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PHARMACEUTICAL ORGANIC CHEMISTRY – I

UNIT 5

TOPIC :

- **Carboxylic acids***

Acidity of carboxylic acids, effect of substituents on acidity, inductive effect and qualitative tests for carboxylic acids, amide and ester Structure and Uses of Acetic acid, Lactic acid, Tartaric acid, Citric acid, Succinic acid. Oxalic acid, Salicylic acid, Benzoic acid, Benzyl benzoate, Dimethyl phthalate, Methyl salicylate and Acetyl salicylic acid

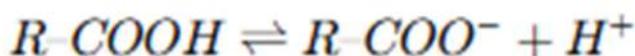
Carboxylic Acids

- Carboxylic acids are organic compounds that contain the carboxyl group (-COOH) as their functional group. The carboxyl group consists of a carbonyl group (C=O) and a hydroxyl group (-OH) attached to the same carbon atom.
- **General formula** : R-COOH
 - (where R = alkyl or aryl group)
- **Examples** :
 - Formic acid (HCOOH) – simplest carboxylic acid
 - Acetic acid (CH₃COOH) – found in vinegar
 - Benzoic acid (C₆H₅COOH) – aromatic carboxylic acid

Acidity of Carboxylic Acids

→ Carboxylic acids are organic compounds containing the -COOH (carboxyl group).

They are acidic in nature because they can donate a proton (H⁺) from the -OH part of the carboxyl group:

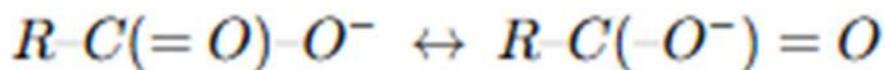


Why Are Carboxylic Acids Acidic

- ▲ The carboxyl group (-COOH) contains an -OH group attached to a C=O group.
- ▲ The electron-withdrawing nature of the carbonyl (C=O) increases the polarity of the O-H bond.
- ▲ This facilitates the release of a proton (H⁺), making the compound acidic.

Resonance Stabilization of Carboxylate Ion :

- After losing a proton, the carboxylic acid forms a carboxylate ion (R-COO⁻).
- This anion is resonance stabilized:



- The negative charge is delocalized over two oxygen atoms, making the carboxylate ion more stable.
- Greater stability of the conjugate base → stronger acidity.

Effect of Substituents on Acidity of Carboxylic Acids

- The acidity of a carboxylic acid (R-COOH) depends on how easily it can lose a proton (H⁺).
- This, in turn, depends on the stability of the carboxylate ion (R-COO⁻) formed after deprotonation.
- Substituents attached to the carbon chain (R-group) affect this acidity by:
 - Stabilizing the carboxylate ion → increases acidity
 - Destabilizing the carboxylate ion → decreases acidity

Types of Substituent Effects :

1. Electron-Withdrawing Groups (EWG):

(e.g., -Cl, -NO₂, -CN)

- Increase acidity
- Pull electrons away from the -COOH group
- Stabilize the carboxylate ion

2. Electron-Donating Groups (EDG):

(e.g., $-\text{CH}_3$, $-\text{OH}$, $-\text{OCH}_3$)

- Decrease acidity
- Push electrons toward the $-\text{COOH}$ group
- Destabilize the carboxylate ion

Inductive Effect

- The Inductive Effect is the electron-withdrawing or electron-donating effect transmitted through sigma (σ) bonds in a molecule due to electronegativity differences between atoms.

Types of Inductive Effect:

- **-I Effect (Electron-Withdrawing Inductive Effect):** Groups like $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$, $-\text{F}$, $-\text{Cl}$ **pull electrons** toward themselves → stabilize negative charges → **increase acidity**.
- **+I Effect (Electron-Donating Inductive Effect):** Groups like $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{OH}$, $-\text{OCH}_3$ **push electrons** toward the chain → destabilize the negative ion → **decrease acidity**.

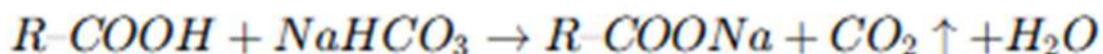
Qualitative Tests for Carboxylic Acids

1. Litmus Test:

- ▲ Carboxylic acids are acidic in nature.
- ▲ Turns blue litmus paper red.
- ▲ Confirms acidic character.

