

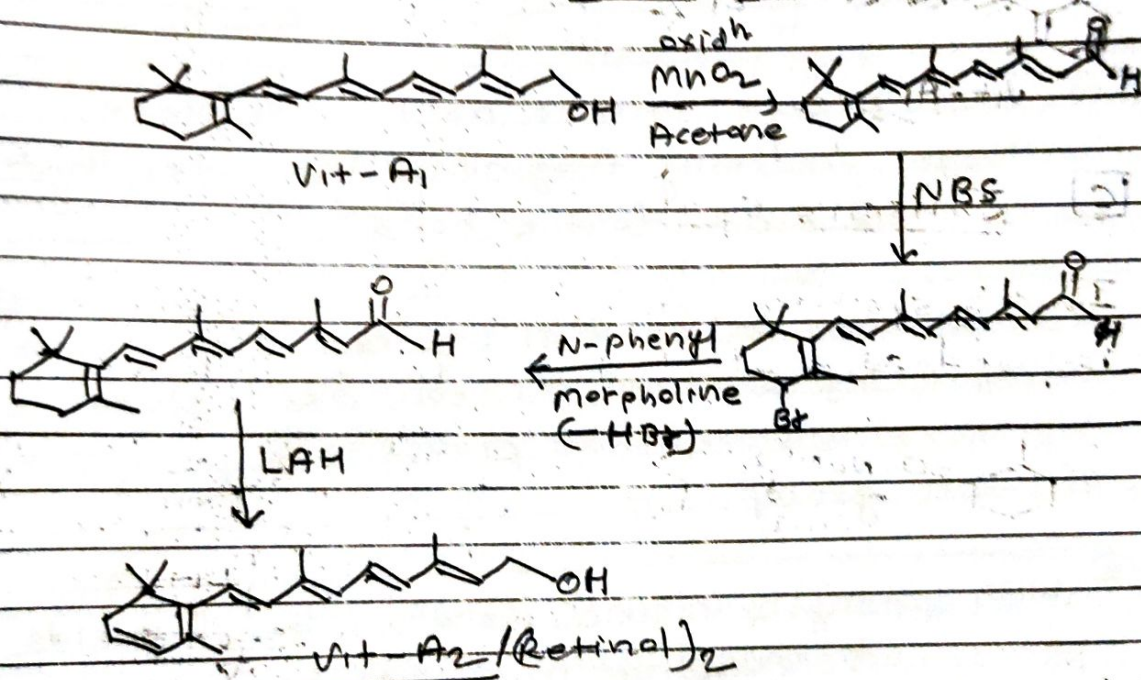
Synthesis of Vitamin-A₂

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- The Vit-A₂ is similar to that of Vit-A₁ but in addition it possesses one more conjugated double bond.
- Also known as (retinol)₂ / 3,4-dehydroretinol
- m.p. = 63-65°C.
- By using UV-spectroscopy, it is clear that Vit-A₂ has two absorption maxima in the UV-region 287 nm and 351 nm, which indicates that Vit-A₂ possesses one more double bond.

* Conversion of Vit-A₁ to Vit-A₂



Vitamin-C

[Ascorbic Acid]

→ Related to the monosaccharides.

→ Deficiency disease - scurvy

mp = 192°C

$[\alpha]_D^{25} = +24^{\circ}$

→ Crystalline solid

*

Constitution:-

① Molecular formula: - $\text{C}_6\text{H}_8\text{O}_6$

② Presence of Keto-Enol system.



③ Ozonolysis of ascorbic acid takes place without producing fragments indicates that it contains one double bond.

④ Vit-C also acts as a strong reducing agent with FeCl_3 solution, ascorbic acid gives violet colouration that proves the presence of $-\text{OH}$ group.

⑤ With phenylhydrazine, ascorbic acid yields phenyl hydrazone that indicates the presence of $\text{C}=\text{O}$ group.



Thus, from the above all points, it is clear that there is a presence of Keto-Enol system.

