# Hydroxy acids

## Monobasic hydroxyacids

### Nomenclature

**Trivial name**: parent carboxylic acid and hydroxyl group represented by Greek letters

**IUPAC name**: position of hydroxyl is indicated by number.

e.g. $CH_3CH(OH)CH_2COOH$ β-hydroxybutyric acid (trivial name),

2-hydroxybutanoic acid or 1-hydroxypropane-1-carboxylic acid (IUPAC)

### Preparation

#### From keto ester

Reduction; Keto-ester → corresponding hydroxyl ester

Hydrolysis: hydroxyl ester →corresponding acids

#### α-hydroxyacids

aldehyde/ketone +KCN → Cyanohydrin → α-hydroxyacids

α-bromoacids → α-hydroxyacids

#### β-hydroxyacids

Reformatsky reaction

α-bromoacid ester + Zn + carbonyl compound → β-hydroxyacids

Aldol reaction followed by oxidation with tollens reagent

Aldehyde → β-hydroxyaldehyde → β-hydroxyacids

Ethylene → ethylene oxide → ethylene glycol → ethylene chlorohydrin → ethylene cyanohydrin- β-hydroxyacids

### Physical properties

$CH_2(OH)COOH$ glycollic acid is solid higher ones are liquid

Highly soluble in water

### Chemical properties

When acid functionality is masked the it behaves as hydroxy compounds when hydroxyl group is protected then it reacts as acid

$CH_2(OH)COOH + PCl5 \rightarrow CH_2(Cl)COCl$

#### Oxidation

α-hydroxyacid: $RCH(OH)COOH + H_2SO_4 \rightarrow RCHO + HCOOH$

α-hydroxyacid: $R_2C(OH)COOH + H_2SO_4 \rightarrow R_2CO + HCOOH$

$RCH(OH)CH_2COOH + KMnO_4 + OH^- \rightarrow RCOCH_3$

### Reduction

$RCH(OH)COOH + HI \rightarrow RCH_2COOH$

### Effect of heat

α-hydroxyacid → Lactides intermolecular cyclic ester

β-hydroxy acid → β,γ- unsaturated acid

γ-hydroxy acids/ δ-hydroxyacids → lactones, intramolecular cyclic ether

Lactones IUPAC –olides e.g δ-valerolactone or 1,5-pentaolide

Tetramethylene glycol → γ-butyrolactone → polyamides

## Glycollic acid, hydroxyacetic acid, $CH_2(OH)COOH$

Source; beet, sugar cane, grapes

### Preparation

Laboratory;

Chloroacetic acid + sodium carbonate +water → Pot. Salt of glycollic acid → glycollic acid

$ClCH_2COOH + Na_2CO_3 + H_2O \rightarrow CH_2(OH)COOK \rightarrow CH_2(OH)COOH$

Formalin + Pot. cyanide + water → Pot. Salt of glycollic acid → glycollic acid

$HCHO + KCN + H_2O \rightarrow CH_2(OH)COOK \rightarrow CH_2(OH)COOH$

Industrial

$HCHO + CO + H_2O \rightarrow CH_2(OH)COOH$ acid catalysed

Use

Glycollic acid → Oxalic acid

$CH_2(OH)COOH + HNO_3 \rightarrow COOHCOOH$

## Lactic acid, α-hydroxypropionic acid, $CH_3CH(OH)COOH$

Source; milk

Preparation

In lab by general procedure

Industrially

Milk + *bacillus acidi lactiti* → Lactic acid

Use

In tanning, dyeing, ethyl lactate as solvent

On chiral center. L(+)-lactic acid m.p. 26℃, from meet, D(-)- Lactic acid m.p. from sugar fermentation, racemic D,L(±)-lactic acid

# Hydroxy – dibasic and polybasic acid

1. Tartronic acid, Hydroxymalonic acid, $CH(OH)(COOH)_2$
2. Malic acid, hydroxysuccinic acid, $CH_2(COOH)C^*H(OH)COOH$
3. Tartaric acid $C^*H(OH)(COOH)C^*H(OH)COOH$

# Tartaric acid

## Source:

grape juice

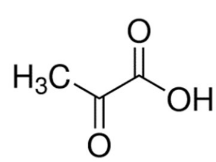
Extraction:

- Grape juice on fermentation give argol, reddish brown crystalline
- Recrystallization of argol gives cream of tartar, white crystal ($KHC_4H_4O_4$)
- $KHC_4H_4O_4 + Ca(OH)_2 \rightarrow CaC_4H_4O_4 \downarrow + K_2C_4H_4O_4 + 2H_2O$
- $K_2C_4H_4O_4 + CaCl_2 \rightarrow CaC_4H_4O_4 \downarrow$
- $CaC_4H_4O_4 + H_2SO_4 \rightarrow H_2C_4H_4O_4 + CaSO_4$