2. Sodium Bicarbonate Test (NaHCO_3 Test):

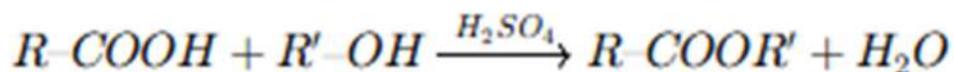
- ▲ Carboxylic acids react with sodium bicarbonate to give effervescence of CO_2 gas.



Observation: Brisk effervescence confirms carboxylic acid group.

3. Reaction with Alcohols (Ester Test):

- ▲ Carboxylic acids react with alcohols in the presence of conc. H_2SO_4 to form esters, which have fruity smell.



Observation : Pleasant fruity odor confirms **ester formation**, hence carboxylic acid presence.

4. Fluorescein Test (for Aromatic Carboxylic Acids):

- ▲ Aromatic carboxylic acids (like phthalic acid) give fluorescent color on heating with resorcinol in conc. H_2SO_4 and then neutralizing with NaOH.
- ▲ Used for detection of aromatic dicarboxylic acids.

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Amides

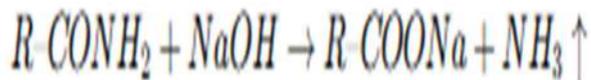
→ Amides are derivatives of carboxylic acids in which the -OH of the carboxyl group is replaced by an -NH₂, -NHR, or -NR₂ group.

→ General formula: R-CONH₂

Qualitative Test for Amides:

1. Heating Test:

- On heating with alkali (NaOH), ammonia gas (NH₃) is released.
- Smell confirms presence of an amide.
- Equation:



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Esters

→ Esters are derived from carboxylic acids and alcohols. The -OH group of the acid is replaced with an -OR group.

→ General formula: R-COOR'

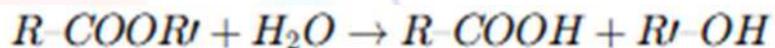
Qualitative Test for Esters:

1. Fruity Smell Test:

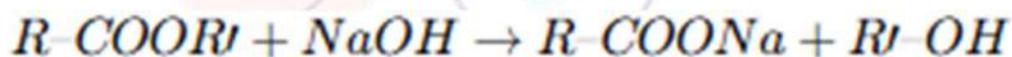
- Esters have a **pleasant, fruity odor**.
- Simple smelling can often identify esters.

2. Hydrolysis Test:

- On hydrolysis with dilute acid or base, esters give back the **acid and alcohol**.
- Acidic hydrolysis:



- Basic hydrolysis (saponification):

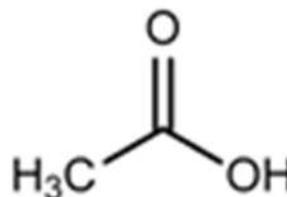


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Acetic Acid

- Molecular Formula: $C_2H_4O_2$ or CH_3COOH
- IUPAC Name: Ethanoic acid
- Common Name: Acetic acid
- Functional Group: Carboxylic acid ($-COOH$)

Structure of Acetic Acid :

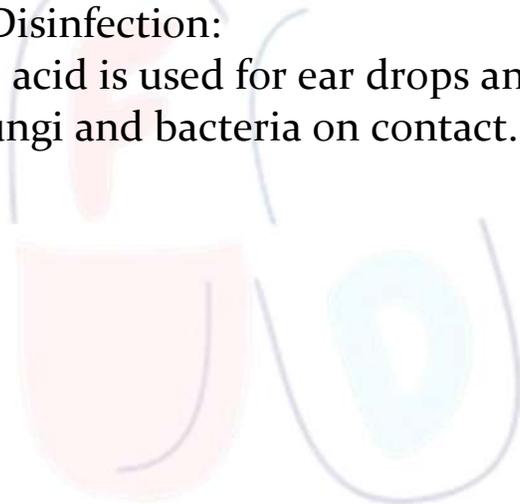


- Contains a methyl group (CH_3) attached to a carboxylic acid group ($-COOH$).
- The carboxylic group includes:
 - A carbon doubly bonded to oxygen ($=O$)
 - A hydroxyl group ($-OH$)

Uses of Acetic Acid:

