Carbohydrates are the major recognition molecules in many cell-cell interaction events in nature.

**Carbohydrates- Chapter 10**

- Introduction and definition monosaccharides
- Aldoses and Ketoses
- Cyclic glycosyl residues, Haworth Projections
- Modified monosaccharides
- Glycosidic bond
- Disaccharides
- Polysaccharides
- Peptidoglycans
- Proteoglycans
- Glycoproteins
Photosynthesis: \(10^{11}\) tons \(\text{CO}_2\) fixed annually

~1/3 in oceans, marine, microorganisms,
~2/3 land plants, efficiency: \(~3\text{-}6\% (0.1\text{-}8\%)

\[ \text{light} \]

\[ 6\text{H}_2\text{O} + 6\text{CO}_2 \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \]

Plant cell walls constitute the bulk of plant biomass:

\(~4\text{-}20\%\) of plant fresh weight

(from measurements of Arabidopsis leaf, silique, stem, inflorescence (Caffall, 2008))

Oxygen

Food

Microbiome

Nutrition

Prebiotic

Fiber

Biologically active glycans/proteoglycans

Resources / Products

Fuels
Nanomaterials
Lumber
Cotton
Chemicals
Pharmaceuticals
Neutraceutics

* Stimulate immune response
* Induce apoptosis in cancer cells
* Regulate sugar metabolism
Carbohydrates

* ___________ organic molecule on earth
* ___________________________________ (or yield these upon hydrolysis)

• __________: energy storage (glycogen, starch)
  (glycogen; animals, bacteria, starch; plants, fungi, bacteria)
  metabolic intermediates (ATP, coenzymes)
  part of DNA & RNA
  structural elements in cell walls of bacteria, fungi & plants
  exoskeleton of arthropods
  extracellular matrix of animals, plants, bacteria and fungi
  cell-cell communication/signaling

• Individual monomeric units are called _______________ (CH₂O)n where n≥3

• ______________ (contain 2-20 monosaccharides)
  ______________ (two linked monosaccharides)

• _________________ (> 20 monosaccharides)

• pure mono- & disaccharides are water-soluble, colorless in solution & sweet

• ____________________________: aldoses & ketoses
_____________: carbohydrate polymer

_____________: carbohydrate derivative where carbohydrate(s) are linked to a peptide, protein or lipid (i.e. proteoglycans, peptidoglycans, glycoproteins, glycolipids)

(contrast with glucoconjugate)

_____________: study of role of glycans and glycoconjugates in living organisms

_____________: compounds with the same molecular formula but different spatial arrangement of their atoms

D & L sugars differ only in steric arrangement of atoms about central C. They are non-superimposable mirror images (i.e. ____________)

They differ in orientation of the crystals, in directions in which solutions rotate polarized light, and in selectivity of reaction with other asymmetric molecules
Fischer projections of: (a) L- and D-glyceraldehyde, (b) dihydroxyacetone

(a) \[
\begin{align*}
\text{L-Glyceraldehyde} & : & \text{H}_2\text{C} = \text{O} & \text{H} - \text{C} - \text{H} & \text{CH}_2\text{OH} \\
& & \text{H} - \text{O} - \text{C} - \text{H} & & \text{CH}_2\text{OH}
\end{align*}
\]

(b) \[
\begin{align*}
\text{D-Glyceraldehyde} & : & \text{H}_2\text{C} = \text{O} & \text{H} - \text{C} - \text{OH} & \text{CH}_2\text{OH} \\
& & \text{H} - \text{O} - \text{C} - \text{H} & & \text{CH}_2\text{OH}
\end{align*}
\]

See pg. 168

Stereo view of L- and D-glyceraldehyde

See pg. 168
<table>
<thead>
<tr>
<th>N (# of Cs)</th>
<th>Name</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>triose</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>tetrose</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>pentose</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>hexose</td>
<td></td>
</tr>
</tbody>
</table>

For sugars with >1 asymmetric (chiral) carbon, D & L refer to chiral C furthest from aldehyde (or ketone) & correspond to D & L glyceraldehyde.

\[ \text{# of stereoisomers} = 2^n \quad \text{where } n = \text{# of chiral C's} \]

__________________: stereoisomers that differ in configuration at only one chiral center

---

**Carbohydrates- Chapter 10**

- Introduction and definition monosaccharides
- **Aldoses and Ketoses**
- Cyclic glycosyl residues, Haworth Projections
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- Peptidoglycans
- Proteoglycans
- Glycoproteins
Structure of the 3-6 carbon **D-aldoses**
(blue are the most common)

You must memorize the structures of all the sugars in blue!