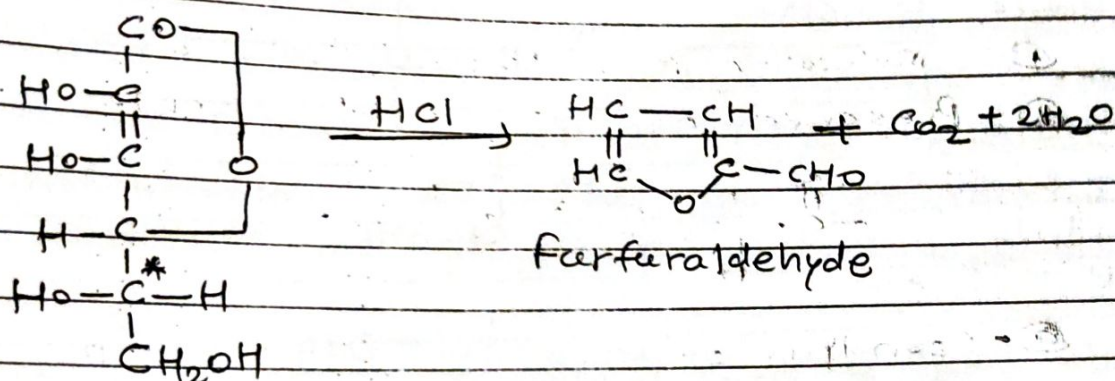
③ Presence of Carboxyl group:

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Vit-C forms monosodium and monopotassium derivative which indicates the presence of $-COO^-$ group. but ascorbic acid vit-C does not give effervescence of CO_2 with $NaHCO_3$ solution. This proves that it does not contain free $-COOH$ group.

④ Nature of C-skeleton:



L-Ascorbic Acid

When vit-C heated with HCl gives furfuraldehyde, this indicates that at least five carbon atoms in its straight chain are present and also that there are no. of hydroxyl groups are present.

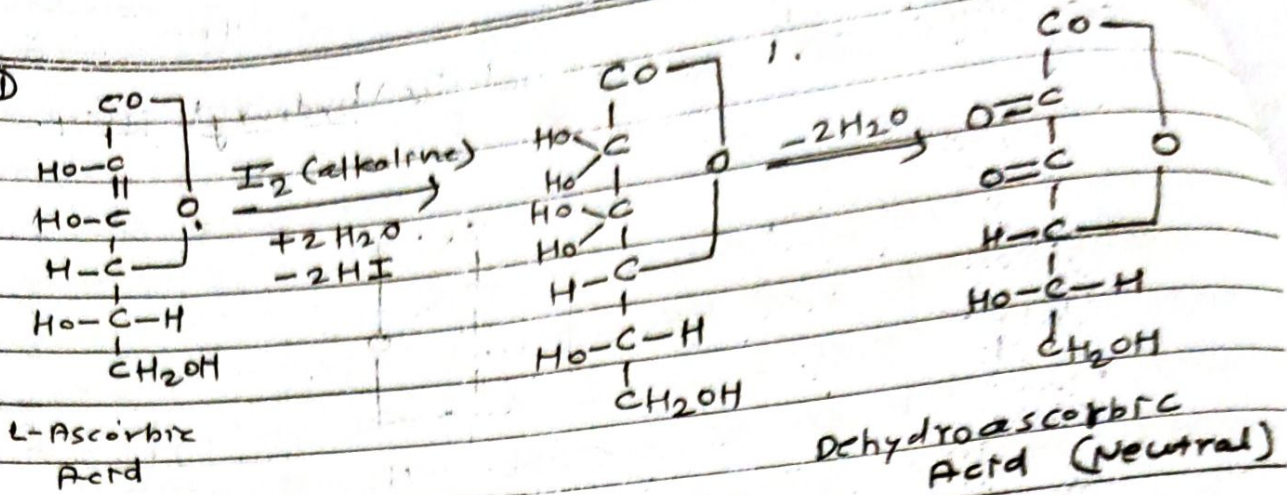
⑤ Presence of hydroxyl groups:

Two types of hydroxyl groups are present in Ascorbic acid structure.