- ✓ **In the Food Industry:**
 - Used as a preservative and flavoring agent (E260).
 - Major component of vinegar (4–8% acetic acid).
 - Gives sour taste to food and acts as an antibacterial agent.
- ✓ **In the Pharmaceutical Industry:**
 - Used in the manufacture of aspirin, acetate esters, and vitamins.
 - Acts as a solvent for many pharmaceutical preparations.
- ✓ **In Organic Synthesis:**
 - A key starting material for preparing:
 - Acetyl chloride
 - Acetic anhydride
 - Esters
 - Cellulose acetate (used in textiles and films)

- ✓ As a Laboratory Reagent:
 - Common solvent and acid used in titrations and chemical reactions.
 - Used in esterification, acetylation, and preparation of carboxylate salts.
- ✓ In Industry:
 - Used in manufacturing:
 - Synthetic fibers (rayon)
 - Rubber and plastics
 - Dyes and inks
- ✓ In Medicine and Disinfection:
 - Dilute acetic acid is used for ear drops and topical antiseptics.
 - Kills some fungi and bacteria on contact.

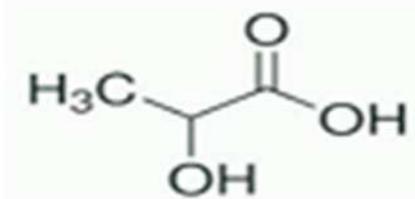


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Lactic Acid

- Chemical Formula: $C_3H_6O_3$
- IUPAC Name: 2-Hydroxypropanoic acid
- Common Name: Lactic acid
- Functional Groups:
 - Hydroxyl group (-OH)
 - Carboxylic acid group (-COOH)

Structure of Lactic Acid :



- It is a hydroxy acid: contains both -OH and -COOH groups.
- Has a chiral center at the second carbon (exists in D- and L- forms).
- Can exist as lactic acid (liquid) or lactate (salt/ion form) in the body.

Uses of Lactic Acid:

- ✓ In the Food Industry:
 - Acts as a preservative and flavoring agent (E270)
 - Provides sour taste in fermented foods like:
 - Yogurt, sauerkraut, pickles, sourdough
 - Used in baking, brewing, and dairy processing
- ✓ In Pharmaceuticals and Medicine:
 - Used in skin-care products (creams, peels) for exfoliation and pH balance
 - Part of oral rehydration therapy (ORT) solutions
 - Used to treat hyperpigmentation, acne, and dry skin

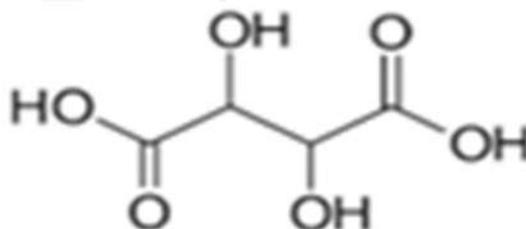
- ✓ In the Body (Biological Role):
 - Produced in muscle cells during anaerobic respiration (exercise)
 - Forms lactate, which is transported to the liver via the Cori cycle
 - Important in energy metabolism
- ✓ In the Cosmetic Industry:
 - Used in lotions, shampoos, and anti-aging creams
 - Improves skin texture and hydration
- ✓ In Biodegradable Plastics:
 - Used in the synthesis of polylactic acid (PLA) — a biodegradable plastic
 - PLA is used in packaging, sutures, implants, etc.
- ✓ In Chemical Industry:
 - Used as a starting material for making:
 - Lactates (salts)
 - Solvents
 - Polymers

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Tartaric Acid

- Chemical Formula: $C_4H_6O_6$
- IUPAC Name: 2,3-Dihydroxybutanedioic acid
- Common Name: Tartaric Acid
- Functional Groups:
 - Two Carboxylic acid groups ($-COOH$)
 - Two Hydroxyl groups ($-OH$)

Structure of Tartaric Acid :



- A dicarboxylic acid with two chiral centers at carbon 2 and 3.
- Exists in three isomeric forms:
 - L-(+)-Tartaric acid (naturally occurring)
 - D-(-)-Tartaric acid
 - Meso-tartaric acid (optically inactive)

Uses of Tartaric Acid:

- ✓ In the Food Industry:
 - Used as an acidulant, flavor enhancer, and preservative
 - Commonly used in baking powders along with sodium bicarbonate
 - Present in aerated drinks, candies, and jams
 - Recognized as a food additive (E334)

