

①

Vitamin A

|| 20/3/00

① mol formula: $C_{20}H_{30}O$

② a forms monoacetate \Rightarrow it contains one OH gp.

③ forms aldehyde or Ox \Rightarrow OH gp is 1° in nature.

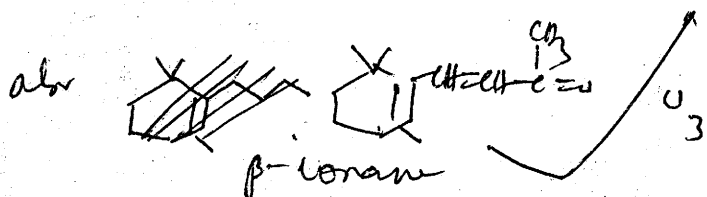
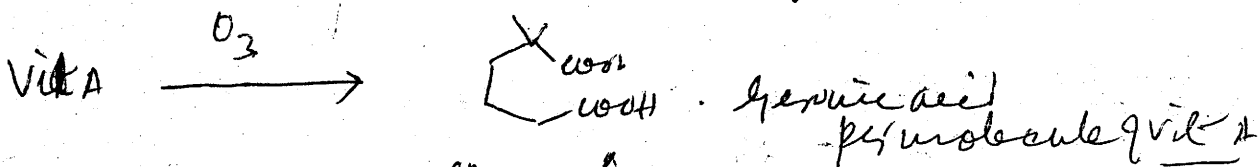
④ it absorbs 10H's on catalytic reduction \Rightarrow it contains 5 DB bonds

③ Fully saturated form contains 20C and 40H
but fully saturated per chain analogue = $C_{20}H_{42}$
no. of missing hydrogens = 2

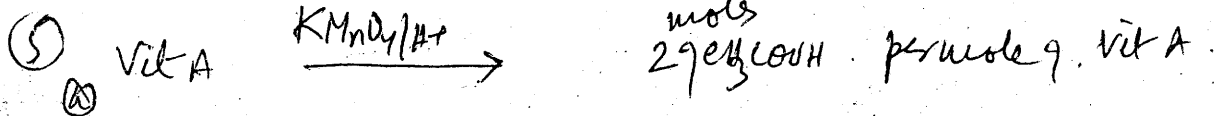
no. of ring = 1 ~~monocyclic~~

\Rightarrow it is a monocyclic compound

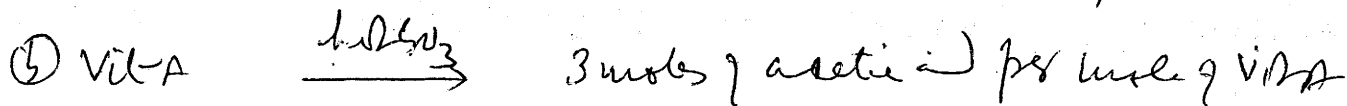
④



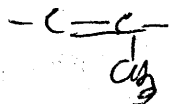
\Rightarrow Vit A should contain β -ionone nucleus.



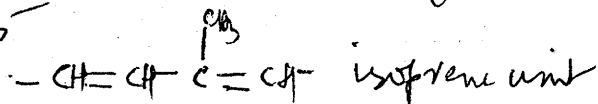
\Rightarrow it contains 2- $C(CH_3)$ group