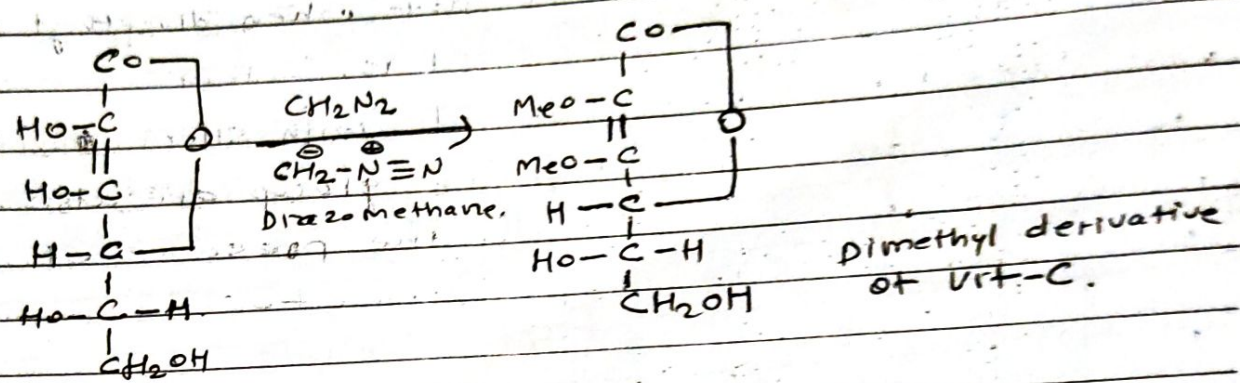
- (a) Enolic hydroxyl group. ($\text{HO}-\text{C}=\text{C}-$) group.
- (b) Alcoholic hydroxyl group ($-\text{OH}$)

① Two-enolic hydroxyl group:-

①



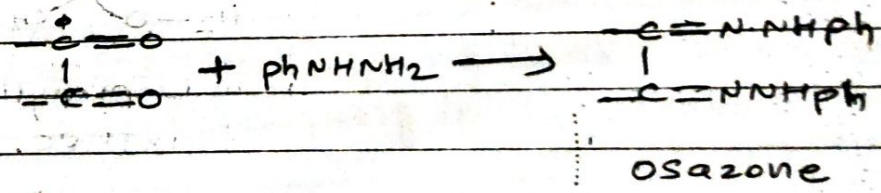
②



As oxidⁿ of vit-c involves the elimination of two hydrogen atoms with the formation of the Neutral dehydroascorbic acid, this indicates that the presence of two enolic hydroxyl group. And formation of dimethyl derivative also indicates the presence of two enolic -OH group.

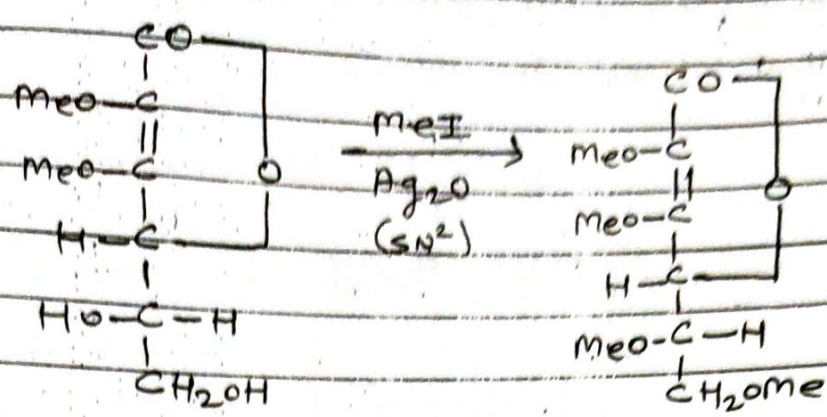
③

Further formation of osazone with phenylhydrazine indicates that two carbonyl group are present at adjacent to each other.

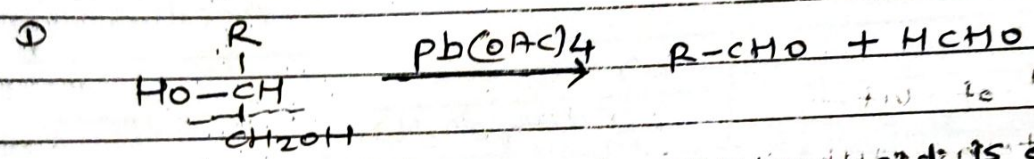


Moreover ascorbic acid yields violet colour with FeCl₃ which is characteristic of enolic group.

2) Presence of two alcoholic hydroxyl group.