- ✓ In Pharmaceuticals:
 - Acts as a stabilizing agent for oral effervescent formulations
 - Used in combination with citric acid in effervescent tablets
 - Improves taste and enhances solubility
- ✓ In Analytical Chemistry:
 - Used as a complexing agent in Fehling's solution
 - Helps in detection of reducing sugars
- ✓ In the Textile and Tanning Industry:
 - Used in dyeing and tanning processes
 - Acts as a mordant to bind dyes to fabrics
- ✓ In Construction:
 - Added to cement and plaster to retard setting time
 - Helps in smooth application and finishing
- ✓ In Cosmetics:
 - Used in skin care products as a natural exfoliant and pH adjuster
 - Part of alpha hydroxy acids (AHAs) used in anti-aging products
- ✓ In Beverages (Wine Industry):
 - Naturally found in grapes and tamarind
 - Helps in maintaining acid balance in wine

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Citric Acid

→ Chemical Formula: $C_6H_8O_7$

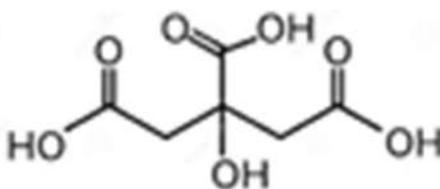
→ IUPAC Name: 2-Hydroxypropane-1,2,3-tricarboxylic acid

→ Common Name: Citric acid

→ Functional Groups:

- Three carboxylic acid groups ($-COOH$)
- One hydroxyl group ($-OH$)

Structure of Citric Acid :



- Tricarboxylic acid with a central carbon bearing:
 - One hydroxyl group
 - Two carboxylic acid groups
- Third $-COOH$ is attached via CH_2 group.

Uses of Citric Acid:

- ✓ In the Food Industry:
 - Used as a preservative, flavoring agent, and acidulant
 - Common in soft drinks, fruit juices, jams, candies, and sauces
 - Food additive code: E330
- ✓ In Pharmaceuticals:
 - Acts as a buffering agent in syrups and tablets
 - Used in effervescent formulations (with sodium bicarbonate)
 - Enhances bioavailability of minerals like iron and calcium

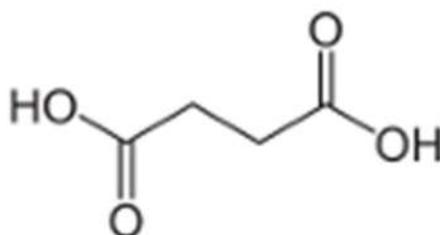
- Mild anticoagulant in blood storage (as citrate salt)
- ✓ In Cosmetics and Personal Care:
 - Used in shampoos, creams, and face washes
 - Helps adjust pH and exfoliate dead skin (AHA – alpha hydroxy acid)
- ✓ In Cleaning Products:
 - Found in bathroom cleaners, descalers, and dishwashing products
 - Chelates metal ions like calcium and magnesium → removes hard water stains
- ✓ In Industrial Applications:
 - Used in the production of citrate salts (e.g., sodium citrate)
 - Acts as a chelating agent in textile and leather industries
 - Used in electroplating and photography
- ✓ In Biotechnology and Fermentation:
 - Used to adjust pH in microbial cultures
 - Often produced industrially via fermentation of *Aspergillus niger*

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Succinic Acid

- Chemical Formula: $C_4H_6O_4$
- IUPAC Name: Butanedioic acid
- Common Name: Succinic acid
- Functional Group:
 - Two carboxylic acid groups ($-COOH$)
- It is a dicarboxylic acid

Structure of Succinic Acid :



- A straight-chain four-carbon dicarboxylic acid.
- Contains two terminal $-COOH$ groups separated by two methylene ($-CH_2-$) units.

Uses of Succinic Acid:

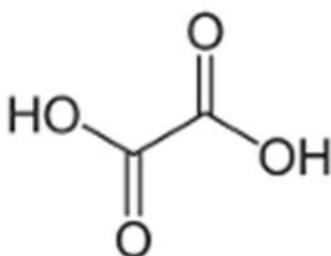
- ✓ In the Pharmaceutical Industry:
 - Used as a buffering agent in drug formulations.
 - Acts as a starting material for synthesizing active pharmaceutical ingredients (APIs).
 - Shows mild anti-inflammatory and antioxidant activity.
 - Used in vitamin supplements, especially Vitamin B complex formulations.
- ✓ In the Food Industry:
 - Used as an acidity regulator (E363)
 - Present in yeast-extract-based products, cheeses, and meat flavorings

