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 - ✓ Unit 4
 - ✓ Unit 5
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- ✓ Unit 1
 - ✓ Unit 2
 - ✓ Unit 3
 - ✓ Unit 4
 - ✓ Unit 5
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- ✓ Unit 1
 - ✓ Unit 2
 - ✓ Unit 3
 - ✓ Unit 4
 - ✓ Unit 5
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- ✓ Unit 1
 - ✓ Unit 2
 - ✓ Unit 3
 - ✓ Unit 4
 - ✓ Unit 5
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NOTES

- ✓ Unit 1
 - ✓ Unit 2
 - ✓ Unit 3
 - ✓ Unit 4
 - ✓ Unit 5
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- ✓ Unit 1
 - ✓ Unit 2
 - ✓ Unit 3
 - ✓ Unit 4
 - ✓ Unit 5
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MEDICINAL CHEMISTRY - III

UNIT 2

TOPIC :

- **Quinolines** : SAR, Quinine sulphate, Chloroquine, *Amodiaquine*, *Primaquine phosphate*, *Pamaquine*, Quinacrine hydrochloride, Mefloquine.



Quinolines (Antimalarial Drugs)

- Quinolines are synthetic antimalarial drugs containing a quinoline nucleus.
- They mainly act as blood schizonticides and are effective against the erythrocytic stage of Plasmodium species.

Classification

A. 4-Aminoquinolines

- Chloroquine
- Hydroxychloroquine
- Amodiaquine

B. 8-Aminoquinolines

- Primaquine
- Tafenoquine

C. Quinoline Methanols

- Quinine
- Quinidine
- Mefloquine

Mechanism of Action

A. 4-Aminoquinolines (Chloroquine)

- Accumulate in parasite food vacuole
- Inhibit heme polymerization
- Toxic free heme accumulates
- Parasite dies

B. 8-Aminoquinolines (Primaquine)

- Act on hepatic stages (hypnozoites)
- Destroy liver forms of *P. vivax* and *P. ovale*
- Also act as gametocidal drugs

C. Quinoline Methanols (Quinine)

- Interfere with DNA replication
- Inhibit heme detoxification
- Act on blood schizonts

Spectrum of Activity

- *Plasmodium vivax*
- *Plasmodium falciparum*
- *Plasmodium malariae*
- *Plasmodium ovale*

Therapeutic Uses

Chloroquine

- ▲ Treatment of chloroquine-sensitive malaria
- ▲ Prophylaxis of malaria

Primaquine

- ▲ Radical cure of *P. vivax* and *P. ovale*
- ▲ Prevention of relapse

Quinine

- ▲ Severe and complicated malaria
- ▲ Drug-resistant *P. falciparum*

Adverse Effects

Chloroquine

- Nausea, vomiting
- Headache
- Retinopathy (long-term use)

Primaquine

- Hemolytic anemia in G6PD deficiency
- GI disturbances

Quinine

- Cinchonism (tinnitus, headache, dizziness)
- Hypoglycemia
- Cardiac arrhythmias

Resistance

- Resistance seen mainly with chloroquine
- Due to decreased drug accumulation in parasite
- Managed by using ACT therapy or alternative drugs

Quinine Sulphate

- Quinine sulphate is a natural antimalarial alkaloid obtained from the bark of *Cinchona* species.
- It is mainly effective against the erythrocytic (blood) stage of *Plasmodium* species.
- Quinine acts as a blood schizonticide and is particularly useful in chloroquine-resistant malaria, especially *Plasmodium falciparum*.
- It has a bitter taste and shows antipyretic and analgesic properties.