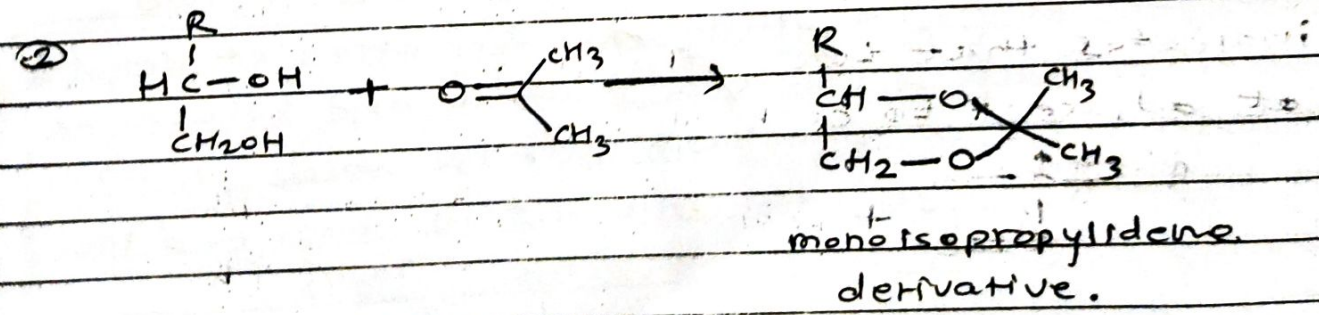


Above reaction indicates that when dimethyl derivative of ascorbic acid is further methylated with methyl iodide with silver oxide gives two remaining alcoholic group are also methylated which indicates the presence of two alcoholic hydroxyl group in vit-C.



When methyl ether of ascorbic acid is oxidised with lead tetraacetate gives formaldehyde and aldehydic group.

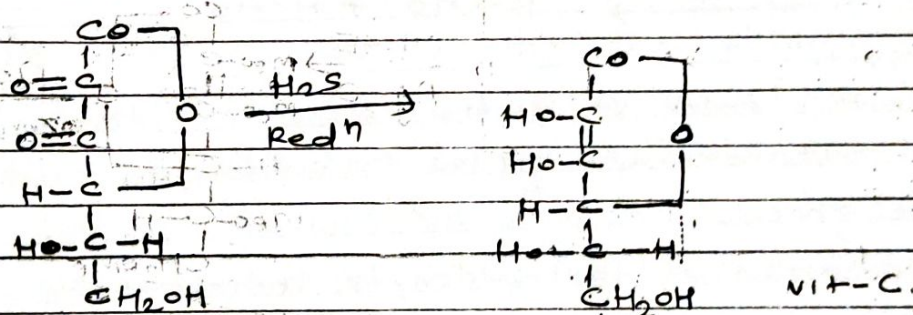
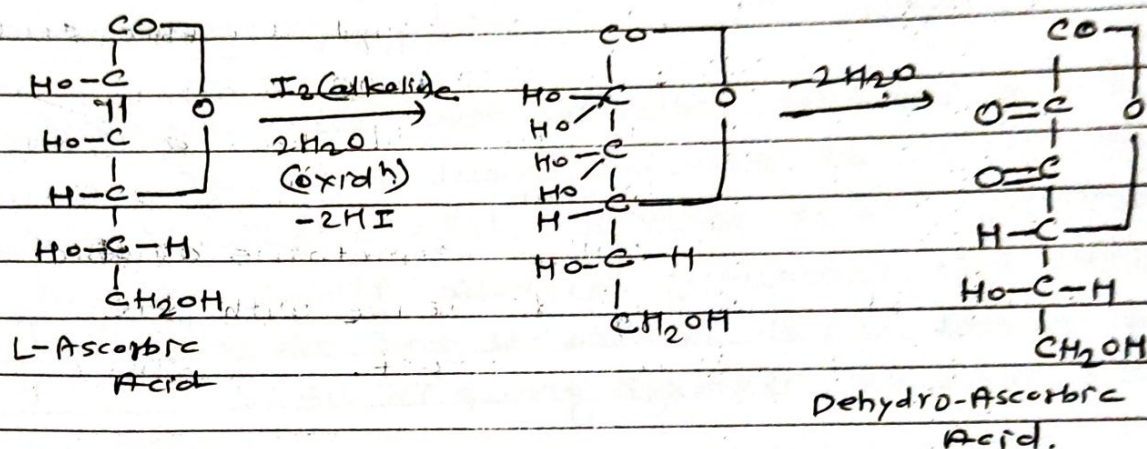
The formation of formaldehyde indicates that one of the presence of hydroxyl group in vit-C structure is primary in nature.