- Used in flavor enhancement (gives umami/savory taste)
- Acts as a precursor for artificial flavoring compounds
- ✓ In the Chemical Industry:
 - Raw material for making:
 - 1,4-Butanediol (BDO)
 - γ -Butyrolactone (GBL)
 - Tetrahydrofuran (THF)
 - Succinic anhydride
 - Used in the synthesis of polyesters and resins
- ✓ In Agriculture:
 - Used in the production of plant growth regulators and fertilizers
 - Improves plant stress tolerance and metabolism
- ✓ In Biotechnology:
 - Succinic acid is a key intermediate in the Krebs cycle (citric acid cycle).
 - Produced biologically by microbial fermentation (e.g., *Actinobacillus succinogenes*)
- ✓ In Cosmetics:
 - Used in lotions, creams, and anti-aging products
 - Acts as a pH regulator and skin-conditioning agent

Oxalic Acid

- Chemical Formula: $C_2H_2O_4$
- IUPAC Name: Ethanedioic acid
- Common Name: Oxalic acid
- Functional Groups:
 - Two carboxylic acid groups ($-COOH$)

Structure of Oxalic Acid :



- It is the simplest dicarboxylic acid.
- Consists of two carboxyl groups directly bonded to each other.

Uses of Oxalic Acid:

- ✓ In Chemical Laboratories:
 - Used as a primary standard in acid-base titrations due to its purity and stability.
 - Acts as a reducing agent in various redox reactions.
- ✓ In the Textile and Leather Industry:
 - Used as a bleaching and cleaning agent for leather and textiles.
 - Helps in removing rust, ink, and tannin stains from fabric and leather.
- ✓ In Metal and Marble Cleaning:

- Removes rust, mineral deposits, and lime scale from metals and stones.
 - Often used in household metal polishes and bathroom cleaners.
- ✓ In Pharmaceutical Industry:
- Used as an intermediate in drug synthesis.
 - Helps in purification and extraction of certain active pharmaceutical ingredients (APIs).
- ✓ In the Preparation of Oxalates:
- Used to make oxalate salts like:
 - Sodium oxalate
 - Calcium oxalate (a component of kidney stones)
 - These salts are used in coordination chemistry and catalysis studies.
- ✓ In Printing and Dyeing:
- Acts as a mordant (binds dyes to fabric).
 - Helps improve color fastness in textiles.
- ✓ In Agriculture:
- Used in beekeeping to control Varroa mites (a honeybee parasite).
 - Acts as a natural pesticide in small, controlled amounts.

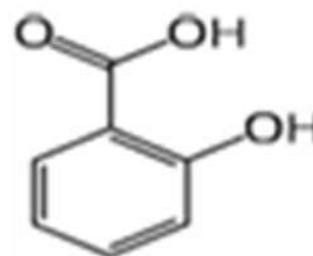
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Salicylic Acid

- Chemical Formula: $C_7H_6O_3$
- IUPAC Name: 2-Hydroxybenzoic acid
- Common Name: Salicylic acid
- Functional Groups:
 - Phenol group (-OH)
 - Carboxylic acid group (-COOH)

Structure of Salicylic Acid :

- A benzene ring substituted with:
 - -OH group at position 2
 - -COOH group at position 1



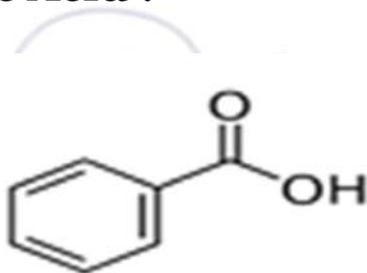
Uses of Salicylic Acid:

- ✓ In Pharmaceuticals:
 - Used in the synthesis of aspirin (acetylsalicylic acid).
 - Acts as a topical keratolytic agent—removes dead skin layers.
 - Used in ointment, lotions, and medicated soaps for:
 - Acne treatment
 - Warts and corns
 - Psoriasis and dandruff
- ✓ In Cosmetics and Skin Care:
 - Commonly included in face washes, toners, and peels.
 - Helps in exfoliating skin, clearing pores, and reducing oiliness.
- ✓ As a Preservative:
 - Acts as a fungicide and bacteriostatic agent.
 - Used in food and beverages in very low concentrations (though limited due to toxicity at higher doses).