Classification

Based on Source

Natural alkaloid

- Cinchona alkaloids

Based on Chemical Nature

- Quinoline alkaloid

Based on Antimalarial Action

- Blood schizonticide

Structure

Quinine consists of:

- Quinoline ring system
- Quinuclidine ring

Important structural features:

- Methoxy group on quinoline ring
- Secondary alcohol group
- Vinyl side chain
- Tertiary amine nitrogen

Molecular formula (quinine sulphate): $C_{20}H_{24}N_2O_2 \cdot H_2SO_4$

Structural Characteristics

- Optically active compound
- Weakly basic in nature
- Forms water-soluble salts (sulphate)

Nomenclature

Quinine → derived from *Cinchona* bark

Sulphate → salt form used for improved solubility

Official name: Quinine sulphate

Stereochemistry

- Quinine contains multiple chiral centers.
- Only the naturally occurring levo-rotatory form is pharmacologically active.
- Stereochemistry is essential for:
 - Antimalarial activity
 - Interaction with parasite heme

Mechanism of Action

- Quinine enters the malarial parasite within infected RBCs.
- Inhibits heme polymerization in the parasite.
- Free heme accumulates and becomes toxic to the parasite.
- Parasite membrane damage occurs.
- Parasite death follows.
- Hence, quinine acts as a blood schizonticide.

Spectrum of Activity

- *Plasmodium falciparum*
- *Plasmodium vivax*
- *Plasmodium malariae*
- *Plasmodium ovale*
- Especially effective against chloroquine-resistant strains

Uses

- Treatment of severe and complicated malaria
- Chloroquine-resistant malaria
- Night leg cramps (limited use)
- Babesiosis (with clindamycin)

Adverse Effects

- Cinchonism
 - Tinnitus
 - Headache
 - Nausea
 - Blurred vision
- Hypoglycemia
- Cardiac arrhythmias
- Hemolysis in G6PD deficiency

Chemical Degradation

1. Acid Degradation

- Stable in acidic conditions

2. Alkaline Degradation

- Decomposition in strong alkali

3. Photodegradation

- Sensitive to light

4. Thermal Degradation

- Heat causes degradation

Prevention

- Store in airtight containers
- Protect from light
- Store in cool, dry place

Structure–Activity Relationship (SAR)

Quinoline Ring

- Essential for antimalarial activity

Quinuclidine Ring

- Required for binding with heme

Methoxy Group

- Enhances antimalarial potency

Tertiary Amine

- Important for accumulation in parasite food vacuole

Optical Activity

- Only natural stereoisomer is active

Chloroquine

- Chloroquine is a synthetic 4-aminoquinoline antimalarial.
- It is highly effective against the erythrocytic stage of Plasmodium species.
- Chloroquine acts as a blood schizonticide and was the drug of choice for prophylaxis and treatment of malaria before resistance emerged.
- It is orally active, inexpensive, and widely used in endemic areas.

Classification

Based on Chemical Class

- 4-Aminoquinoline derivative

Based on Antimalarial Action

- Blood schizonticide

Based on Origin

- Synthetic antimalarial

Structure

Chloroquine contains:

- ▲ Quinoline ring system
- ▲ Chloro-substituted aromatic ring
- ▲ Side chain with tertiary amine

Important structural features:

- 7-chloro substitution on quinoline ring
- Terminal diethylamino group
- Weakly basic side chain

Molecular formula: $C_{18}H_{26}ClN_3$

Structural Characteristics

- Lipophilic, weak base
- Forms water-soluble salts (phosphate or hydrochloride)
- Accumulates in parasite food vacuole

Nomenclature

Chloro → chlorine substituent on quinoline ring

Quine → derived from quinoline derivative

Available forms:

Chloroquine phosphate

Stereochemistry

- ⇒ Chloroquine has one chiral center in its side chain (optional for exams)
- ⇒ Racemic mixture is used clinically
- ⇒ Activity is mainly due to the quinoline ring and basic side chain

Mechanism of Action

- ▲ Chloroquine diffuses into infected RBCs.
- ▲ Accumulates in parasite food vacuole.
- ▲ Inhibits heme polymerization → heme accumulates as toxic free heme.
- ▲ Free heme destroys parasite membranes.
- ▲ Parasite death occurs.
- ▲ Hence, chloroquine is a blood schizonticide.

Spectrum of Activity

- *Plasmodium falciparum* (chloroquine-sensitive strains)
- *Plasmodium vivax*
- *Plasmodium malariae*
- *Plasmodium ovale*

Note: Ineffective against chloroquine-resistant *P. falciparum*.