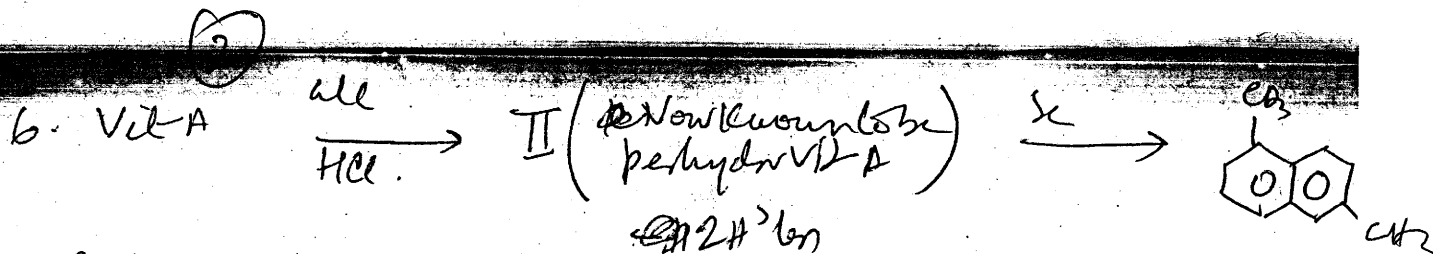


\Rightarrow it contains 3- $C(CH_3)$ -group \rightarrow the form



⑦ Since presence of one such grouping can be accounted for in the β -ionone nucleus. So the other two should be in the side chain. The presence of $-C(CH_3)-$ group in the side chain has been suggested by the fact that ~~Vit A~~ most of the carotenoids contain isoprene units





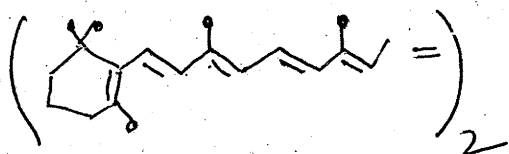
This also suggests the

⇒ there are 2 isoprene units in the side chain
(also suggested by the formation of 2 moles of acetic acid per mole of vit A by rxn 5@)

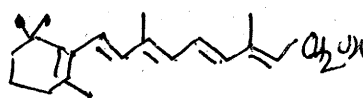
Since vit A has been found to resemble, in physiological property/action, with ~~β-carotene~~ β-carotene.

6@ rate of hydrolysis requires it to be of molecular weight half to that of the β-carotene.

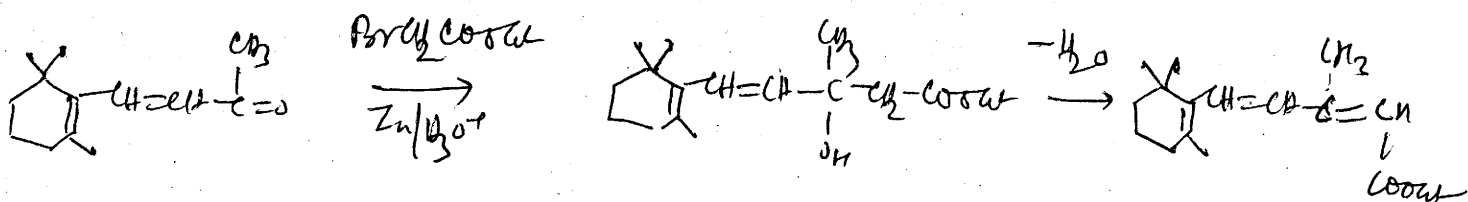
The structure of β-carotene is known & established and can be represented as.



So the structure of vit A with should be

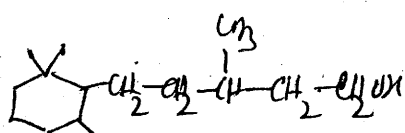


Support for this structure can be found in the fact that perhydrovit A has been ~~found to~~ synthesized from ~~β-carotene~~ β-ionone and shown to be identical with reduced form of vit A. Structure of perhydrovit A is established by following synthesis

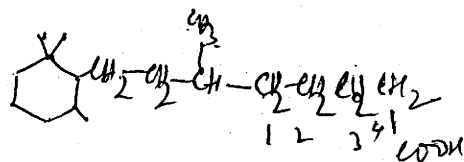


Completed^{ly}

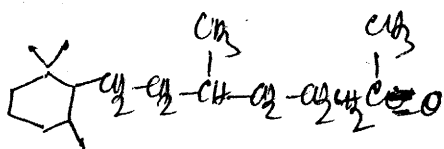
$\xrightarrow[\text{Alcohol}]{\text{Mg/H}_2}$



