/heinrich2004\\_fund\\_pharm\\_part.djvu](http://ashipunov.info/shipunov/school/biol_310/heinrich2004_fund_pharm_part.djvu)

**Pages 60–105.**