Uses

- ▲ Treatment of acute malaria (sensitive strains)
- ▲ Malaria prophylaxis
- ▲ Extraintestinal amebiasis (limited use)
- ▲ Sometimes combined with primaquine for radical cure of *P. vivax* and *P. ovale*

Adverse Effects

- Gastrointestinal upset: nausea, vomiting
- Pruritus (especially in dark-skinned individuals)
- Retinopathy (long-term use)
- Cardiotoxicity at high doses
- Headache, dizziness
- Rare: hemolysis in G6PD deficiency

Chemical Degradation

1. Acid Degradation

- Stable in acidic medium

2. Alkaline Degradation

- Hydrolysis of side chain possible

3. Photodegradation

- Sensitive to light

4. Thermal Degradation

- Heat accelerates degradation

Prevention

- Store in cool, dry place
- Protect from light and moisture

Structure–Activity Relationship (SAR)

Quinoline Ring

- ▲ Essential for antimalarial activity

Chloro Substitution (C-7)

- ▲ Enhances activity against parasites

Tertiary Amine Side Chain

- ▲ Basic side chain allows accumulation in parasite vacuole
- ▲ Diethyl substitution increases potency

Lipophilicity

- ▲ Promotes tissue penetration
- ▲ Enhances oral absorption

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Amodiaquine

- Amodiaquine is a synthetic 4-aminoquinoline antimalarial closely related to chloroquine.
- It acts primarily as a blood schizonticide, effective against the erythrocytic stage of *Plasmodium* species.
- Amodiaquine is especially useful in areas with chloroquine-resistant *Plasmodium falciparum*.
- It is often used in combination therapy to reduce resistance development.

Classification

Based on Chemical Class

- 4-Aminoquinoline derivative

Based on Antimalarial Action

- Blood schizonticide

Based on Origin

- Synthetic antimalarial

Structure

Amodiaquine contains:

- Quinoline ring system
- Chlorine-substituted aromatic ring
- Aminoalkyl side chain

Important structural features:

- 7-chloro substitution on quinoline ring
- Amino group on side chain
- Hydroxy substitution on aromatic ring (enhances activity)

Molecular formula: $C_{20}H_{22}ClN_3O$

Structural Characteristics

- Lipophilic weak base
- Forms water-soluble salts for oral use
- Accumulates in parasite food vacuole

Nomenclature

Amo → from amino group

Diaquine → quinoline derivative

Marketed as:

Amodiaquine hydrochloride

Fixed-dose combination with artesunate

Stereochemistry

- Contains one chiral center in the side chain
- Racemic mixture used clinically
- Stereochemistry is essential for interaction with parasite heme

Mechanism of Action

- ▲ Amodiaquine accumulates in the food vacuole of infected RBCs.
- ▲ Inhibits heme polymerization, leading to accumulation of toxic free heme.
- ▲ Free heme damages parasite membranes.
- ▲ Parasite death occurs.
- ▲ Acts as a blood schizonticide.

Spectrum of Activity

- ◆ *Plasmodium falciparum* (including some chloroquine-resistant strains)
- ◆ *Plasmodium vivax*
- ◆ Mainly active against erythrocytic forms

Uses

- ✓ Treatment of uncomplicated *P. falciparum* malaria
- ✓ Used in combination therapy (e.g., amodiaquine + artesunate)
- ✓ Effective in chloroquine-resistant malaria

Adverse Effects

- Gastrointestinal disturbances: nausea, vomiting, diarrhea
- Hepatotoxicity (rare but serious)
- Agranulocytosis (rare)
- Pruritus
- Rare hypersensitivity reactions

Chemical Degradation

1. Acid Degradation

- Stable in acidic conditions

2. Alkaline Degradation

- Hydrolysis of side chain possible

3. Photodegradation

- Sensitive to light

4. Thermal Degradation

- Heat accelerates degradation

Prevention

- Store in cool, dry place
- Protect from light

Structure–Activity Relationship (SAR)

Quinoline Ring

- Essential for antimalarial activity

7-Chloro Substitution

- Increases activity against *P. falciparum*

Side Chain Amino Group

- Required for vacuole accumulation and activity

Hydroxy Substitution on Aromatic Ring

- Enhances potency and reduces toxicity

Lipophilicity

- Facilitates oral absorption and tissue penetration

Primaquine Phosphate

- Primaquine phosphate is a synthetic 8-aminoquinoline antimalarial.
- It is the only widely used drug effective against the liver stages (hypnozoites) of *Plasmodium vivax* and *P. ovale*.
- Primaquine is mainly gametocidal and prevents relapse by eradicating dormant liver forms.
- It is used in radical cure and prophylaxis of malaria.

