

Carbohydrates: Interface between Chemistry and Biology

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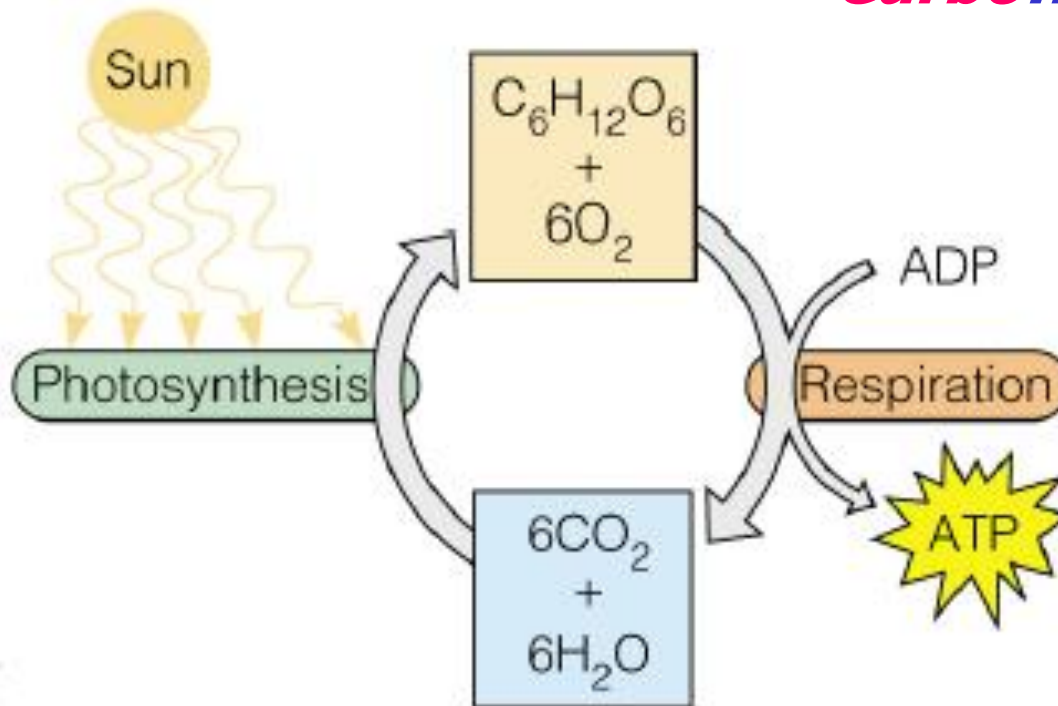
Maharana Pratap Govt. P.G. College, Hardoi

What is carbohydrate

General formula: $C_nH_{2n}O_n$

C H₂O

*Carbo*hydrate



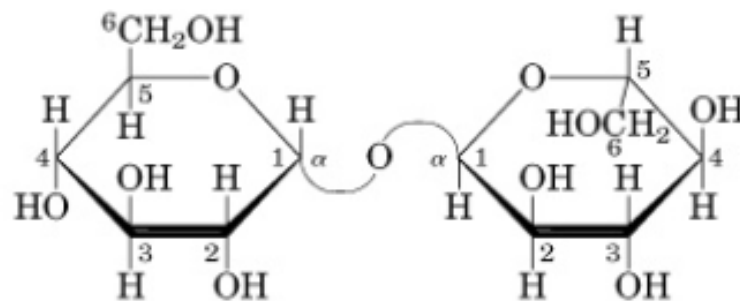
- The most abundant biomolecules on Earth
 - 100 billion tons/year of CO₂ & H₂O into cellulose & other plant products via
- Most simple general formula:
 - = C_n(H₂O)_n where n ≥ 3
- Occur as:
 - monosaccharides - simple sugars (eg glucose)
 - oligosaccharides - 2 to 11 linked monosaccharides
 - disaccharides, tri, tetra, penta etc
 - polysaccharides - 12 to millions of linked monosaccharide units
- General name ending is often -ose:
 - glucose, lactose, cellulose BUT not always:
 - starch, glycogen, chitin

Why carbohydrates are so important

- Energy Transport Molecules - Mono & Disaccharides
- Energy Storage - Polysaccharides
- Plant & Animal Structure - Polysaccharides
- Informational Molecules - Oligosaccharides

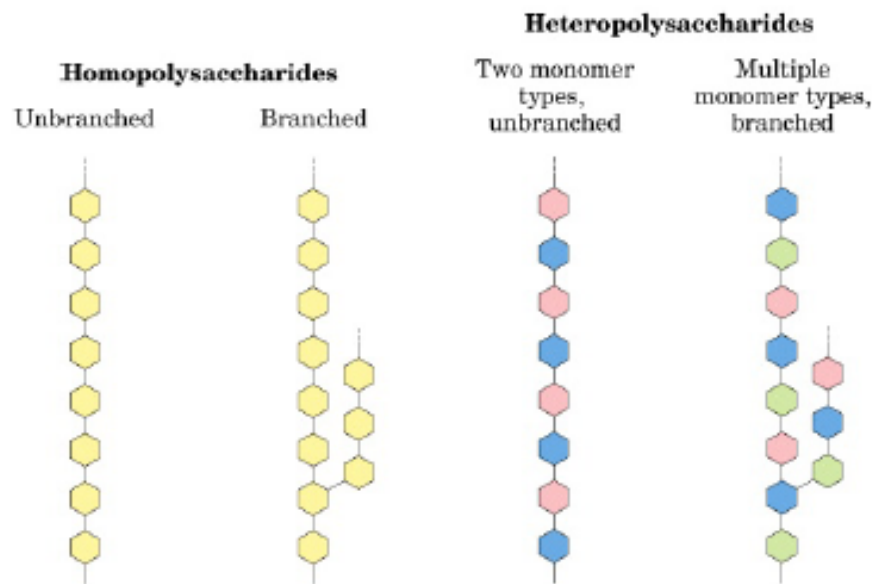
Energy Transport Molecules

- Glucose: monosaccharide, in vertebrate blood
- Lactose: β -linked disaccharide, in mammalian milk
- Sucrose: $\alpha\beta$ -linked disaccharide, in plants
- Trehalose: $\alpha\alpha$ -linked glucose disaccharide, in insects