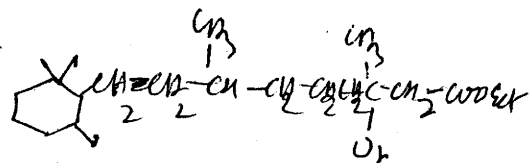
1. PBr_3
2. $\text{Mg}^+\text{CH}_3\text{COOH}$
3. $\text{H}_3\text{O}^+/\text{D}$



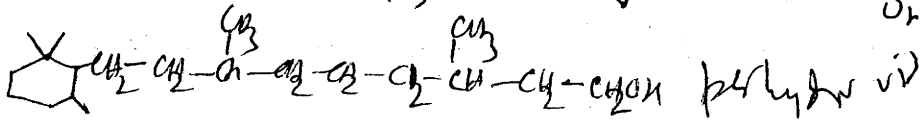
$\xrightarrow[\text{Et}_3\text{Li}]{\text{Suzuki}}$



$\xrightarrow[\text{Zn/H}_3\text{O}^+]{\text{Perhydrovit A}}$



$\xrightarrow[\text{Alcohol}]{\text{NH}_4^+/\text{H}_2}$

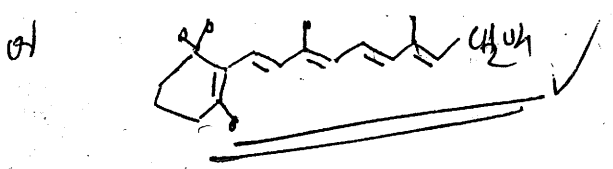