Classification

Based on Chemical Class

- 8-Aminoquinoline derivative

Based on Antimalarial Action

- Liver stage (hypnozoitocidal) agent
- Gametocidal agent

Based on Origin

- Synthetic antimalarial

Structure

Primaquine contains:

- Quinoline ring system
- Substituted amino side chain at position 8

Important structural features:

- Terminal primary amino group
- Alkyl side chain
- Quinoline ring with weakly basic properties

Molecular formula (primaquine phosphate): $C_{15}H_{21}N_3O \cdot H_3PO_4$

Structural Characteristics

- Highly lipophilic
- Weakly basic → accumulates in liver
- Forms water-soluble phosphate salt for oral use

Nomenclature

Prima → primary amino group

Quine → quinoline derivative

Available as:

Primaquine phosphate (oral)

Stereochemistry

- Primaquine has no chiral centers.
- Racemic mixture is used clinically.
- Activity depends mainly on side chain substitution for liver stage activity.

Mechanism of Action

- Primaquine is absorbed orally and reaches the liver.
- Accumulates in hepatocytes.
- Acts on dormant hypnozoites of *P. vivax* and *P. ovale*.
- Produces reactive oxygen species → parasite death.
- Also kills gametocytes of *P. falciparum* in blood.
- Hence, primaquine is liver schizonticide and gametocide.

Spectrum of Activity

- Liver stages of *P. vivax* and *P. ovale* (hypnozoites)
- Gametocytes of *P. falciparum*
- Minimal activity against erythrocytic stages

Uses

- Radical cure of *P. vivax* and *P. ovale* malaria
- Malaria prophylaxis (prevents relapse)
- Gametocidal action in *P. falciparum* infections

Adverse Effects

- Hemolysis in G6PD-deficient patients (major concern)
- Gastrointestinal disturbances: nausea, vomiting, abdominal pain
- Headache, dizziness
- Rare: methemoglobinemia

Chemical Degradation

1. Acid Degradation

- Relatively stable

2. Alkaline Degradation

- Sensitive to strong base

3. Photodegradation

- Sensitive to light

4. Thermal Degradation

- Heat accelerates degradation

Prevention

- Store in cool, dry place
- Protect from light

Structure–Activity Relationship (SAR)

Quinoline Ring

- Essential for antimalarial activity

8-Amino Substitution

- Crucial for liver-stage activity

Alkyl Side Chain

- Increases lipophilicity
- Enhances hepatocyte penetration

Lipophilicity

- Promotes liver accumulation
- Oral absorption

Phosphate Salt

- Increases water solubility for oral formulation

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Pamaquine

- Pamaquine is a synthetic 8-aminoquinoline antimalarial.
- It is primarily used as a liver schizonticide, targeting the dormant hepatic stages (hypnozoites) of *Plasmodium vivax* and *P. ovale*.
- It also exhibits gametocidal activity against *Plasmodium falciparum*.
- Pamaquine is less commonly used today due to its toxicity, with primaquine largely replacing it.