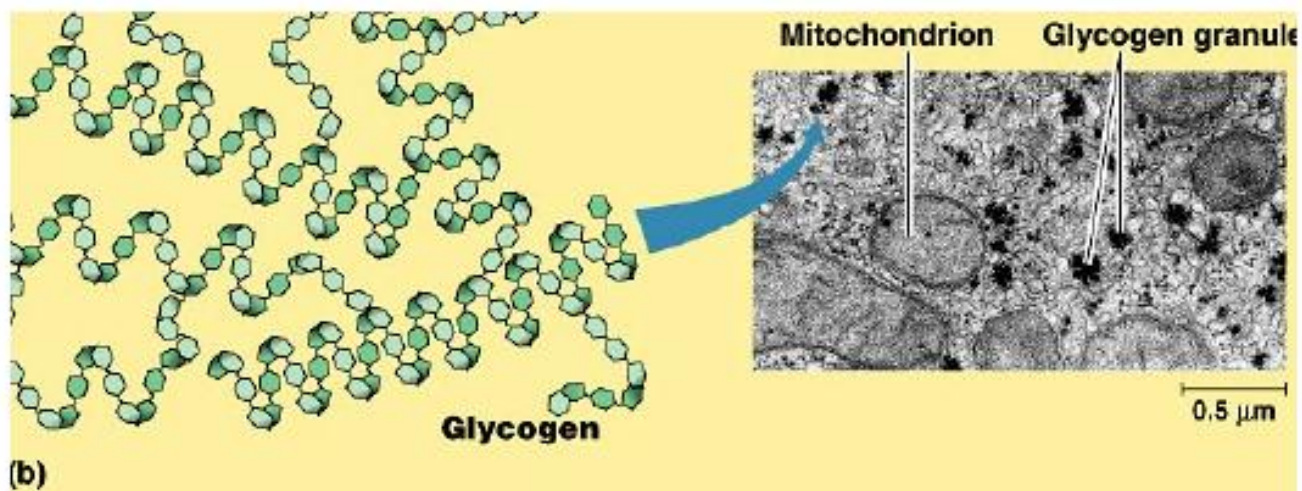
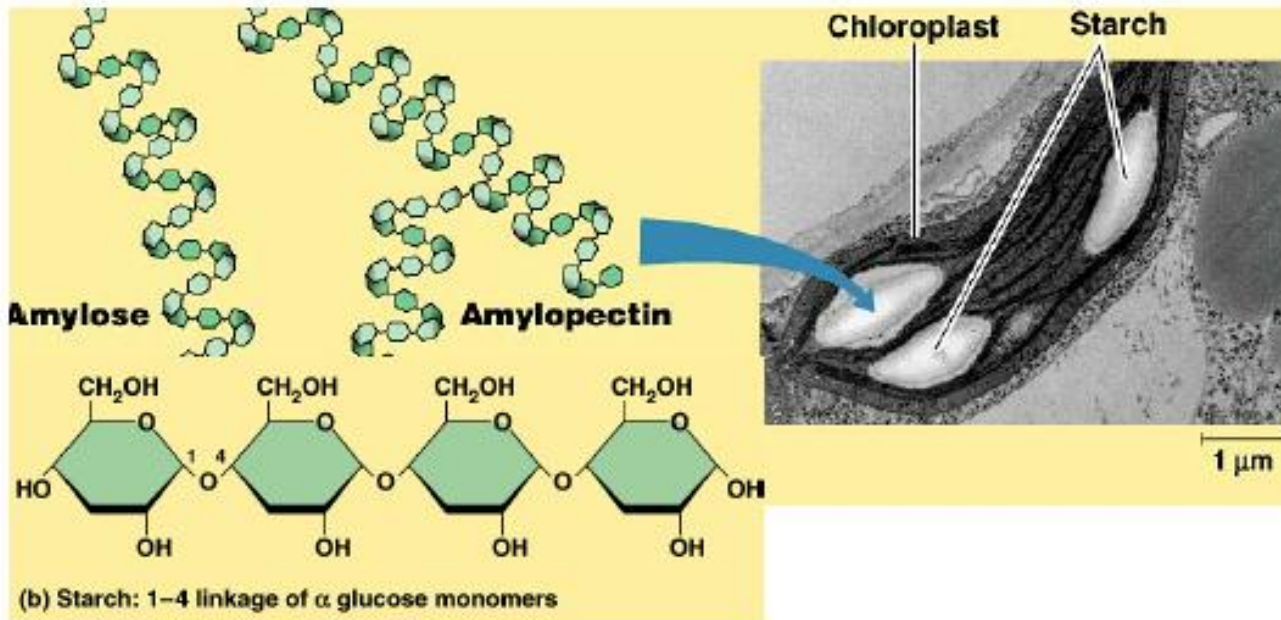
Trehalose
 α -D-glucopyranosyl α -D-glucopyranoside
 $\text{Glc}(\alpha 1 \leftrightarrow 1\alpha)\text{Glc}$

Polysaccharides: Energy Storage or Structural

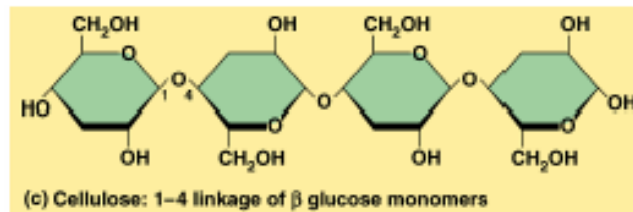


- Long polymeric chains of monosaccharides. Typically thousands to millions of residues in length
- Homopolysaccharides = one type of monosaccharide only
- Heteropolysaccharides = more than one type (commonly 2)
- May be linear or branched
- May be neutral or may be negatively charged
- May be soluble, gum-like, granular or fibrous

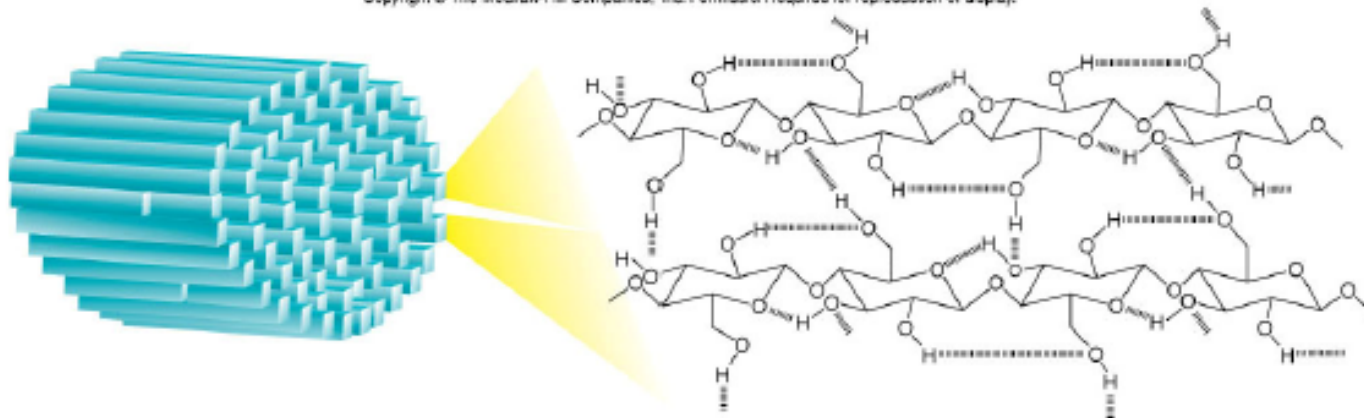
Amylose : A Homopolysaccharide of Glucose



Cellulose (Disaccharide is Cellobiose)