Benzoic Acid

- Chemical Formula: $C_7H_6O_2$
- IUPAC Name: Benzenecarboxylic acid
- Common Name: Benzoic acid
- Functional Group:
 - Carboxylic acid group ($-COOH$) attached to a benzene ring

Structure of Benzoic Acid :



- Composed of:
 - A benzene ring (C_6H_5-)
 - A carboxylic acid group ($-COOH$)

Uses of Benzoic Acid:

- ✓ As a Food Preservative:
 - Used to preserve acidic foods such as:
 - Fruit juices
 - Soft drinks
 - Pickles
 - Jams and sauces
 - Prevents growth of molds, yeasts, and bacteria
 - Food additive code: E210
- ✓ In the Pharmaceutical Industry:
 - Used in the preparation of benzoyl derivatives.
 - Mild antiseptic and antifungal agent.
 - Present in ointments and lotions for fungal skin infections.

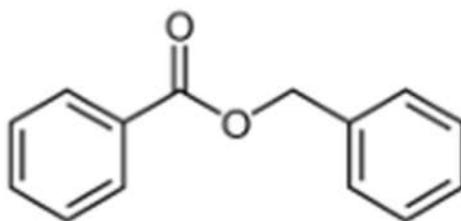
- Used in cough syrups and expectorants (as sodium benzoate).
- ✓ In Cosmetics and Toiletries:
 - Found in toothpastes, deodorants, face washes, and creams.
 - Acts as a preservative and fragrance additive.
- ✓ In Chemical Industry:
 - Used as a starting material for synthesis of:
 - Dyes
 - Perfumes
 - Plasticizers
 - Benzoyl chloride, phenol, and benzoate esters
- ✓ In Laboratory Use:
 - Acts as a standard substance in chemical analysis.
 - Used to measure heat of combustion in calorimetric experiments.

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Benzyl Benzoate

- Molecular Formula: $C_{14}H_{12}O_2$
- IUPAC Name: Phenylmethyl benzoate
- Common Name: Benzyl benzoate
- Type: Ester (formed from benzoic acid and benzyl alcohol)

Structure of Benzyl Benzoate :



Contains:

- A **benzene ring** attached to **COO-** (benzoate group)
- A **benzyl group** ($CH_2-C_6H_5$)

Uses of Benzyl Benzoate:

- ✓ In Pharmaceuticals and Medicine:
 - Used as a topical antiparasitic agent, especially in treatment of:
 - Scabies (caused by *Sarcoptes scabiei*)
 - Pediculosis (lice infestation)
 - Kills mites and lice by penetrating their exoskeletons and disrupting nervous function.
- ✓ In Skin Lotions and Ointments:
 - Acts as a skin penetrant, helping other drugs absorb better.
 - Used as a soothing base in some dermatological preparations.
- ✓ In Cosmetics and Perfumes:
 - Used as a fixative and solvent in:
 - Perfumes
 - Hair oils

- Lotions and creams

In Textile and Plastic Industry:

- Used as a plasticizer for cellulose materials and synthetic resins.
- Enhances flexibility and durability of plastics and fabrics.

In Veterinary Medicine:

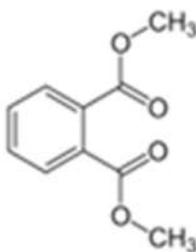
- Used in sprays and ointments for parasite control in animals.
- Found in some animal shampoos for treating mites and fleas.



Dimethyl Phthalate (DMP)

- Chemical Formula: $C_{10}H_{10}O_4$
- IUPAC Name: Dimethyl benzene-1,2-dicarboxylate
- Common Name: Dimethyl phthalate
- Type: Diester of phthalic acid with methanol

Structure of Dimethyl Phthalate



- A benzene ring with two methyl ester ($-COOCH_3$) groups at ortho (1,2) positions.

Uses of Dimethyl Phthalate:

- ✓ As a Plasticizer:
 - Widely used to improve flexibility and durability of plastics such as:
 - Cellulose acetate
 - PVC
 - Makes plastics soft and less brittle.
- ✓ As an Insect Repellent:
 - Used as an active ingredient in mosquito repellents.
 - Effective against mosquitoes, flies, and gnats.
 - Present in lotions and sprays (now less common due to safer alternatives).

✓ In Pharmaceutical Formulations:

- Used as a coating agent in enteric-coated tablets to control drug release.
- Helps in masking the taste and protecting drugs from stomach acid.