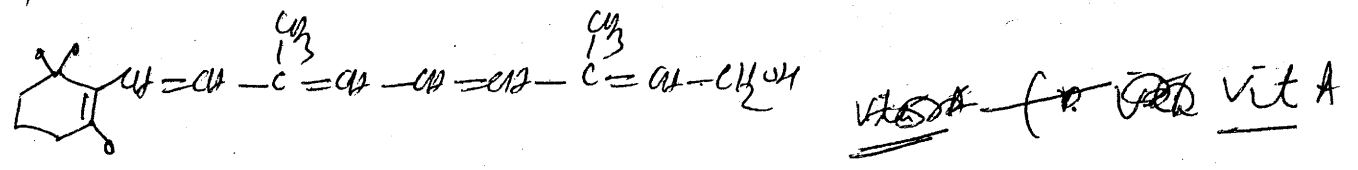
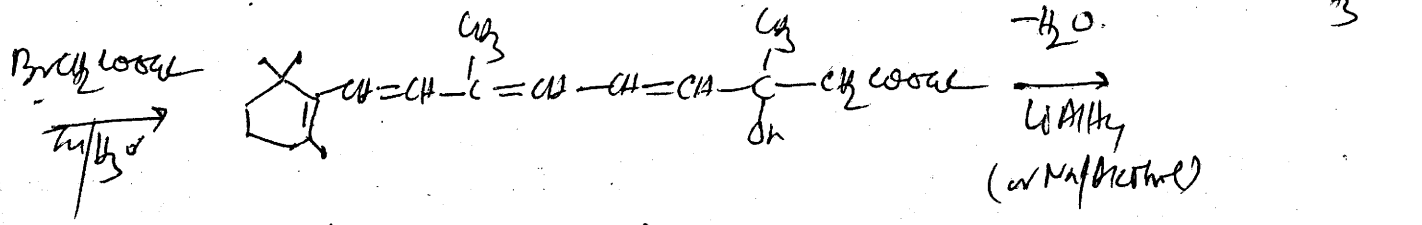
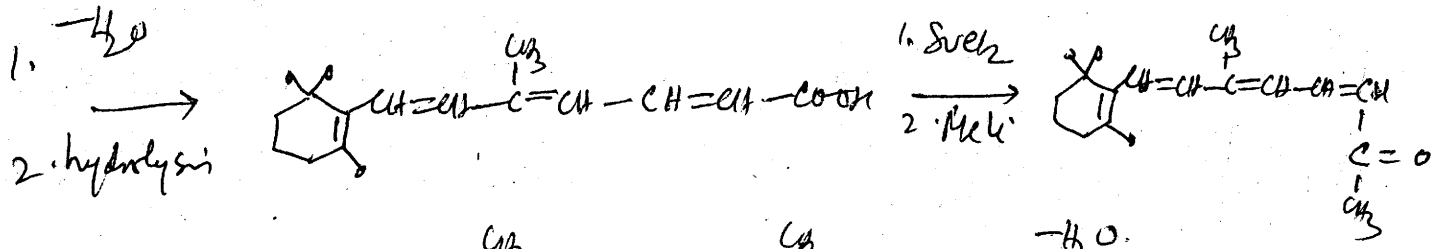
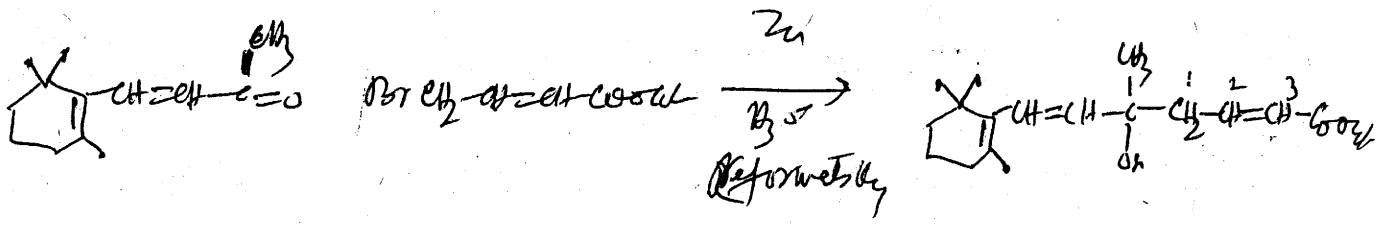
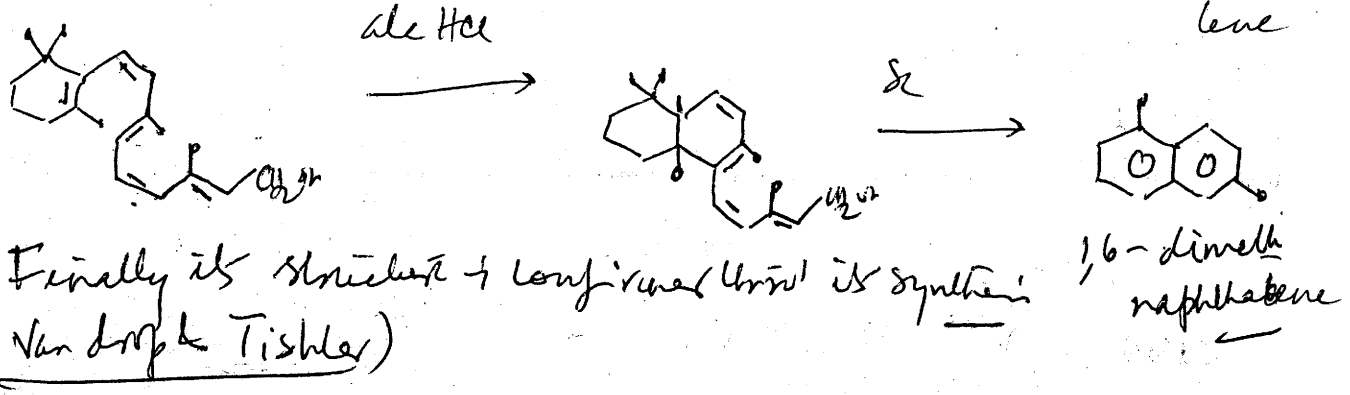


3

Vit A $\xrightarrow{5H_2}$

perhydrovit A

Above structure of vit A explains the formation of 1,6-dimethyl naphthalene



~~Vit A~~ \rightarrow ~~Vit A~~ Vit A

4, 4/2

①

Vitamin C

10.00

① mol formula $C_6H_8O_6$.