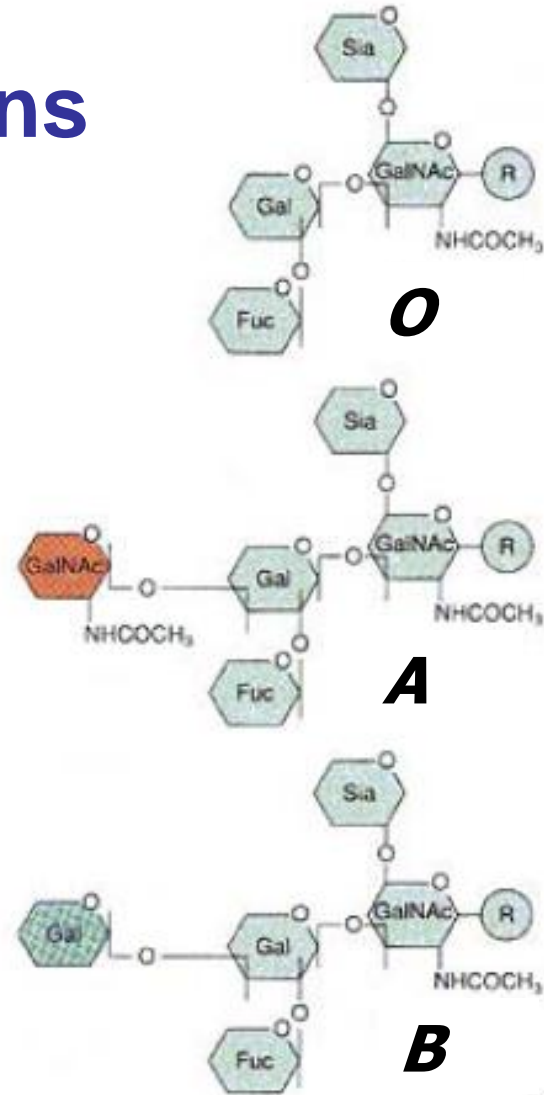
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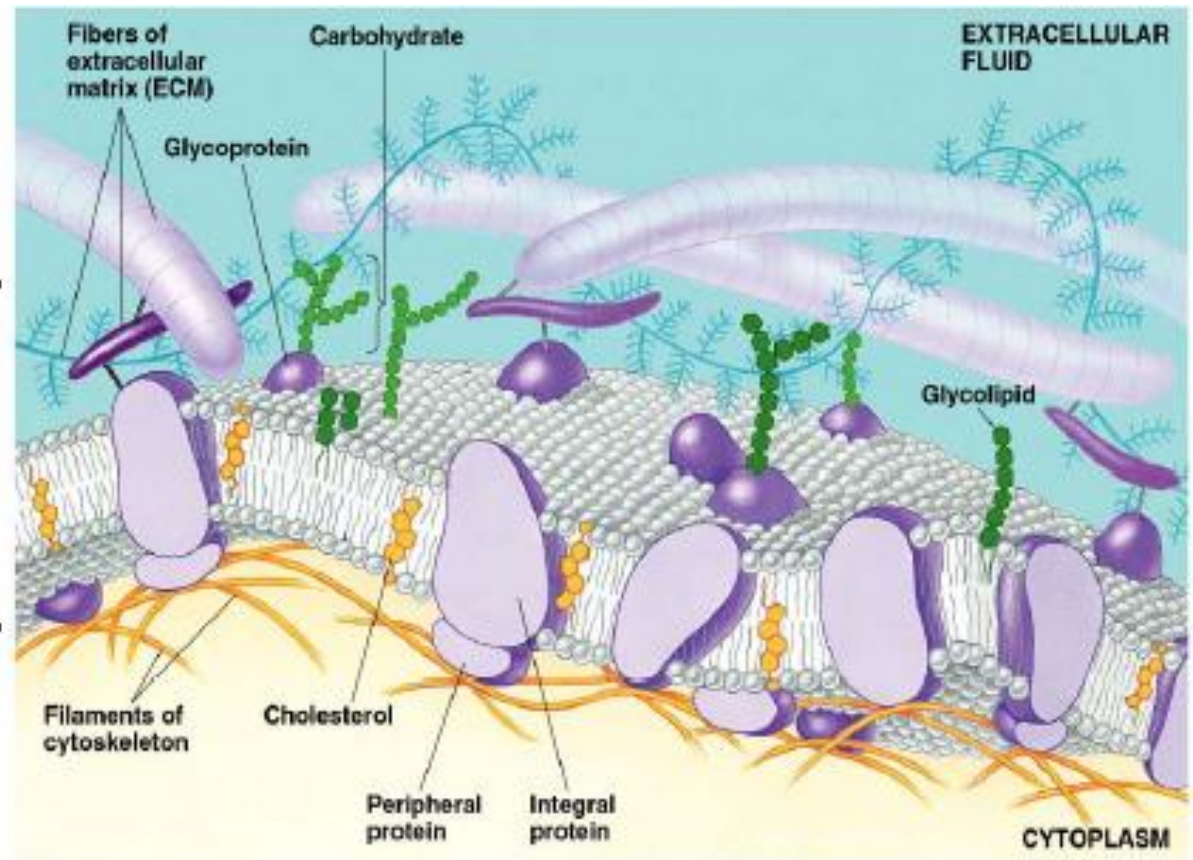
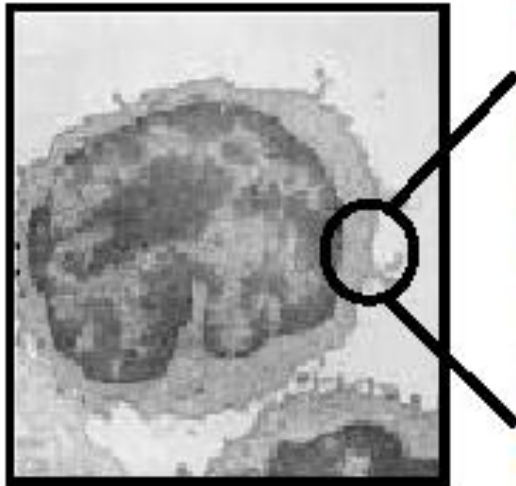
- Cellulose is the main structural component in wood, paper, cotton etc
- Most animals do not have an enzyme that attacks $\beta(1-4)$ O-glycosidic linkage in cellulose
- Herbivores carry bacteria that produce $\beta(1-4)$ cellulase
- Some termites, crabs etc may produce this enzyme