Ascorbic acid as well as dimethyl derivative condense with acetone which produce monoiso-propylidene derivative indicates that the presence of two alcoholic hydroxyl group in vit-C are adjacent to each other.

- ② Moreover the presence of four hydroxyl groups in vit-C structure indicates that vit-C reacts with Ac_2O gives tetra-acetate derivative or methylation gives tetramethyl ether derivative.

⑥ Presence of Lactone Ring:-



During oxidⁿ of vit-C, there is a removal of two hydrogen atoms, resulting the formation of dehydro-ascorbic acid which is a neutral and behaves as the lactone of monobasic hydroxyl acid.

Also ~~dehydro-~~ vit-C on reduction with H_2S is converted into ascorbic acid (vit-C).

As above oxidⁿ-redⁿ process is carried out with mild reagent, it concludes that vit-C like its oxidation product dehydroascorbic acid is lactone not an acid.

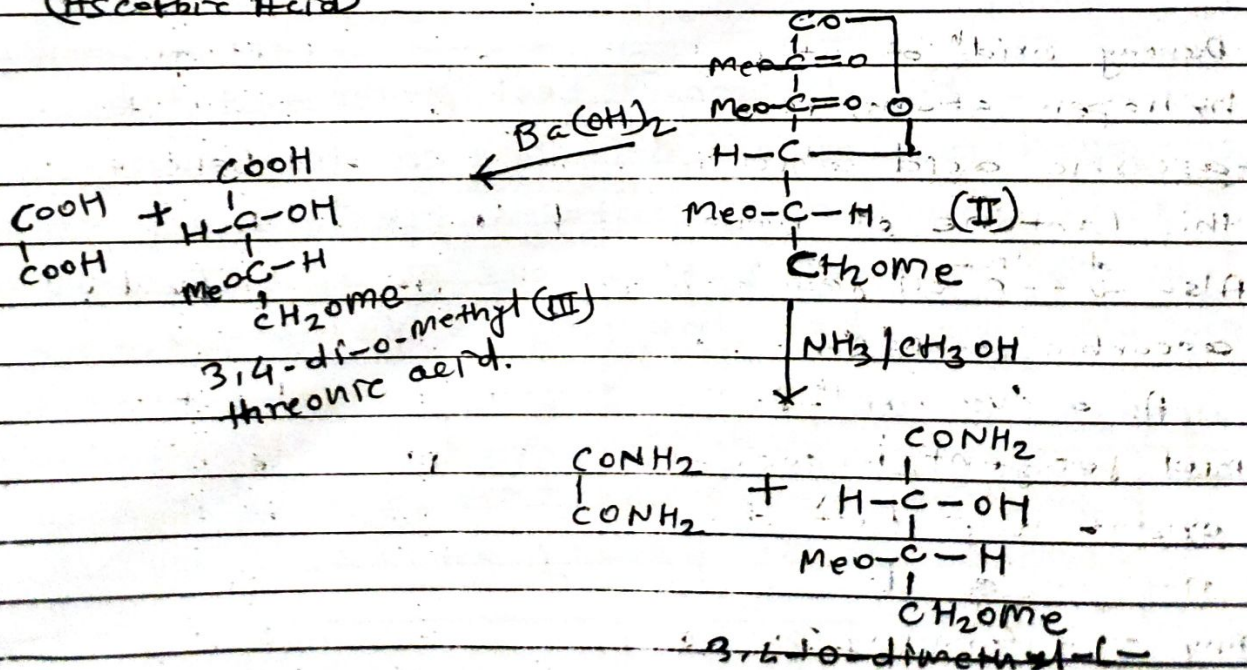
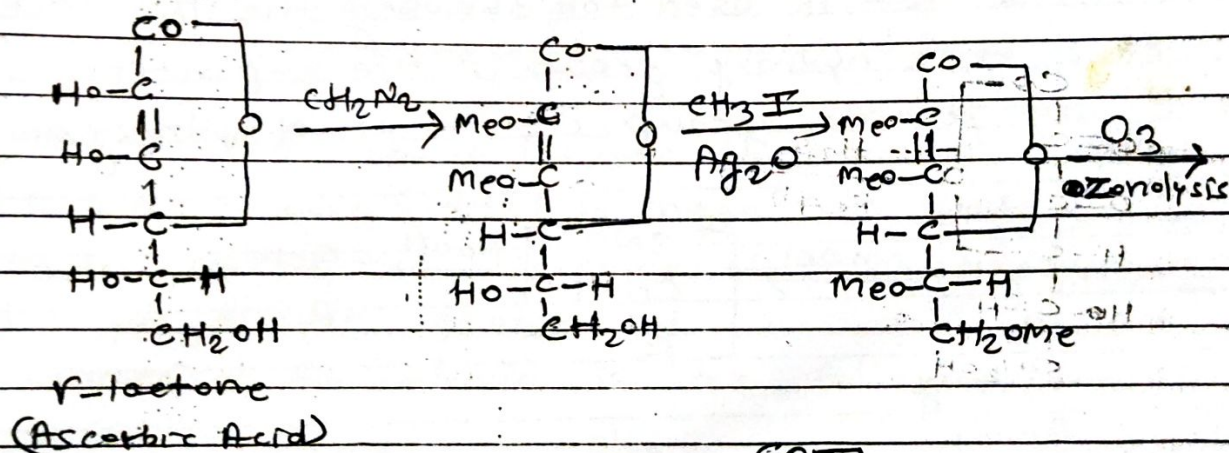
Any salt forming property due to the presence of ~~lactone~~ group.