(aldoses continued)
Fisher projections of the 3 to 6 carbon D-ketoses (blue structures are most common)

**Ketotriose**

\[
\text{CH}_2\text{OH} \\
\text{C} = \text{O} \\
\text{CH}_2\text{OH}
\]

Dihydroxyacetone

\[
\downarrow
\]

**Ketotetrose**

\[
\text{CH}_2\text{OH} \\
\text{C} = \text{O} \\
\text{H} - \text{C} - \text{OH} \\
\text{CH}_2\text{OH}
\]

D-Erythrulose
(ketoses continued)

Ketopentoses

CH$_2$OH
C═O
H—C—OH
H—C—OH
CH$_2$OH
d-Ribulose

CH$_2$OH
C═O
HO—C—H
H—C—OH
CH$_2$OH
d-Xylulose

Ketohexoses

CH$_2$OH
C═O
H—C—OH
H—C—OH
H—C—OH
CH$_2$OH
d-Psicose
d-Fructose
d-Tagatose

CH$_2$OH
C═O
H—C—OH
H—C—OH
H—C—OH
CH$_2$OH
d-Tagatose
d-Sorbose
Cyclization of Aldoses and Ketoses

Reaction of an alcohol with:
(a) An aldehyde to form a hemiacetal
(b) A ketone to form a hemiketal

Formation of a hemiacetal

Formation of a hemiketal

See pg. 170

Carbohydrates- Chapter 10

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(a) Pyran and (b) Furan ring systems

(a) Pyran

(b) Furan

(a) Six-membered sugar ring is a "__________"
(b) Five-membered sugar ring is a "__________"

Cyclization of D-glucose to form glycopyranose

See pg. 169-170

See pg. 170
(cyclization of D-glucose, continued)

**Haworth Projection**

- Reaction of C-5 hydroxyl with one side of C-1 gives α, reaction with the other side gives β

* anomic carbon
* α and β refer to the anomic configurations

See Fig. 10.3

---

**D-Fructose**

(open-chain form)

**α-D-Fructofuranose**

(a cyclic form of fructose)

---

Figure 10.4

*Biochemistry, 4th Short Course, Second Edition
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**Fig. 10.4**
Aldoses where \( C_n (n \geq 5) \) or ketoses \( (n \geq 6) \) yield cyclic hemiacetals (or hemiketals) in solution

6 member ring = __________
5 member ring = __________

________ C = most oxidized C of cyclic monosaccharide. It is chiral (i.e. \( \alpha \) or \( \beta \)) = anomeric configuration

*** In solution the ring & linear form of monosaccharides are in equilibrium!
Example: D-glucose at 31°C
64% \( \beta \)-D-pyranose
36% \( \alpha \)-D-pyranose
< 1% furanose or linear
Cyclization of D-ribose to form α- and β-D-ribopyranose and α- and β-D-ribofuranose

Continued on next slide

(Cyclization of D-ribose continued)

Continued next slide
(Cyclization of D-ribose continued)

**Conformations of Monosaccharides**

**Conformations of β-D-ribofuranose**

Ten possible envelope & ten possible twist conformations

see Fig. 10.6
Conformations of β-D-glucopyranose

* Axial substituent: perpendicular to plane of ring

** Equatorial substituent: parallel to plane of ring

(b) Stereo view of chair (left), boat (right)

2 possible conformations (generally more stable)

6 possible conformations

*Axial substituent:
perpendicular to plane of ring

** Equatorial substituent:
parallel to plane of ring

Top conformer is more stable because it has the bulky hydroxyl substituents in equatorial positions (less steric strain)
Carbohydrates- Chapter 8

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Derivatives of Monosaccharides

- Many sugar derivatives are found in biological systems
- Some are part of monosaccharides, oligosaccharides or polysaccharides
- These include sugar phosphates, deoxy and amino sugars, sugar alcohols and acids
Be sure to know these abbreviations