2 ② gives intense colouration with TETRA NITRO MET
- a specific reagent of D bond.

③ on 'O₃' treatment gives monozoneide of composite
 $C_6H_8O_6 \cdot O_3$.

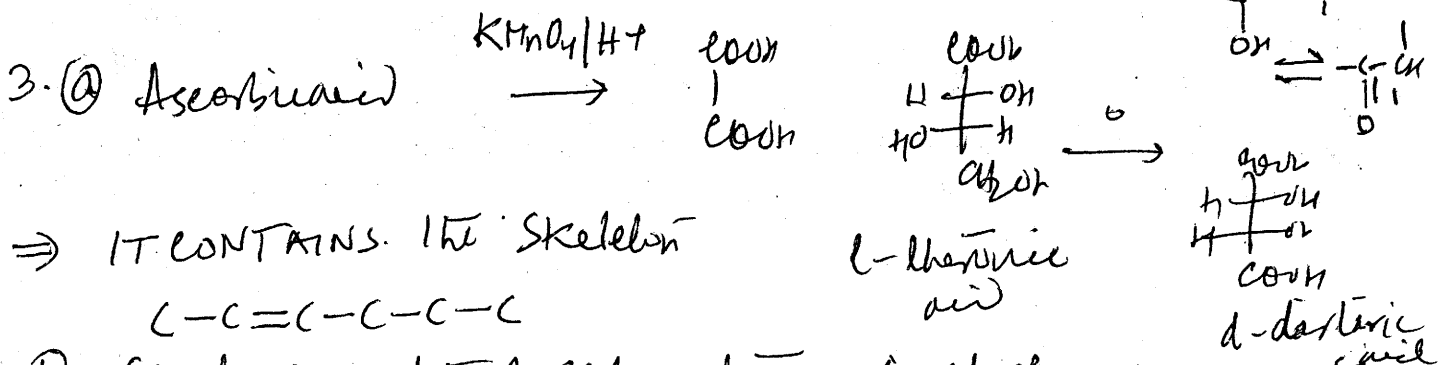
④ behaves as a strong reducing agent despite sh
-ve test for C=O sp (no colouration with Schiff's bc

⑤ gives intense colouration with $FeCl_2$ solⁿ

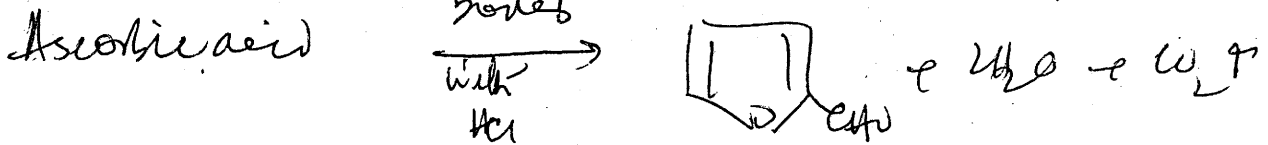
⑥ forms diphenylhydrazone with phenyl hydrazine

⇒ 1. IT CONTAINS ONLY ONE DOUBLE BOND.

