hello everyone welcome to third class of biomolecules ah first i will ah like to ah give you a recap of ah last class in last class we discussed about ah structure of you know aldosis particularly configuration of ill doses and there we talked about d l doses particularly and then we also discussed about the configuration of ketosis and there we discussed different type of ah d ketosis and finally we were talking about the structure of structural formula of monosaccharides ah while talking structure of formula of monosaccharides we we discussed the different kind of you know representations particularly ah fischer projection ah formula and there we learnt that how sugar molecule can be represented in a two dimensional format fischer projection formula is also known as cross formulation why it is known as curve formulation because of the way of presentation is like you know ah we keep the main functional group on the vertical line and ah hydroxyl group we keep on the carbon chain i have already given you example of the d glucose so ah today i will ah show you some models and through that we will try to understand in a better way the meaning of formulas can be seen through the use of molecular model and here you can see that i have taken here this you know carbon chain carbon chain here stands for like you know carbon number one which has the aldehyde functional group carbon number two which has you know hydroxyl on the right hand side and hydrogen on the left hand side then carbon number three which has you know hydroxyl on the left hand side and hydrogen on the right hand side similarly you know carbon number four where hydroxyl is on the you know right hand side and hydrogen on the left hand side and carbon number carbon number five has ah you know hydroxyl again on the right hand side of the carbon chain and hydrogen on the left hand side and finally the last carbon c h two o h is attached

so if you look over this molecular model you can see here that how this aldehyde group is projecting away from us whereas you know um hydroxyl and hydrogen are ah projecting towards us

so high aldehyde group and this ch2oh which is going you know away from us and if we leave it freely then it tries to approach towards the ah you know ld hyde group this ah ch2oh you know attached ah hydroxyl group

so now again ah you know i will i would like to talk about that you know if we leave this open chain conformation you know it it tries to you know attain a kind of you know cyclic or spiral structure and that basically you know has been absorbed in the structure of glucose that it does not remain as a like you know linear form it attains a cyclic form all right

so what are those cyclic forms we have already discussed about the fischer projection formula which is a linear form the other possibility from the fischer projection formula that one can attain is cyclic form and that is also known as howarth formulas which is cyclic in nature

so i will show you this is the fischer projection formula which is cross formulation and there we also learned about that waste line dash base formula now i am talking about the you know the cyclic formula which is you know having a six membered ring and that six membered ring having oxygen as a hetero atom and other five members of the six membered ring are carbon now i will explain it that how this six membered ring is forming i have already mentioned that the linear form the fischer projection firm what we have discussed already it does not remain in reality

so this is the cyclic form cyclic form again i am taking here the linear form through this you know chain of carbons ok and i am leaving it if you see that you know when i leave it freely then again this aldehyde is approaching towards the hydroxyl of you know hydroxyl of the you know fifth carbon and that structural arrangement leads to the cyclic structure of the you know sugar basically of the you know glucose but in particularly in this case

so what are we doing we we we are just putting it in a free form and that free form gets the cyclic structure now once this hydroxyl approaches the aldehyde of this carbon chain it reacts with the aldehyde and as we know that reaction of aldehyde and alcohol leads to the formation of acetyl and that basically the cyclic structure is acetyl in other words we can say that the glucose which we consider as a linear form its not linear its mixture of cyclic as well as the linear form here i have drawn from the linear form the i have drawn here the cyclic form this solid line representation means if we consider the pyron ring in plane this ah the solid line comes towards us where as the oxygen containing part is going away from us and on this ring you know different substituents are there

so one possibility if aldehyde group attacks aldehyde group gets attacked by the hydroxyl it can lead to the hydroxyl down and other possibility where the hydroxyl can go up

