Chapter 2

Steroids

Includes:

a-Sterols b-Steriod hormones c-Vitamines d-Bile acids;

e-The adrenal cortex hormones;

f-Some carcinogenic hydrocarbons

g-....etc

Steriods are compounds most of them isolated from animal sources and some of them isolated from plant source.

Steroids produces Diels hydrocarbon and small amount of chrysene on distillation with Se/ at 360° C If distillation carried out at 420° C, chrysene.

Is the mainly product with small amount os picene.

All steroids containing perhydrocyclopentenophenanthrene with M.F. C_nH_{2n-6}

Preparation of Diels hydrocarbon (3'-methyl-1,2-cyclopentenophenanthrene)

Some nomenclature of steroids:

For substituents:

Dotted line refers to α -configuration;

Solid line refers to β -configuration;

Wavy line refers to unknown configuration

A)Sterols

They are present in animal and plant in oils and fats, three types:

a-Zoosterols: They are sterols of animals,

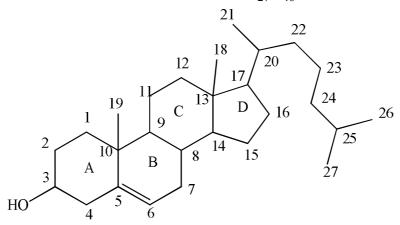
b-Phytosterols: They are sterols of plants

c-Mycosterols: They are sterols of yeast and fungi

All sterols are containing Diel's hydrocarbon nucleus or

perhydrocyclopentenophenanthrene with M.F. $C_nH_{2n-2} = C_{17}H_{28}$

1- Cholesterol C₂₇H₄₆O



It is present in the animal cell free or as fatty esters especially in the brain and spinal cord

Color reactions of cholesterol:

A solution of cholesterol in chloroform gives a red color with $c.H_2SO_4$ and gives greenish color with $c.H_2SO_4$ / (CH₃CO)₂O.

a-Structure of the ring system (Tetracyclic form of cholesterol):

HO cholesterol C₂₇H₄₈O CrO₃

Cholestane
$$C_{27}H_{48} = C_{n}H_{2n-6}$$

$$C_{17}H_{48}O$$

$$C_{17}H_{48}O$$

$$C_{17}H_{48}O$$

$$C_{17}H_{48}O$$

$$C_{17}H_{48}O$$

Formation of cholestanol from cholesterol indicates the presence of one double bond in cholesterol.

Reduction of cholestanone to cholestane indicates the presence of a secondary hydroxyl group in cholesterol.

Consequently, cholesterol is a tetracyclic ring compound with one double bond and secondary hydroxyl group.

Distillation of cholesterol with selenium give Diels hydrocarbon, indicates the presence of this nucleus in it.

b- Position of the hydroxyl group(at C-3):

 3^- ,7-dimethyl-1,2-cyclopentenophenanthrene

Thus, the hydroxyl group in cholesterol at C-3.

c-Position of the double bond can be indicated by the following reactions:

Consequently ,the double bond at C_5 --- C_6 in the ring .

ÓН

d- *The nature and position of the side chain in cholesterol*: It has been found that:

The side chain is methylisohexylketone (C8) and the nucleus is (C19)

Barbier-Wieland degradation (B.W.) Ме EtOH/HC1 R i)MeMgI ·CO₂H ii)H₂O monocarboxylic acid ester ΗÓ Мe tert.alcohol | c.H₂SO4 Ме Ме CrO_3 RCO₂H monocarboxylic acid alkene ÌИе Ме EtOH /HC1 i)MeMgI -CO₂H $CO_2C_2H_5$ НÓ Мe $\underset{\mid c.H_2SO4}{\text{tert.alcohol}}$ Me Ме CrO₃ Мe Мe alkene ketone CrO₃ H_2/Pt ΌH Na(Hg)/HCl OH cholesterol cholestanol cholestanone Н

cholestane

H coprostane

Degradative oxidation for the side chain in coprostane

Formation of acetone means that the side chain of cholesterol ends with isopropyl group.

The last reactions indicates that the side chain consists of eight carbons attached with the ring D which is a five membered ring .

Also, formation of Diel's hydrocarbon on heating cholesterol with Selenium, indicate that the side chain attached to the nucleus at C-17.

Formation of 1,2-dimethylphenanthrene indicate that there is an angular methyl at C-13.

e-Presence of an angular methyl at C-10:

The carboxylic group at C-10 resists esterification and resists decarboxylation, this is due to the presence of an angular methyl group and the carbon is tertiary carbon.

f- Presence of an angular methyl group at C-13:

 $cholesterol \ + \ H_2 \ / \ Pt \ \rightarrow cholestanol$

 $cholestanol + CrO_3 \quad \rightarrow cholestanone$

cholestanone + Na (Hg) / HCl → cholestane