Blood Group Antigens

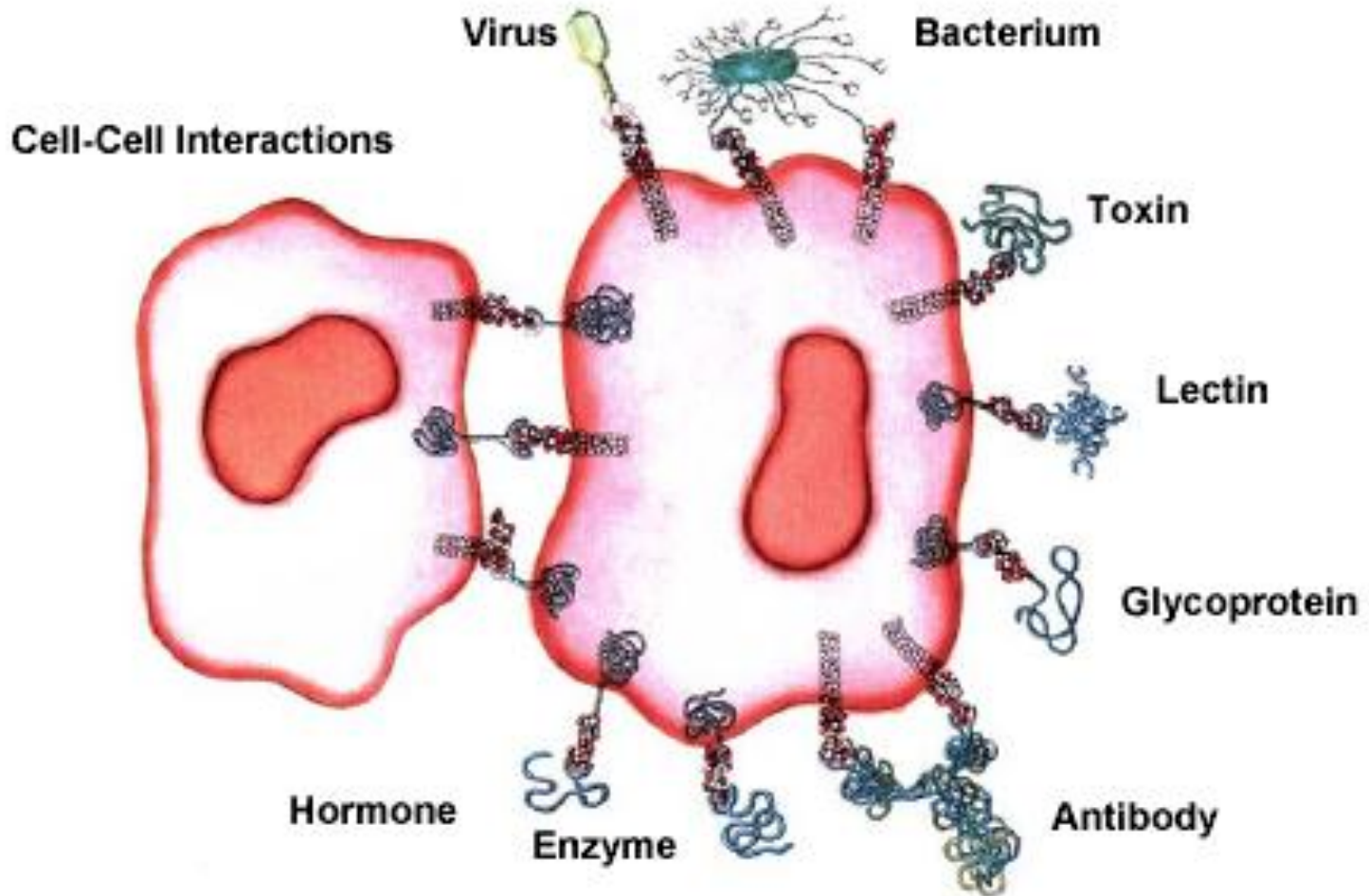
- ABO blood groups are determined by Oligosaccharides O-linked to proteins and lipids in the RBC membrane.
- Oligosaccharides typically carry additional groups eg amino sugars such as *N*-Acetylgalactosamine (GalNAc)
- Type A & B each elicit antigens that cause RBCs to “clump” together.



Carbohydrates serve as recognition sites for other biomacromolecules



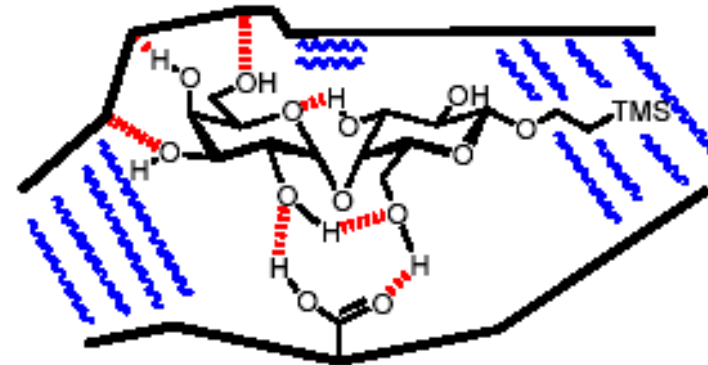
Cell-cell interaction



Lectin-carbohydrate interaction



A)



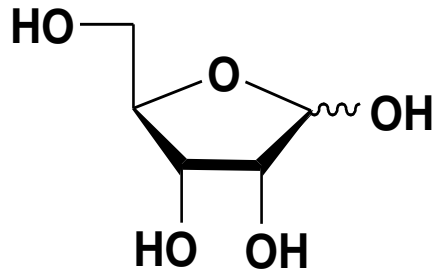
B)

Hydrogen bond

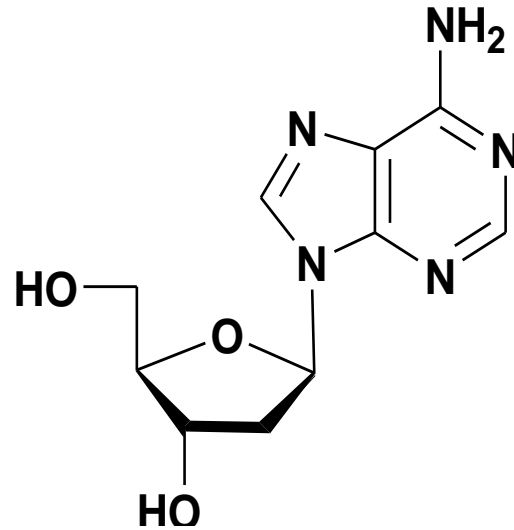
Hydrophobic area

Fig. 1.11. Carbohydrate - lectin interactions. A) From Weis, W. I. and Drickamer, K. Trimeric structure of a C-type mannose-binding protein. *Structure* **1994**, 2, 1227. B) Model of the galabiose binding site of PapG_{J96}.