so i will draw the other possibility again i am putting this solid

line just to make you feel that this part of the ring is towards earth then other part is away from us the rest you know two
so what is happening here
the o h group of c two is placed on the right side and that of c3 on the left side and those of c4 and c5 on the right side this cyclic form the cyclic representation
basically is known as how earth formula how earth formula and these two cyclic form where hydroxyl is you know opposite to the orientation of c h two o h that is known as you know alpha d gluco pyranose and where the hydroxyl is on the same side
of the c h two o h then it is called beta d glucose pyranose now i will rather chair conformation of these structures to make you understand in a better way
so i am drawing here chair conformation
so in the alpha d gluco pyranos hydroxyl is axial at the first carbon and in the case of beta d glucopyranose it is equatorial all right now ah i am assuming that you have
better concept of you know cyclic structure that have earth formula which i explained you
ah with the help of the model that you know how this cyclic structure forms first i talked
about the fischer projection formula where the which is also known as class formulation where
we can see that on the carbon chain basically ah hydroxyl and hydrogen are on the both the sides
and if we leave it freely then ah hydroxyl of a fifth carbon comes closer to the ah ld hydric
group and it reacts and forms the acetyl and that leads to the formation of cyclic structure which
is acetyl in nature and that acetyl can be the you know alpha form or alpha cyclic form or
it can be the beta cyclic form and based on the you know sugar particularly we started
with the gluco glucose
so here glucopyranose alpha d glucopyranose and beta d glucopyranose ah these are the two cyclic structures are possible the cyclic form of the you know alpha d
glucopyranose and the beta d gluco pyranose where the orientation of hydroxyl group is you know ah
detrimental that you know from which class at the carbon number one there only it just varies if you
look over the you know these two cyclic structure leaving all other stereo center or chiral center
only you know the stereochemistry varies at the carbon number one basically at one position only
in both these forms you know ah stereochemistry is different rest of the carbons are having
same you know stereo chemistry and that is why the this you know in carbohydrate
chemistry the diastomer differing only at the hemiacetal r acetyl carbon are called enomars
so in carbohydrate chemistry diastromers differing only at only at the hemi acetyl are acetyl carbon are called enomers are called anomers and the hemiacetal are still carbon atom atoms carbon atom is called the anomaly carbon

atom numeric carbon atom
so the diastomers differing only at the hemiacetal
or acetyl carbon are called enomers and the   hemistolar estral carbon atoms
carbon atom
is called the enormic carbon atom the cyclic   structures for the glucose
enomors are called
havarth formula which i have already shown you and   each of these you know
glucose alpha and beta are
different at the you know particularly acetyl ah   carbon which farms after the
reaction of hydroxyl
at the c5 position and the aldehydic group now it is not fixed that this
cyclization will lead to the only   six membered cyclic structure
as we have seen in the case of   glucose it can also lead to the formation of
five membered ring
so if the monosaccharide ring ring is six membered after the acetyl formation
cyclic stick form
ester formation then it is known as pyranose here i will draw the structure of
pyram a pyron and if if the monosaccharide ring is ring is five membered phi
membered the compound is designated as furanose
so if the monosaccharide ring is five
membered the compound is designated as   furanose i am talking about the
acetyl cyclic acetyl formation
so this is the structure of furan and that is why
the cyclic you know structure is called furanose   now ah i will on the two
dimensional
representation i will show you that you know   how the formation of this
cyclic structure is taking place   ah first i will draw the fischer projection
formula and then ah i will show you that you know   what reaction is taking
place in reality i have
already shown you the howard projection formula   and ah i have also shown you
the alpha
and beta i mean chair structure of this   ah corresponding have earth projection
formula
ah
so let me write the structure of glucose
so here i am writing the structure
of glucose as we know that it has six carbons and aldehyde in its framework and
multiple
hydroxyl group particularly you know   ah five hydroxyl group on the carbon
chain   this is the glucose this is the plane projection
formula and this is the model for you know this   plane projection formula if
you see here this
is the model exactly i have drawn you can see let me arrange it in a proper way
this way this is the you can just pay attention that its very difficult to keep
it in a you know let me put it again trying to yeah in this case you can see
that c s two o
h c h two s this is the c h two h and this is   aldehyde basically this is the
aldehyde
group attached to the carbon and this is the   you know ch2 is the last one this
is what
i am you know dangling basically c s two   o h this is the c s two h and this is
the
aldehyde and rest of the carbons are you know   substituted with the hydroxyl
and hydrogen

you can see that carbon second is hydroxyl right side carbon two hydroxyl is left side carbon
three hydroxyl is right side and carbon four hydroxyl is right side and finally the ch2oh group
is you know going again away from us if if i leave it freely then as i mentioned that you know the
carbon at the five position is coming closer to the aldehyde group you can see here one two three
four five five position is coming closing closer to the alihide group
so let me draw the cyclic
structure to make you understand in a better way
so first i am writing the same open chain form and then to explain it in a two dimensional format i will show
you that you know how to rotate the bonds to ah
so this is the carbon which is attached with the aldehyde
so that be the aldehyde carbon number
one carbon number two carbon number three carbon number four five and six now
as i mentioned that what happens that you know carbon hydroxyl attached with the carbon
number five comes closer in this you know cyclic presentation you can see here that this is coming
closer this is the aldehyde
so one two three four five i just i have tilted like this
so that it can
react and this is this job i am going to
so what i am doing basically i am rotating along this carbon
carbon bond this carbon carbon bond thats what i am writing over here that if we rotate along
this carbon carbon bond carbon four and five carbon four and five if i rotate then
hydroxyl will take the position of c s two h and c h two o s
will take the position of hydrogen and hydrogen will take the position
of hydroxyl alright and
so let me rewrite with the rotated structure rest of the thing will remain
same and only the position of c s two o h and o h will get change all right
so after this bond rotation c four
c five bond rotation we get this structure now stage is set for the acetyl formation
so this lone
pair will attack on the carbonyl of the aldehyde and again o minus whatever the alkoxide will
form that will abstract the hydrogen from the alcohol one thing i will like to mention
here that this hydrogen abstraction is not intramolecular the proton transfer
steps occur between separate molecule the proton transfer step occurs between
separate molecules it is not inter intra molecular are concerted it is not intra molecular or concerted
here it appears just for the sake of you know clarity i have written like that but
generally it happens you know intermolecular
so after this cyclic acetyl formation
what will be the structure i am going to write the structure here first i will
draw the pyron ring and the enomeric carbon here is the anomeric
carbon in one case the newly formed hydroxyl group is on the same side where