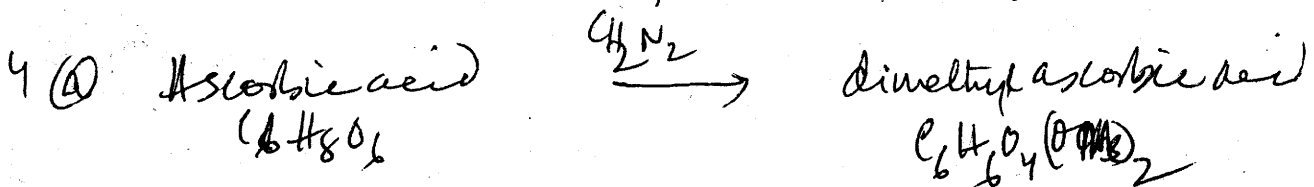
2. ALSO A KETO-ENOL SYSTEM



② St chain nature of carbon atoms is atwist by the rea

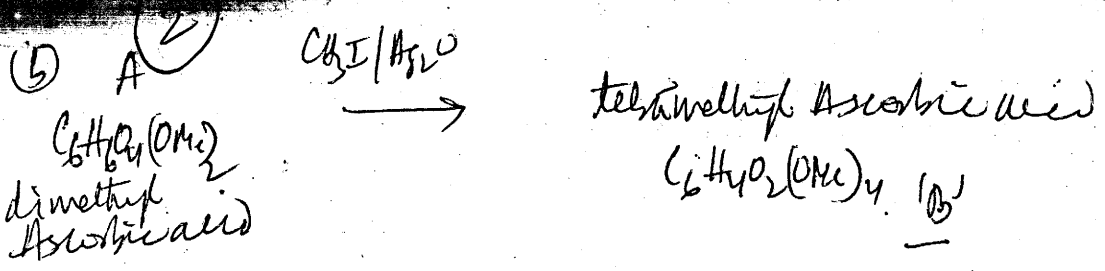


beside showing the presence of a no of OH sps

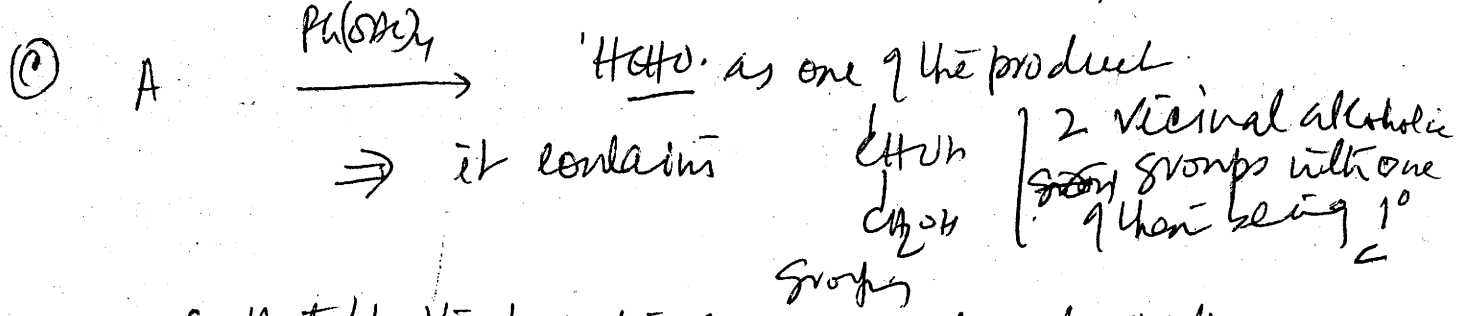


as CH_3N_2 is a specific reagent for methylating
enol OH.

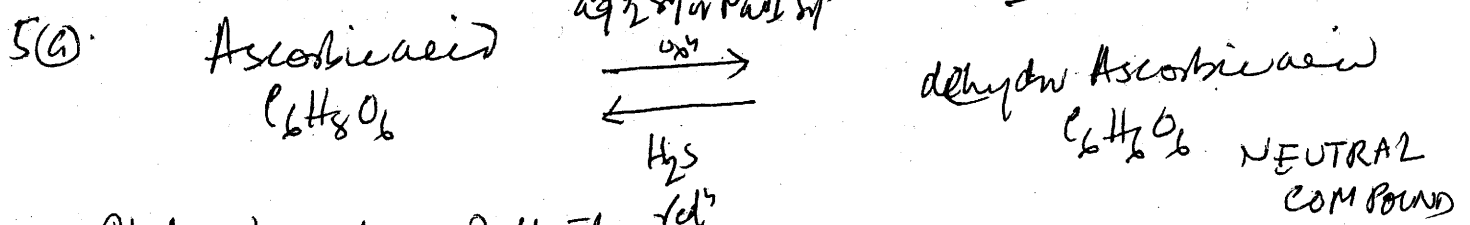
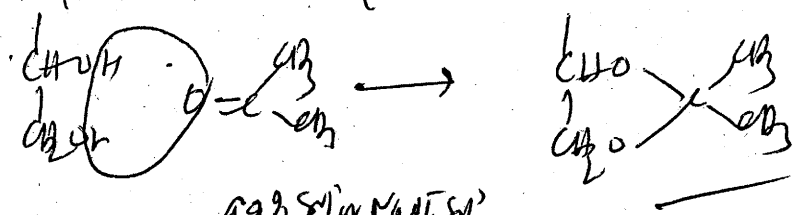
⇒ IT CONTAINS ONLY TWO ENOLIC HYDROXYL
GROUPS.