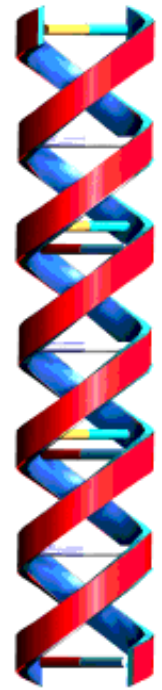
Carbohydrates are important for the storage of genetic information



D-ribose



Adenosine



DNA

Synthesis of Oligosaccharides



The challenge

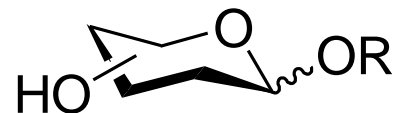
Building Blocks

MONO



P = Hydroxyl Protection

MONO

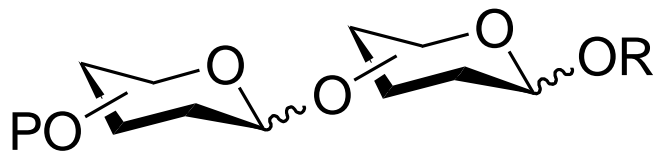


DONOR

Promoter



ACCEPTOR



DI



DONORS



P = Hydroxyl Protection

Activating group

Thioalkyl

SMe, SEt, SPh, STol

Halo

F, Cl, Br, I

Others: *n*-Pentenyl

Acetimidates

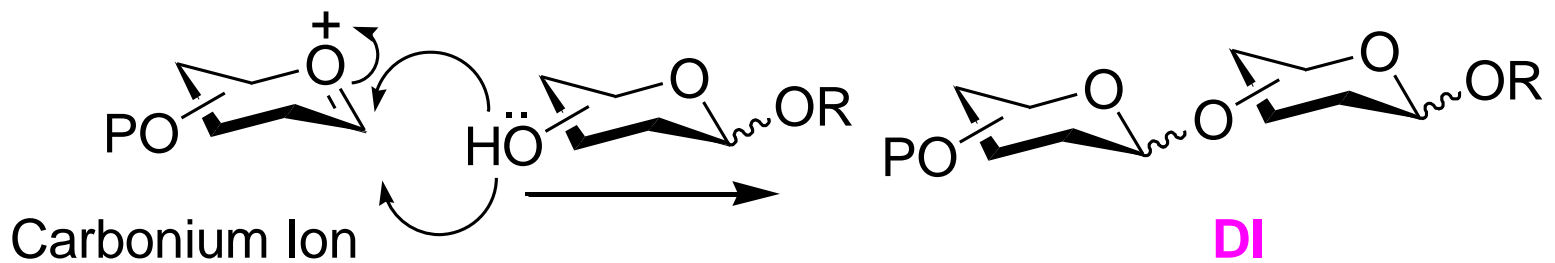
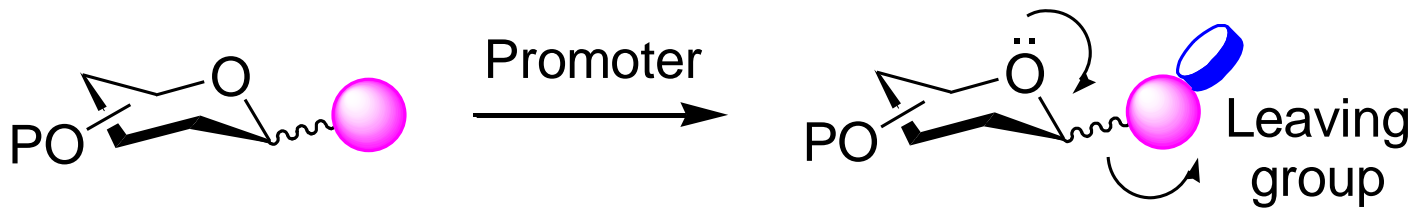
Trichloroacetimidate

Trifluoroacetimidate

Seleno

SePh

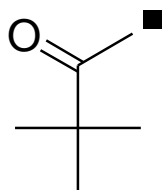
Glycosylation



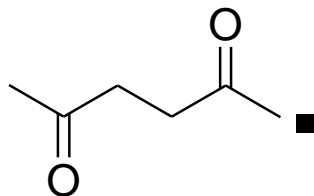
Choice of hydroxyl protection

Acyl protection

Acetate
Benzoate
Pivaloate
Levulonate



Pivaloate

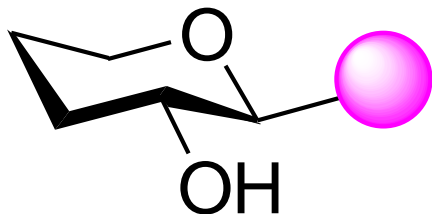


Levulonate

Alkyl/aryl protection

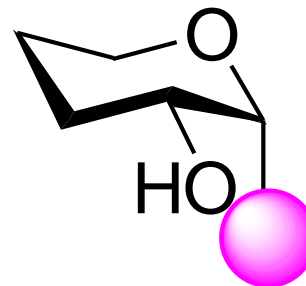
Methyl
Benzyl
4-methoxybenzyl
4-nitrobenzyl

Stereochemistry of Glycosylation



1,2-*trans*

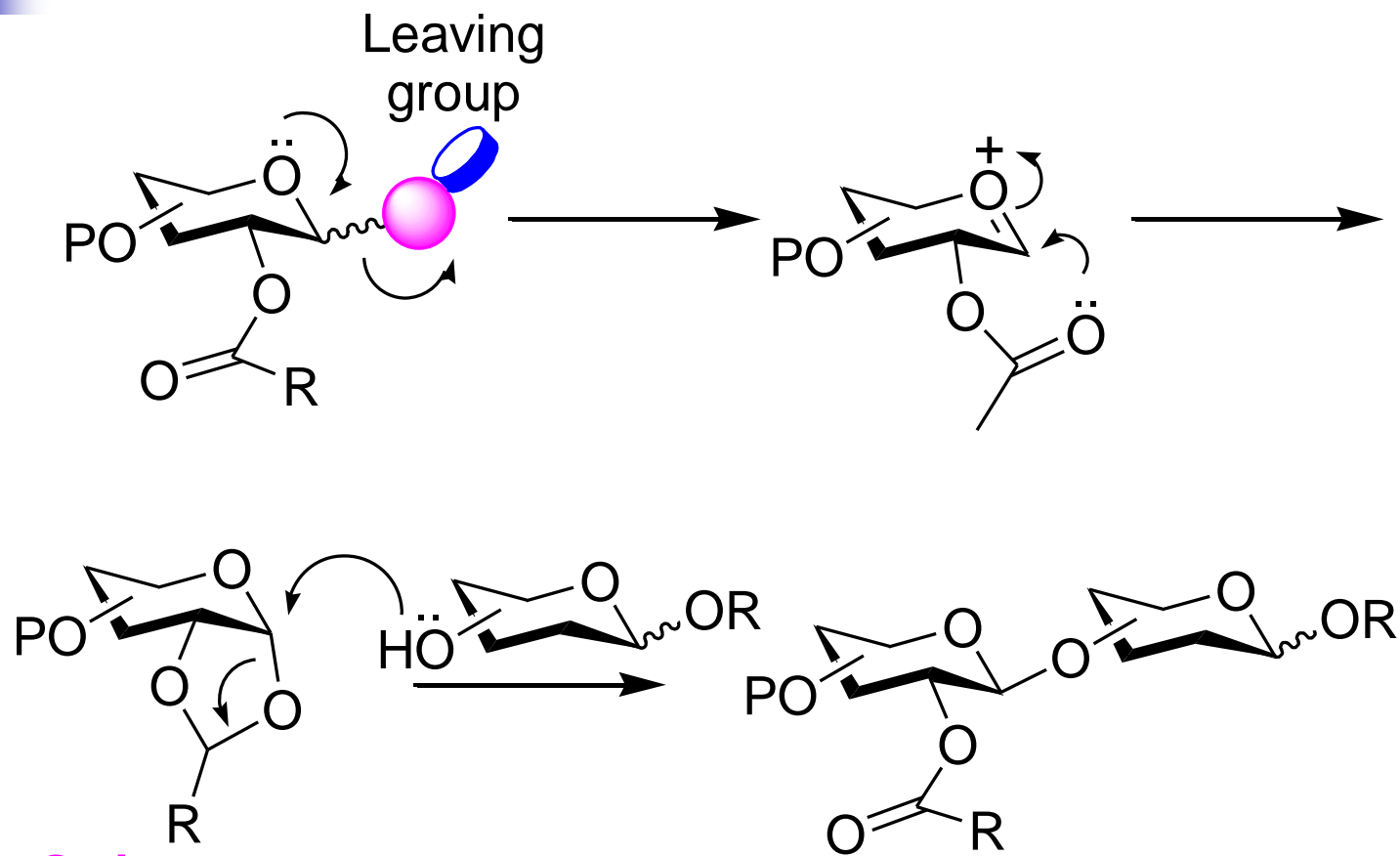
**Sterically favoured
kinetic controlled**