the c s two o h and in other case it is on the
opposite side let me draw the by rendering here also
so in this case it is on the
opposite side of the c h two o h i will also like to mention that in both these cyclic structure what is common is
that leaving this enomeric carbon which has the you know different stereo chemistry all the c two
c three c four and c five have the same chirality same stereochemistry
so this is
alpha d gluco pyranose alpha d co pyranose and beta d glucopyranose glucopyranose now let us take a practice
problem how to draw these you know cyclic structure from the
fissor projection formula are from the you know cyclic structure or the from the chair ah ah form of ah structure how one can draw the fischer projection formula
just for the practice
so let us take a problem draw the beta pyron firm beta pyranose form of below given compound compound a and a fisher projection firm form of compound b let me draw these
two structure let first a
so this is the fischer projection formula again
i will draw it in the you know cyclic format so for drying in the cyclic format i will take
first aldehyde
so let me make the aldehyde and then first carbon attached to it
so it has hydroxyl group on the right hand side then the
third carbon which has again hydroxyl group and the right hand side and then fourth carbon
where the hydroxyl group is on the left hand side and the fifth carbon which has hydroxyl group on the right hand side and c h two o h group now this after acetyl formation i it has been
mentioned that you know beta pyranose form
so ah i will not consider alpha pyronose i
will directly write the beta pyranose form in the beta pyranose form i am putting the all chiral center
so this is the for the beta pyronose form of the
given fischer projection formula the structure here now i think you have better
understanding once you know that you know fischer projection formula then
you can translate easily into the howard projection formula the cyclic one for the
acetyl formation now the second question is the b draw the fischer projection formula for a chair
form of fischer projection for cyclic structure
so i have now you can see on this structure this is b let
us open it up
so that we can we can translate it into the fischer projection formula
so what i
am doing that ah i am going to open this this is the carbonyl carbon which reacts with the five
position hydroxyl group
so just i will put the c h two o h this is first second third fourth
five fifth sixth and seventh
so c s two o h and then again carbonyl which is involved in the here

it is basically involved in the kettle formation and
so the other third carbon third carbon is
having hydroxyl again on the right hand side and fourth also having
hydroxyl in the right hand side and then again the fifth
hydroxyl is on the left hand side and finally the sixth one is having on the
right hand side and c h two o it h very clear that how you know the
carbonyl this ketose is reacting with the you know um hydroxyl of the carbon
chain
and that leads to the the cyclic structure now i will talk about the you know
muta rotation muta rotation as i mentioned that glucose in open chain is very
different from
the you know ah cyclic structure and in reality it remains as a mixture of the
cyclic re structure
the acetyl structure what just now i discussed with you because of the you
know cycle formation
due to the reaction of aldehyde and hydroxyl of same molecule muta rotation we
can defined
with the chiral nature of this you know ah sugar molecule particularly in case
of
glucose if we consider open chain firm and consider its ability to
rotate plane polarized light i am assuming that you are well familiar with
the you know concept of chirality as we know that chiral molecule has ability
to rotate plane
polarizalized
so this is the open chain form open chain form of d glucose d glucose and this
open chain form have given a specific rotation plus 52.
7 whereas i also showed you the
cyclic acetyl structure and cyclic style structure i am drawing
here in the chair conformation
so one is having hydroxyl group towards
the same side where the c h two o h we have already discussed that
is known as beta d glucopyranose this is beta d glucopyranose and the other
possibility where it is opposite to the c s two o h
so this is c h
two h and opposite to that this acetyl is known as alpha d glucopyranose now
these two crystalline structure can
be separated and it has been observed that alpha d glucopyranose which has
melting
point these two are basically diastromer because the if you see the carbon one
which
is you know having different stereo center otherwise all the other one two
three four
four chiral centers are having the same ah stereo chemistry only the enomeric
carbon
is having the different stereo chemistry and that is why alpha d gluco
pyranose has melting
point 146 degree centigrade and specific rotation close to plus one one two
whereas
beta d gluco pyranose which has melting point one hundred fifty degree
centigrade and specific rotation is plus eighteen point seven
so if you leave alpha
d gluco pyranose as it is you you see here we are having equilibrium among all
these structures from
the open chain to the these two cyclic structure