\Rightarrow IT CONTAINS TWO EXTRA -OH GROUPS. ~~THAT MUST~~ WHICH MUST BE ALCOHOLIC otherwise CH_3I should be able to methylate all the four OH groups directly.



supported by the formation of monoacetal derivative



It has been found that

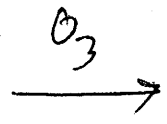
- (i) the product of forward reaction - dehydro Ascorbic acid is a neutral compound,
- (ii) behaves as a lactone of monobasic, hydroxy acid
- (iii) the process is reversible, & more importantly
- (iv) the ~~eff~~ reversibility is effected by even mild reagents

\Rightarrow Ascorbic acid is itself a lactone rather than a as suggested earlier on its ability to form mono K/Na salt. Salt forming ~~less~~ ability may possibly be due to the enolic -OH gr's whose presence has ~~also~~ been ~~proved~~.

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5

B.
tetramethyl
ascorbic acid
 $C_6H_4O_2(OMe)_4$

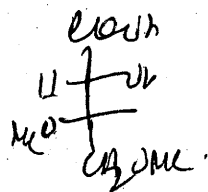
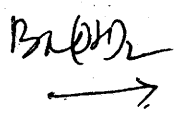


C. NEUTRAL
containing same no of carbon atoms

Since ozonolysis (=) bond is known to completely break that linkage;
⇒ there must be a ring system to hold the fragments

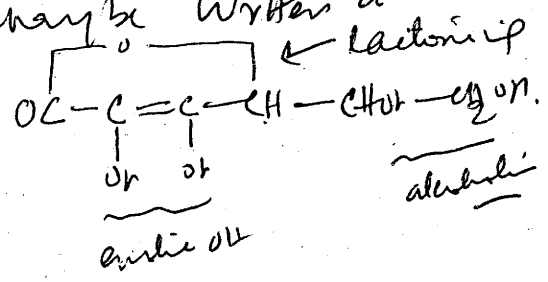
6

P C



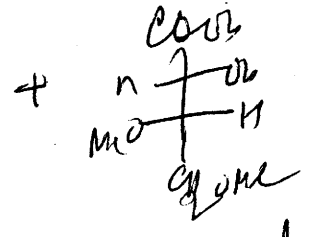
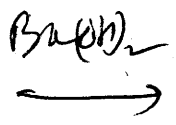
This line contains 3 COOH gr.
Since ozonolysis ~~with~~ is known to produce only 2 COOH gr's ⇒ the third should already be present in Ascorbic acid itself as lactone, because ~~the latter~~ Ascorbic may behave as a neutral comp.

~~On the basis of above facts and finding a tentative~~
On the basis of above facts and finding a tentative structure vit C may be written as



Although there are evidences showing the nature of the lactone ring to be γ rather than δ (stability towards alkali) a final confirmation of the ring size is necessary and is achieved through following ~~example~~ ~~with~~ reaction sequences.

6(a) 'C'
oxidized product
of tetramethyl
ascorbic acid
(B)



dimethyl-l-threo
ne