1,2-*cis*

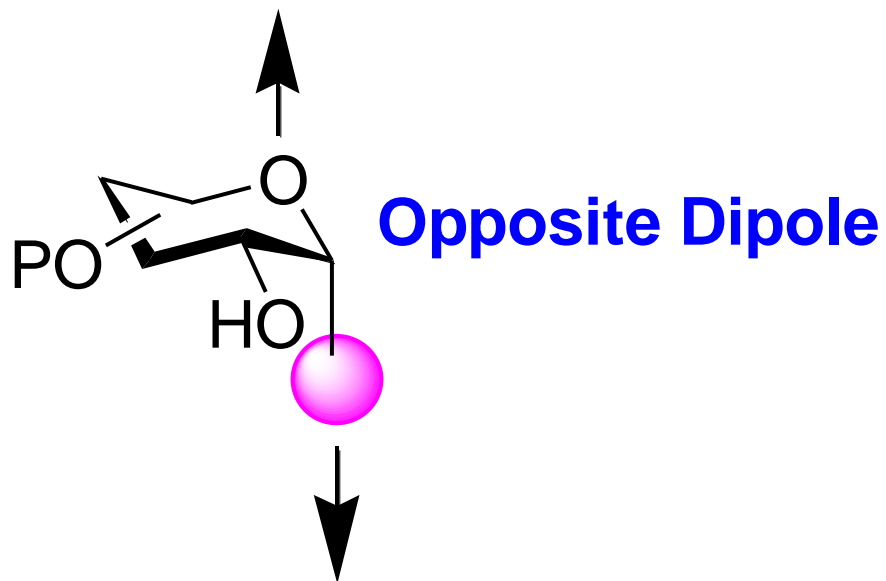
**Thermodynamic
controlled**

1,2-*trans* Glycosylation



Orthoester
through NGP

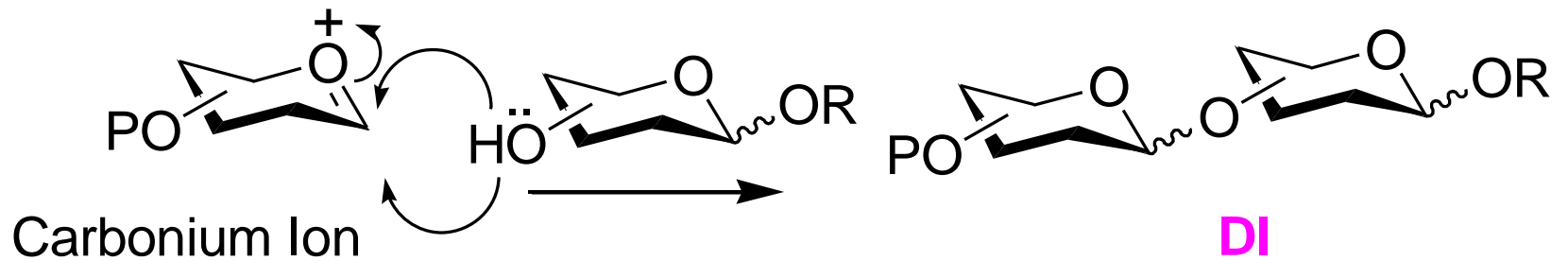
1,2-*cis* Glycosylation



Anomeric effect

Thermodynamically controlled

1,2-*cis* Glycosylation



CONDITIONS

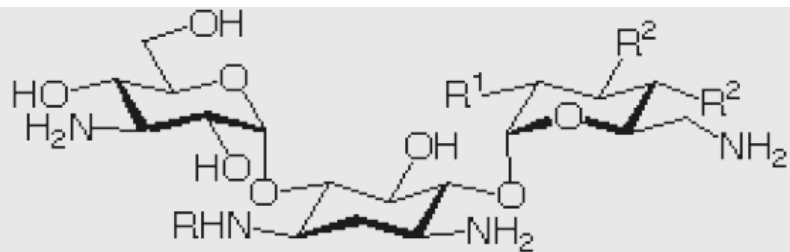
No participating group in 2-position

Low temperature

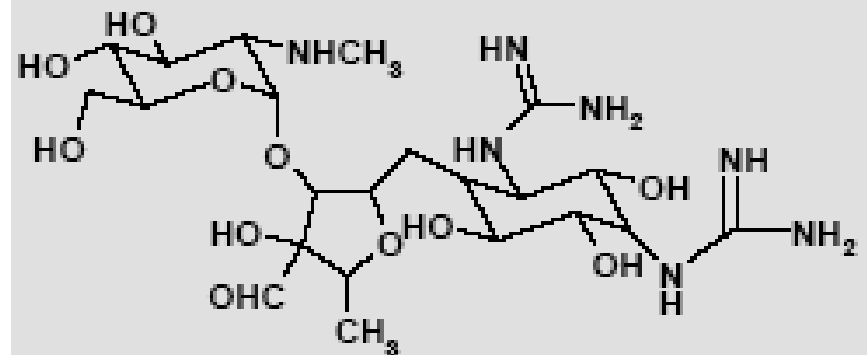
Non-polar solvent

Promise of Carbohydrates

Medicinal ???