Classification

Based on Chemical Class

- 8-Aminoquinoline derivative

Based on Antimalarial Action

- Liver stage (hypnozoiticidal) agent
- Gametocidal agent

Based on Origin

- Synthetic antimalarial

Structure

Pamaquine contains:

- Quinoline ring system
- 8-amino substituted side chain

Important structural features:

- Primary amino group at position 8
- Alkyl side chain for lipophilicity
- Quinoline nucleus for antimalarial action

Molecular formula: $C_{15}H_{21}N_3$

Structural Characteristics

- Lipophilic weak base
- Forms salts for oral administration
- Accumulates in liver tissue

Nomenclature

- Pama → derived from aminoquinoline modification
- Quine → quinoline derivative
- Administered as pamaquine phosphate (oral salt)

Stereochemistry

- Pamaquine has no chiral centers
- Racemic mixture used clinically
- Activity depends on 8-amino substitution

Mechanism of Action

- ✓ Pamaquine is absorbed orally and reaches the liver.
- ✓ Accumulates in hepatocytes infected with *Plasmodium* hypnozoites.
- ✓ Causes oxidative damage in parasite cells.
- ✓ Kills dormant liver forms and prevents relapse.
- ✓ Also kills gametocytes of *P. falciparum*.
- ✓ Hence, Pamaquine is liver schizonticide and gametocide.

Spectrum of Activity

- Liver stages of *P. vivax* and *P. ovale* (hypnozoites)
- Gametocytes of *P. falciparum*
- Minimal or no effect on erythrocytic stages

Uses

- Radical cure of *P. vivax* and *P. ovale* malaria
- Malaria prophylaxis (prevents relapse)
- Gametocidal agent in *P. falciparum* infection

Adverse Effects

- Hemolysis in G6PD-deficient patients
- Gastrointestinal upset: nausea, vomiting, abdominal pain
- Headache, dizziness
- Rare: methemoglobinemia

Chemical Degradation

1. Acid Degradation

- Relatively stable

2. Alkaline Degradation

- Sensitive in strong alkali

3. Photodegradation

- Light-sensitive

4. Thermal Degradation

- Heat accelerates degradation

Prevention

- Store in cool, dry place
- Protect from light

Structure–Activity Relationship (SAR)

Quinoline Ring

- Essential for antimalarial activity

8-Amino Substitution

- Crucial for liver-stage (hypnozoite) activity

Alkyl Side Chain

- Enhances lipophilicity and liver accumulation

Lipophilicity

- Facilitates oral absorption and hepatocyte penetration

Phosphate Salt

- Improves water solubility for oral use

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Quinacrine Hydrochloride

- Quinacrine hydrochloride is a synthetic acridine derivative used as an antimalarial drug.
- It was one of the earliest synthetic antimalarials, historically used in chloroquine-resistant malaria.
- Quinacrine is primarily effective against the erythrocytic stage of *Plasmodium* species.
- It is also known as Atabrine.

Classification

Based on Chemical Class

- Acridine derivative

Based on Antimalarial Action

- Blood schizonticide

Based on Origin

- Synthetic antimalarial

Structure

Quinacrine contains:

- Acridine nucleus (three fused aromatic rings)
- Aminoalkyl side chain
- Hydroxy and methoxy substitutions on aromatic rings

Important structural features:

- Acridine chromophore (responsible for intercalation with DNA)
- Side chain tertiary amine (basic, lipophilic)
- Hydroxy/methoxy groups enhance solubility

Molecular formula: $C_{23}H_{30}ClN_3$

Structural Characteristics

- Highly lipophilic
- Weakly basic → accumulates in parasite food vacuole
- Forms water-soluble hydrochloride salt for oral administration

Nomenclature

- Quina → originally derived for antimalarial use
- Crine → from acridine structure
- Marketed as quinacrine hydrochloride (oral tablet)

Stereochemistry

- Quinacrine hydrochloride is achiral
- Activity depends on side chain substitution and acridine chromophore
- Racemic mixture used clinically

Mechanism of Action

- Quinacrine accumulates in infected erythrocytes.
- Intercalates with parasite DNA, inhibiting replication and transcription.
- Inhibits heme polymerization in the parasite food vacuole.
- Accumulation of free heme leads to parasite death.
- Acts as a blood schizonticide.