✓ In Personal Care and Cosmetic Products:

- Used as a solvent and fixative in:
 - Perfumes
 - Hair sprays
 - Nail polishes

✓ In Industrial Applications:

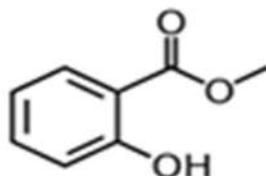
- Used in paints, varnishes, and polishes as a solvent.
- Helps in improving film-forming properties and enhancing adhesion.

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Methyl Salicylate

- Chemical Formula: $C_8H_8O_3$
- IUPAC Name: Methyl 2-hydroxybenzoate
- Common Name: Methyl salicylate
- Other Name: Oil of Wintergreen
- Functional Groups:
 - Ester group ($-COOCH_3$)
 - Phenol group ($-OH$)

Structure of Methyl Salicylate :



- A benzene ring substituted at:
 - Position 1: $-OH$ group (phenol)
 - Position 2: $-COOCH_3$ group (methyl ester)

Uses of Methyl Salicylate:

- ✓ As a Counterirritant in Topical Pain Relief:
 - Used in ointments, creams, sprays, and liniments for:
 - Muscle pain
 - Joint pain (arthritis)
 - Backache and strains
 - Produces a warming sensation that distracts from deeper pain.
- ✓ In Pharmaceutical Preparations:
 - Used in the formulation of balms like:
 - Iodex
 - Moov

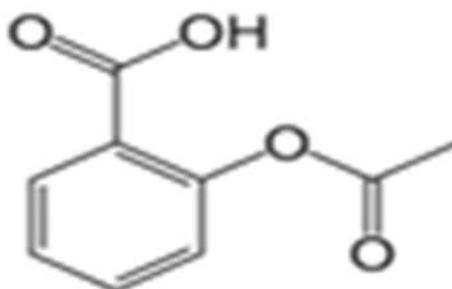
- Tiger Balm
 - Helps in blood circulation stimulation at the site of application.
- ✓ In Flavoring and Fragrance Industry:
 - Added in minty-flavored gums, candies, and mouthwashes (in very small quantities).
 - Commonly used in toothpaste and perfumes for its refreshing aroma.
- ✓ In Analytical and Chemical Uses:
 - Acts as an intermediate in the synthesis of dyes, pesticides, and other esters.
 - Used in testing for iron(III) salts, which give a violet complex with phenolic groups.
- ✓ As a Preservative:
 - Mild antiseptic and fungistatic properties.
 - Sometimes used in preserving cosmetic products and formulations.
- ✓ In Veterinary Medicine:
 - Used in pain-relief sprays and creams for animals like horses and cattle.

Learn and Educate

Acetyl Salicylic Acid (Aspirin)

- Chemical Formula: $C_9H_8O_4$
- IUPAC Name: 2-Acetoxybenzoic acid
- Common Name: Aspirin
- Type: Ester derivative of salicylic acid

Structure of Acetyl Salicylic Acid :



- A benzene ring substituted at:
 - Position 1: -COOH (carboxylic acid)
 - Position 2: -OCOCH₃ (acetyl ester group)

Uses of Acetyl Salicylic Acid (Aspirin):

- ✓ As an Analgesic (Pain Reliever):
 - Used to relieve mild to moderate pain such as:
 - Headache
 - Toothache
 - Menstrual pain
 - Muscle aches
- ✓ As an Antipyretic (Fever Reducer):
 - Reduces body temperature by acting on the hypothalamus.

- ✓ As an Anti-inflammatory Agent:
 - Inhibits the enzyme cyclooxygenase (COX), reducing production of prostaglandins.
 - Used in arthritis, bursitis, and other inflammatory conditions.
- ✓ As an Antiplatelet Agent:
 - Prevents formation of blood clots by inhibiting thromboxane A₂ synthesis.
 - Used in low doses for:
 - Prevention of heart attacks
 - Stroke prevention
 - Post-angioplasty care
- ✓ In Rheumatic Conditions:
 - Used in treating rheumatic fever and acute gout attacks.
- ✓ In Pharmaceutical Preparations:
 - Available as:
 - Tablets, chewable tablets
 - Enteric-coated formulations (to prevent stomach irritation)
- ✓ Industrial and Analytical Uses:
 - Used as a starting material for other salicylates and derivatives.
 - Sometimes used in quality control tests as a reference standard.