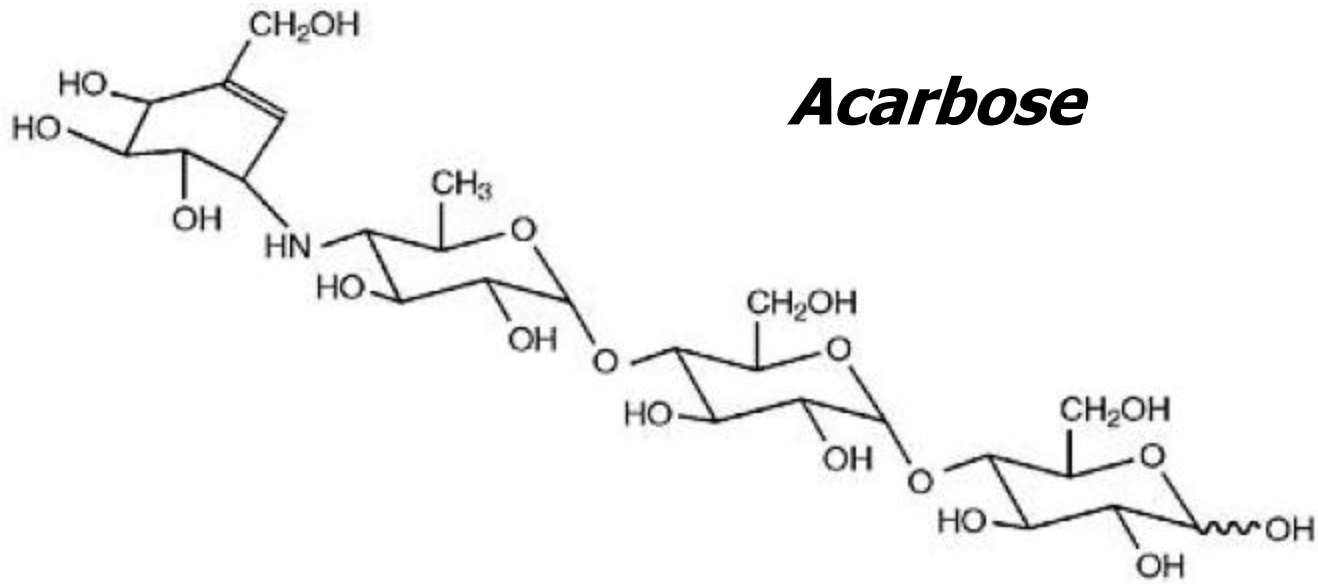


	R ¹	R ²	R
Kanamycin	OH	OH	H
Kanamycin B	NH ₂	OH	H
Dibekacin	NH ₂	H	H
Arbekacin	NH ₂	H	COCH(OH)CH ₂ CH ₂ NH ₂ (S)