so the specific rotation of one firm will
decrease until unless it reaches to this 52.
7 whereas if you are having
pure beta d glucopyranose the specific rotation of beta d glucopyranose
will again increase until it reaches to the 52.
7 this is the normal d glucose which
i have represented in the open chain form which gives the 52.
7 as a specific rotation
so a solution of ordinary glucose has an initial specific rotation as plus one one two it
decreases down until un unless it reaches to the you know ah plus fifty two point seven r i can say
that a pure solution of beta d glucopyranose which has specific rotation plus 18.
7 increases
until unless unless it reaches to the 52.
7 assuming that the concentration
of the open chain is negligible we can ah figure out that percentage of cyclic structures available in
the solution
so if we assume that the concentration of open chain is zero concentration of open chain firm is negligible or zero with the help of specific rotation by specific rotation we can calculate that in a given solution
how much is the alpha d glucopyranose and how much is the beta d gluco pyranose
so i am just
writing here the you know the these percentage
so if the open chain is giving 50 plus 52.
7
that can be obtained from the from a mixture of alpha d pyranose where hydroxyl is axial and beta d-gluco-pyranose where hydroxyl is equatorial now as we know that beta d glucopyranose has you know a
specific rotation of plus 18.
7 and the you know d glucose where the you
know mixture of both has 52 point 52.
7
so how much of the you know beta d
glucose over there and how much is the alpha d here we can easily calculate if we consider
that open chain form is negligible then 36 percent of the alpha d gluco pyranose
and 64 percent of beta d gluco pyranose beta gluco paranos is available there at equilibrium at equilibrium here i will like to again add one more point that the in this case we can see that you know 64 percent is the higher quantity
so it is not
true that always beta n omer is the most stable i will show you another example where alpha anomer is more stable
so the beta anomal of a
pyranose is not always the more stable as we saw that in a mixture based on the calculation of the specific rotation ah we saw that 64 percent of beta d gluco pyranose
is there and 36 percent of alpha d glucopyranose this should not reflect that beta d glucopyranose is the are you know beta d pyranoside is

the more stable form now i will write here always more stable let me write here
a structure where alpha d glucopyranose is more stable
so here alpha d alpha d mano pyranose alpha d minor pianos and the beta d mano
pyranose beta d mano paranose here it has based on the
specific rotation it has been observed that it has 69 percent of the alpha
d mano pyranose at equilibrium and thirty one percent of beta demand
pyranose at equilibrium in a mixture now this enumeric effect is believed to be
caused by hyper conjugation this anomeric effect is believed to be caused by
hyper conjugation i am assuming that
you all are familiar with the hyper conjugation basically what happens that an
axial oriented
orbital axial oriented orbital associated with the non burning electron of the
ring oxygen
non bonding electron of the ring oxygen can overlap with the you know sigma
star orbital of the axial exocyclic co hemi acetyl band and that is the
ah you know reason for the stability of this ah you know enormous carbon ah
where
this ah overlap between the orbitals of the um you know um sigma star
arbitrage
of c o hemiacetal bond ah with the ah vacant non burning orbital of the
ring oxygen leads to the stabilization now ah i will talk about the glycoside
formation
so let us talk about the glycoside formation what is glycoside glycoside if you
treat d glucose with acidic methanol acidified
methanol or you can say that acidic methanol
so d glucose i am not indicating that it has
alpha d glucose or beta d glucose just simply if you take d glucose and react
it reacted with the acidified methanol what happens basically two gluco
glucopyranoside
forms let me draw this structure first two gluco pyranosite forms
so this is methyl alpha d gluco pyronoside
again here the orientation at the enomeric carbon and ah the ch2oh group will
define the type of glucopyranide since here it is in opposite side
so it becomes the
alpha one
so methyl alpha d gluco pyranoside side and the other possibility where if ocs
three is equatorial then it becomes methyl beta d glucose pyranosine now i will
discuss the mechanism that how is it
happening basically its a two step protocol what happens that in the presence
of a seed hydroxyl
group gets protonated and then it leaves and forms the corresponding
carbocation and that carbocation
gets reacted with the methanol and since this is sp 2 hybridized
so it has 2 possibility that
it can attack from the either this side or the you know opposite side and
hence it leads to
the you know these two glucopyranoside alpha d are ah beta glucopinocyte
so let me write here
the mechanism of ah mechanism further reaction
so carbohydrate acetyls acetyls are generally called glycosides and an acetal
of glucose is called glucoside glucoside similarly acetyl of mannose is called
mano side and acetola fructose is called fructoside
so these are the you know glycoside
formation let let me talk about the mechanism how does it ah happens

so i will stop here i will
discuss the mechanism in the next class ah thank you very much for the
attention ah we will meet
again ah with the mechanism of glycoside formation you