<table>
<thead>
<tr>
<th>Monosaccharide or derivative</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentoses</td>
<td></td>
</tr>
<tr>
<td>Ribose</td>
<td>Rib</td>
</tr>
<tr>
<td>Xylose</td>
<td>Xyl</td>
</tr>
<tr>
<td>Hexoses</td>
<td></td>
</tr>
<tr>
<td>Fructose</td>
<td>Fru</td>
</tr>
<tr>
<td>Galactose</td>
<td>Gal</td>
</tr>
<tr>
<td>Glucose</td>
<td>Gle</td>
</tr>
<tr>
<td>Mannose</td>
<td>Man</td>
</tr>
<tr>
<td>Deoxy sugars</td>
<td></td>
</tr>
<tr>
<td>Aboquose</td>
<td>Abe</td>
</tr>
<tr>
<td>Fucose</td>
<td>Fuc</td>
</tr>
<tr>
<td>Amino sugars</td>
<td></td>
</tr>
<tr>
<td>Glucosamine</td>
<td>GlcN</td>
</tr>
<tr>
<td>Galactosamine</td>
<td>GalN</td>
</tr>
<tr>
<td>N-Acetylgalactosamine</td>
<td>GalNAc</td>
</tr>
<tr>
<td>N-Acetylglucosamine</td>
<td>GlcNAc</td>
</tr>
<tr>
<td>N-Acetylneuraminic acid</td>
<td>NeuNAc</td>
</tr>
<tr>
<td>N-Acetylmuramic acid</td>
<td>MurNAc</td>
</tr>
<tr>
<td>Sugar acids</td>
<td></td>
</tr>
<tr>
<td>Glucuronic acid</td>
<td>GlcUA, GlcA</td>
</tr>
<tr>
<td>Idurononic acid</td>
<td>IdoA</td>
</tr>
<tr>
<td>Galacturonic acid</td>
<td>GalUA, GalA</td>
</tr>
</tbody>
</table>

![Chemical Structures](image)

**Figure 10.7**

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Some important sugar phosphates

- Dihydroxyacetone phosphate
- D-Glyceraldehyde 3-phosphate

- In deoxy sugars an H replaces an OH

Deoxy sugars
• An amino group replaces a monosaccharide OH
• Amino group is sometimes acetylated
• Amino sugars of glucose and galactose occur commonly in glycoconjugates

Several _______________

• Amino and acetylamino groups are shown in red

\[
\text{α-ᴅ-Glucosamine} \quad \text{N-Acetyl-α-ᴅ-galactosamine} \quad \text{GalNAc}
\]
Sialic acids (e.g. N-acetyleneuraminic acid, Neu5A, which is typical in human glycoproteins) are important in animal glycoproteins (formed from ManNAc + pyruvate) [derived from N-acetylmannosamine and pyruvate]. Note: The specific structures of the sialic acids can be different in different species!

(polyhydroxy alcohols)

- Sugar alcohols: carbonyl oxygen is reduced

Several sugar alcohols:

- Glycerol
- myo-Inositol
- D-Ribitol
• Sugar acids are carboxylic acids
• Produced from aldoses by:
  (1) Oxidation of C-1 to yield an **aldonic acid**
  (2) Oxidation of the highest-numbered carbon to an **alduronic acid** (also called uronic acid)

Sugar acids derived from glucose
(example of an aldonic acid)

A lactone is a cyclic ester in organic chemistry. It is the condensation product of an alcohol group and a carboxylic acid group in the same molecules.
(continued)
(example of an alduronic acid)

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Disaccharides and Other Glycosides

- primary structural linkage in all polymers of monosaccharides
- glucose provides the anomeric carbon
- a general term meaning that a carbohydrate provides the anomeric carbon

Glucopyranose + methanol yields a glycoside

Under acidic conditions alcohols, amines or thiols can condense with the anomeric C to form a glycosidic bond
Carbohydrates- Chapter 8

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Structures of Disaccharides

Structures of (a) maltose, (b) cellobiose

(a) β-anomer of maltose
(α-D-Glucopyranosyl-1→4)-β-D-glucopyranose

(b) β-anomer of cellobiose
(β-D-Glucopyranosyl-1→4)-β-D-glucopyranose

__________ is a hydrolysis product of amylose (starch)
__________ is a degradation product of cellulose

see Fig. 10.8
Name the structure starting at the non-reducing end
Structures of Disaccharides (continued)
Structures of (c) lactose, (d) sucrose