⑦

Size of lactone ring:-

The size of lactone ring is γ -lactone due to the following facts.

- ① Rate of hydrolysis of dehydroascorbic acid is comparable to a γ -lactone.
- ② I.R spectrum of ascorbic acid shows a band 1760 cm^{-1} of γ -lactone.
- ③ On treatment with diazomethane ascorbic acid yields methyl derivative with the lactone ring remains intact.

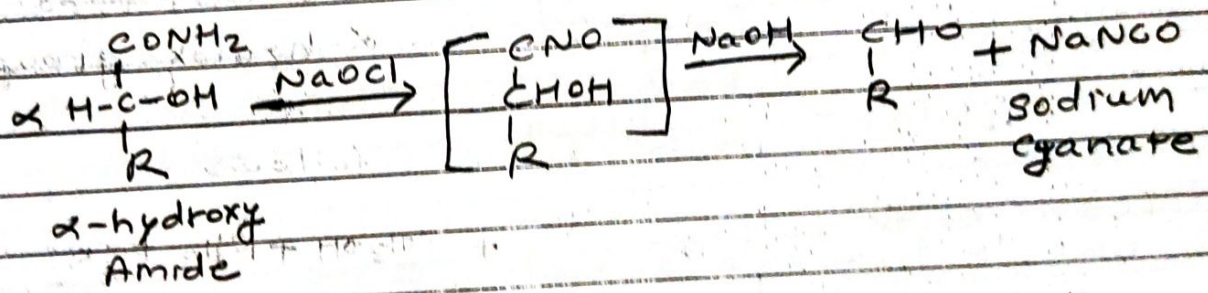


- Ozonolysis of tetramethyl derivative of Vit-C yields (II) neutral compound which has the same no. of carbon atoms showing the presence of ring system.
- When the compound (II) is hydrolysed with Ba(OH)₂ solution, yields oxalic acid. The formation of three carboxylic groups on ozonolysis clearly shows that the starting compound contains lactone.
- Moreover, the compound (II) is converted to amide on treatment with methanolic ammonia which gives 3,4-di-O-methyl-L-threonamide (IV). Thus the formation of compound (IV) are responsible for Weerman's test.

* Weerman's Test:

indicated the presence of α -OH gr.
 [α -hydroxy amides on treatment with sod. hypochlorite gives sod. cyanate]

This test is used for showing the presence of a free hydroxyl group in the α -position to an amide group i.e. in an α -hydroxy amide.



The Weerman's test proves that the compound (IV) contain α -hydroxy amide group. Thus the compound (II) contains free hydroxyl group. Thus the formation of above III and IV compounds possible only when the ring is γ -lactone.

Indication:- L-Ascorbic acid (γ -lactone) shows positive Weerman's test due to the presence of α -hydroxy amide derivative in (IV).