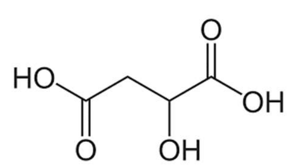
Mol formula: $C_4H_6O_6$

## Structure elucidation

1. Thermal decarboxylation: Tartaric acid + heat → pyruvic acid($CH_3COCOOH$) + $CO_2$ + $H_2O$

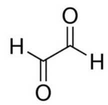



2. Reduction dehydroxylation: Tartaric acid +HI → malic acid $CH_2(COOH)C^*H(OH)COOH$




## Synthesis

Glyoxal + HCN → Glyoxal cyanohydrin



CHOCHO +HCN → CH(OH)(CN)CH(OH)(CN)

Glyoxal cyanohydrin + $H_2O$ → Tartaric acid

CH(OH)(CN)CH(OH)(CN) + $H_2O$ → CH(OH)(COOH)CH(OH)(COOH)

(α, α'-dihydroxysuccinic acid or 2,3-dihydroxybutanedioc acid)

C*H(OH)(COOH) C*H(OH)(COOH)

## Stereochemistry

Two chiral carbons.

four ($2^2$) enantiomers possible.

Have centre of symmetry so two isomers are meso forms.

So D(+)-Tartaric acid, L(-)-tartaric acid, meso-tartaric acid and DL-tartaric acid or racemic tartaric acid

Ambiguity in stereochemistry

1. Building up, carbohydrate Chemistry

   D(+)-Glyceraldehyde → (-)-Tartaric acid; so (-) is D form and (+)- form is L form

2. Stepping down

   (+)-tartaric acid → D(-)-Glyceric acid;  so (+) is D form and (-) is L form

D(+) Tartaric acid, (R,R) tartaric acid

# Citric acid

**Source**: citrus fruit

Isolation

Lemmon juice + 10%NaOH added till brown ppt forms. Filter

10% $CaCl_2$ PPt filter

Residue is washed in hot water and filtered

Acidified with sulphuric acid filtered.

Filtrate is concentrated and crystallized.

## Structure elucidation

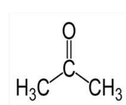
**Mol formula**; $C_6H_8O_7$

Mono acetyl derivative; so mono hydroxyl

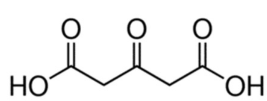
Three series of salts; tribasic acid

Oxidation:

Citric acid + Concetrated $H_2SO_4 \rightarrow CO_2 +$ A; α-hydroxy is present.

A → $2CO_2$ + Acetone 

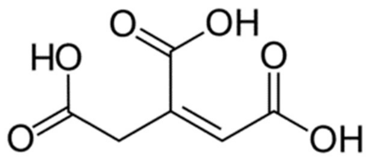

Hydroxyl is present in position of carbonyl. A is acetonedicarboxylic acid



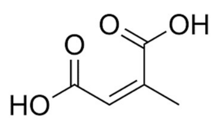

$(COOH)CH_2C(O)CH_2(COOH)$

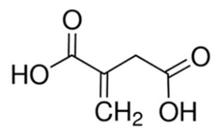
Dehydration: Citric acid + $H_2SO_4$

On heating or treatment with concentrated $H_2SO_4$, citric acid forms aconitic acid (It has a nutty flavour, which makes it useful as an artificial nut flavour.) and a molecule of water; β-hydroxy acids is present.

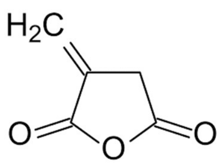



On pyrolysis E/Z-aconitic acid,  Z-citraconic acid (mesaconic acid), itaconic acid and their anhydrides.




Formation of anhydrides show citraconic and itaconic acids are 1,2-dicarboxylic acid. Aconitic acid upon decarboxylation produce citraconic acid and itaconic acid, isomers differing in position of double bond.




Over all reaction

Citric acid → aconitic acid → Citraconic acid + Itaconic acid

↓ ↓ ↓

Acetonedicarboxylic acid citraconic anhydride Itaconic anhydride

↓

Acetoacetic acid → acetone

Synthesis

Glycerol +n HCl → 1,3-dichloro-2-propanol

1,3-dichloro-2-propanol + [O] → 1,3-dichloroacetone

1,3-dichloroacetone +HCN →1,3-dichloroacetocyanohydrin

1,3-dichloroacetocyanohydrin + KCN →1,3-dicyanoacetocyanohydrin

1,3-dicyanoacetocyanohydrin +$H_2O$ → citric acid