Spectrum of Activity

- *Plasmodium falciparum* (including some chloroquine-resistant strains)
- *Plasmodium vivax*
- *Plasmodium malariae*
- Mainly effective against erythrocytic stages

Uses

- Treatment of chloroquine-resistant malaria
- Prophylaxis in endemic areas (historical use)
- Sometimes used in combination therapy with other antimalarials

Adverse Effects (Important for Exams)

- ▲ Gastrointestinal upset: nausea, vomiting, diarrhea
- ▲ Yellow discoloration of skin and urine
- ▲ Headache, dizziness
- ▲ Itching and rash
- ▲ Rare: hepatic toxicity and neurotoxicity

Chemical Degradation

1. Acid Degradation

- Stable in acidic medium

2. Alkaline Degradation

- Decomposition in strong alkali

3. Photodegradation

- Sensitive to light

4. Thermal Degradation

- Heat accelerates decomposition

Prevention

- ▲ Store in cool, dry place
- ▲ Protect from light

Structure–Activity Relationship (SAR)

Acridine Nucleus

- Essential for DNA intercalation
- Required for antimalarial activity

Side Chain Tertiary Amine

- Basic group facilitates accumulation in parasite vacuole

Hydroxy/Methoxy Substitutions

- Improve solubility and bioavailability

Lipophilicity

- Ensures tissue penetration and oral absorption

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Mefloquine

- Mefloquine is a synthetic quinoline-methanol antimalarial.
- It is effective against chloroquine-resistant strains of *Plasmodium falciparum*.
- Mefloquine acts as a blood schizonticide and is used both for treatment and prophylaxis of malaria.
- It has a long half-life, allowing weekly dosing for prophylaxis.

Classification

Based on Chemical Class

- Quinoline-methanol derivative

Based on Antimalarial Action

- Blood schizonticide

Based on Origin

- Synthetic antimalarial

Structure

Mefloquine contains:

- Quinoline nucleus
- Hydroxy- and trifluoromethyl-substituted side chain
- Chiral centers in side chain

Important structural features:

- 2-piperidyl-methanol side chain
- Trifluoromethyl group at C-8 of quinoline ring

Molecular formula: $C_{17}H_{16}F_6N_2O$

Structural Characteristics

- Highly lipophilic
- Basic side chain facilitates accumulation in parasite food vacuole
- Long tissue and plasma half-life

Nomenclature

Me → methanol side chain

Floquine → fluorine-substituted quinoline

Available as: Mefloquine hydrochloride (oral)

Stereochemistry

- Mefloquine has two chiral centers
- Used as a racemic mixture clinically
- Stereochemistry influences antimalarial potency and toxicity

Mechanism of Action

- ⇒ Mefloquine accumulates in the parasite food vacuole of infected RBCs.
- ⇒ Inhibits heme polymerization, leading to accumulation of toxic free heme.
- ⇒ Free heme damages parasite membranes, causing parasite death.
- ⇒ Effective against erythrocytic stages of *P. falciparum*.
- ⇒ Hence, mefloquine is a blood schizonticide.

Spectrum of Activity

- *Plasmodium falciparum* (including chloroquine-resistant strains)
- *Plasmodium vivax*
- Active against erythrocytic stages

Uses

- ▲ Treatment of chloroquine-resistant *P. falciparum* malaria
- ▲ Prophylaxis in areas with resistant malaria (weekly dosing)
- ▲ Sometimes combined with artesunate for combination therapy

Adverse Effects

- Gastrointestinal: nausea, vomiting, diarrhea
- Neuropsychiatric: dizziness, insomnia, anxiety, vivid dreams
- Rare: seizures, psychosis, arrhythmias

Chemical Degradation

1. Acid Degradation

- Stable in acidic medium

2. Alkaline Degradation

- Sensitive to strong alkali

3. Photodegradation

- Sensitive to light

4. Thermal Degradation

- Heat accelerates decomposition

Prevention

- Store in cool, dry place
- Protect from light and moisture

Structure–Activity Relationship (SAR)

Quinoline Nucleus

- ▲ Essential for antimalarial activity

Trifluoromethyl Substitution

- ▲ Enhances activity against chloroquine-resistant strains

Piperidyl-Methanol Side Chain

- ▲ Basic group allows accumulation in food vacuole

Lipophilicity

- ▲ Promotes oral absorption and tissue penetration

Chirality

- ▲ Influences potency and adverse effects

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