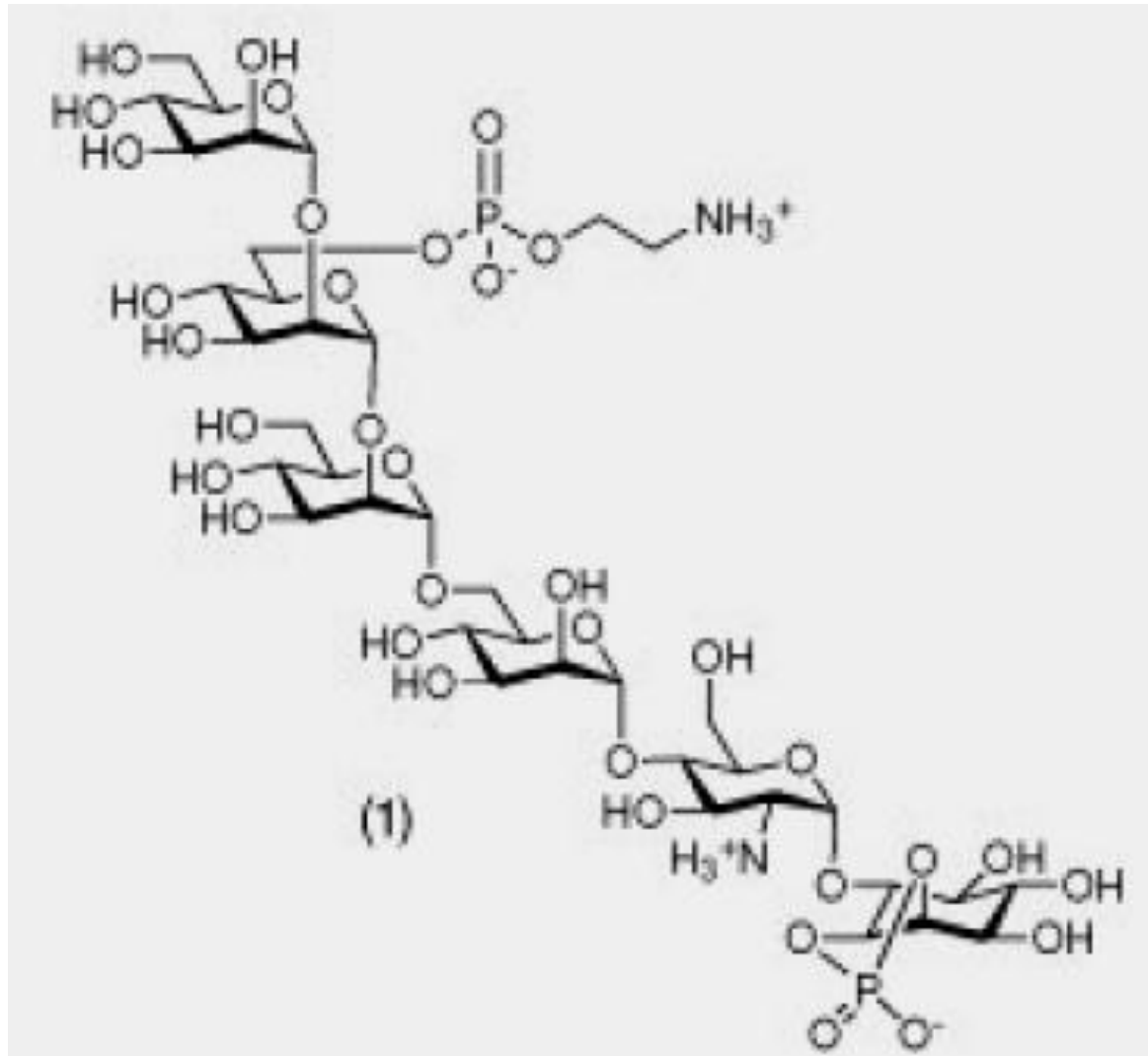
Streptomycin

Anti tuberculosis

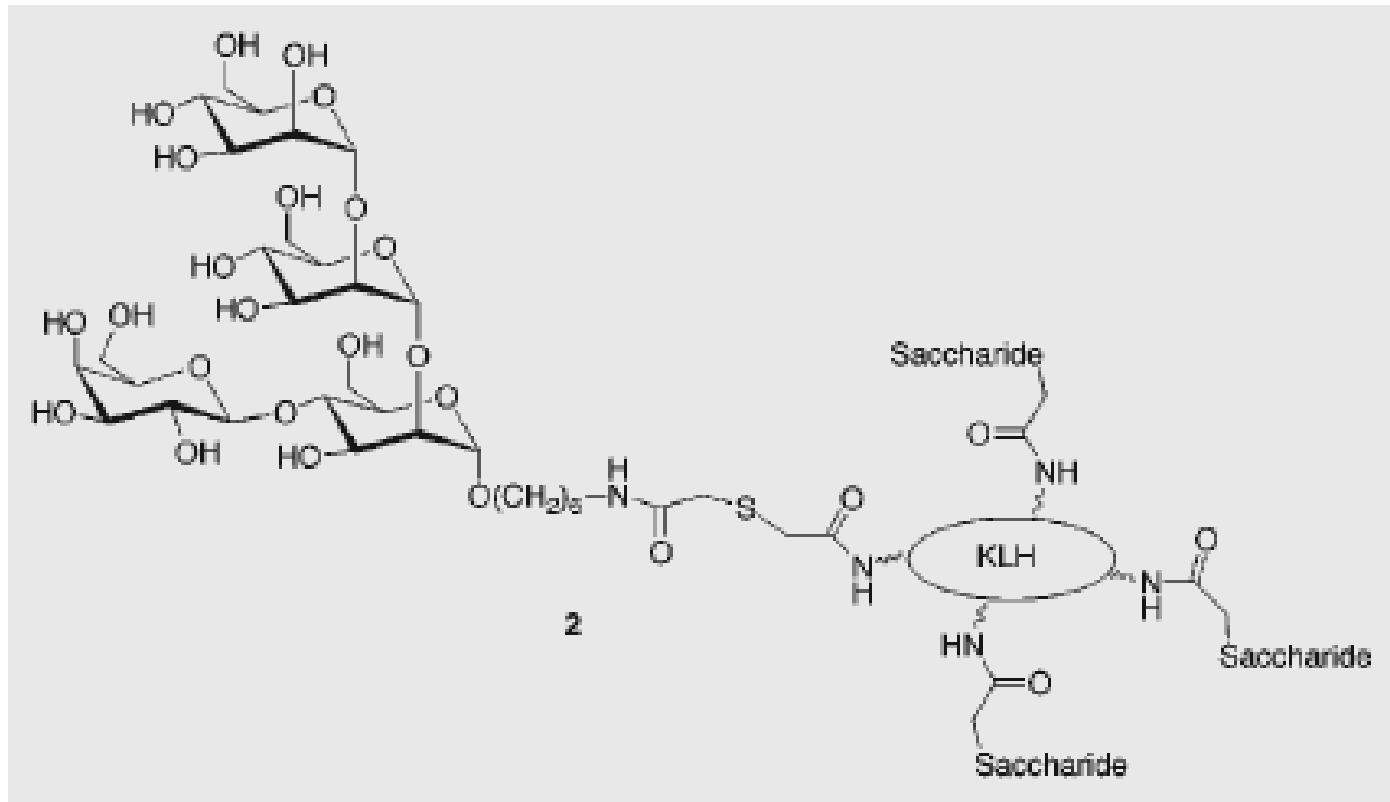


Acarbose

Anti Diabetic



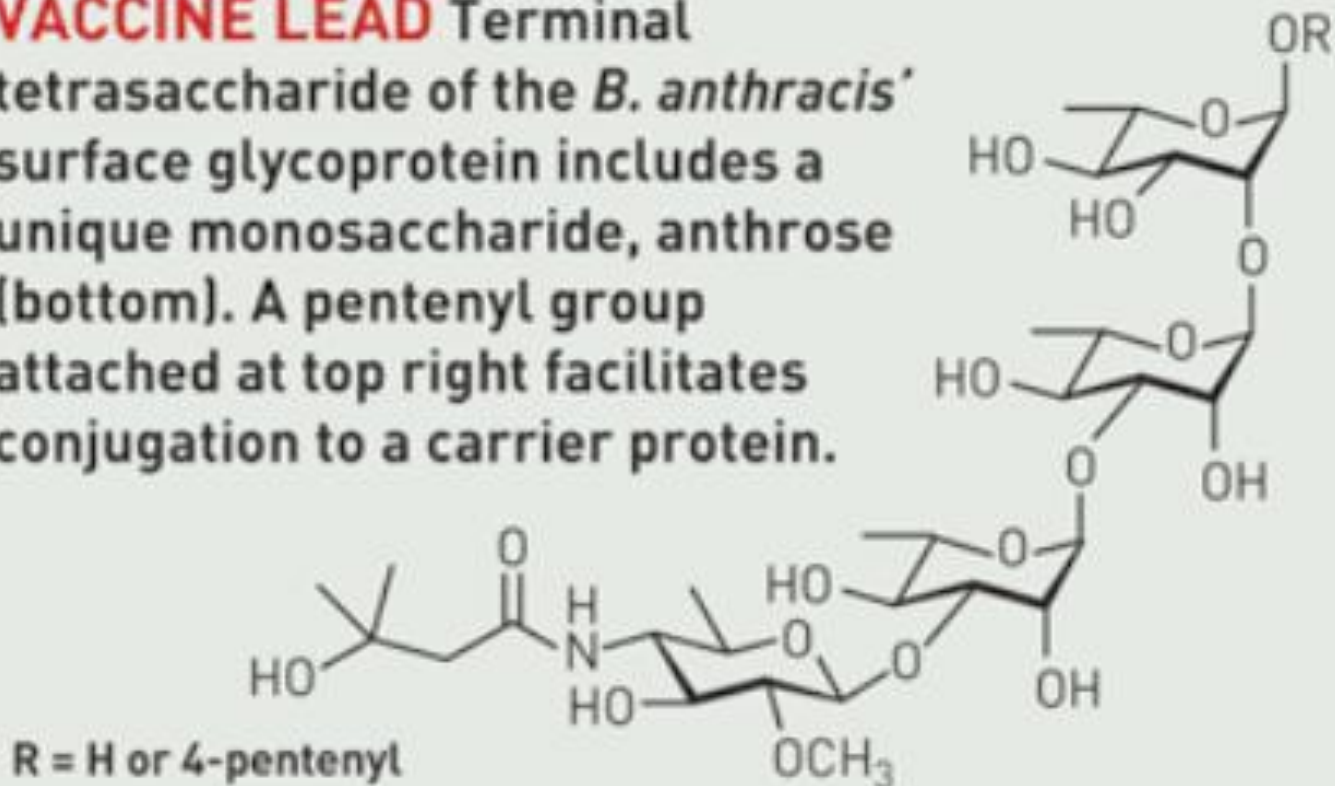
Anti Malaria (Pete Seeberger)



keyhole limpet hemocyanin (KLH)

Anti Leishmania (Pete Seeberger)

VACCINE LEAD Terminal tetrasaccharide of the *B. anthracis* surface glycoprotein includes a unique monosaccharide, anthrose (bottom). A pentenyl group attached at top right facilitates conjugation to a carrier protein.



Anthrax antigen (Pete Seeberger)

THANKS