(c) \( \beta-\text{Galactopyranosyl}(1 \rightarrow 4)-\alpha-\text{Glucopyranose} \)
(d) \( \text{Sucrose} \)

\[ \text{\textbf{c}} \quad \text{(c) lactose} \]
\[ \text{\textbf{d}} \quad \text{(d) sucrose} \]

\text{\textbf{c}}: \text{\textbf{c}} \quad \text{\textbf{d}}: \text{table sugar, most abundant disaccharide in nature, synthesized only in plants}

Reducing and Nonreducing Sugars

- Carbohydrates with a reactive carbonyl (i.e. aldoses with free C1) are called \textbf{Reducing Sugar} because they can reduce metal ions (e.g. \( \text{Cu}^{2+}, \text{Ag}^{+} \))

- Carbohydrates with no free anomeric Carbon are called \textbf{Nonreducing Sugar} (e.g. sucrose)

\text{see Pg. 172}
Nucleosides and Other Glycosides

• Anomeric carbons of sugars can form glycosidic linkages with alcohols, amines and thiols

• ___________: nonsugar molecule attached to the anomeric sugar carbon

• ___________: compound containing glycosidic bonds

• _________ + _________ = ______________

Structures of three glycosides
Carbohydrates- Chapter 10

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Polysaccharides

• ____________ - homopolysaccharides containing only one type of monosaccharide
• ____________ - heteropolysaccharides containing residues of more than one type of monosaccharide

• Lengths and compositions of a polysaccharide may vary within a population of these molecules
Starch and Glycogen

- D-Glucose is stored intracellularly in polymeric forms
- Plants and fungi - starch
- Animals - glycogen
- Starch is a mixture of amylose (unbranched) and amylopectin (branched)

Structure of amylose

(a) Amylose is a linear polymer of D-glucose in an \(\alpha-1,4\)-linkage; DP of 100-1000

(b) Assumes a left-handed helical conformation in water

DP: degree of polymerization: number of monomeric units in a macromolecule or polymer or oligomer molecule
Structure of amylopectin

Amylopectin is amylose strands connected by an \( \alpha-1,6 \)-linkage; DP of 300-6000

Comparison of between amylopectin and glycogen

- Both are energy storage forms of glucose
- Both are strands of \( \alpha-1,4 \)-linked glucose connected by \( \alpha-1,6 \)-linkages
- **Amylopectin**: found in plants; DP 300-6000, crystallin, \( \alpha-1,6 \)-linkages branches occur 1/25 residues
- **Glycogen**: found in animals; DP \( \leq 50,000 \), NOT crystallin, \( \alpha-1,6 \)-linkages branches occur 1/8 to 1/12 residues
Action of α- and β-amylase on amylopectin (both cleave α-1,4-glucan)

• α-amylase cleaves random internal α-(1-4) glucosidic bonds (endoglycanase) [This is the amylase in your saliva and your pancreatic amylase, also in plants & other organisms]

• β-amylase acts on nonreducing ends, exoglycosidase, releases dimers [Only synthesized by bacteria, fungi and plants]

Cellulose: most abundant organic molecule on earth, DP 300 - >15,000, synthesized by plants & some bacteria, cell wall polysaccharide

Structure of cellulose (β-1,4-linked glucose homopolymer)

(a) Chair conformation

(b) Haworth projection

see Fig. 10.14
**Stereo view of cellulose fibrils**

*Individual cellulose chains interact to give cellulose microfibrils and bundles*

- Intra- and interchain H-bonding gives strength

---

**Cellulose chains interact via H-bonds to form microfibrils and fibers.**

---

*www.emc.maricopa.edu/.../BIOBK/BioBookCHEM2.html*
In plants a cellulose synthase rosette complex of 6 X 6 cellulose synthase subunits synthesizes a cellulose microfibril of ~18 individual cellulose molecules bound together by H-bonds.

Doblin et al., 2002, Plant Cell Physiol. 43:1407
Structure of chitin: exoskeleton of spiders & crustaceans, insects & in cell wall sf some fungi & algae

- Repeating units of $\beta$-(1-4)GlcNAc residues

![Structure of chitin](image)

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**Peptidoglycans**

- **Peptidoglycans** - heteroglycan chains linked to peptides
- Major component of bacterial cell walls
- Heteroglycan composed of alternating GlcNAc and N-acetylmuramic acid (MurNAc)
- $\beta-(1 \rightarrow 4)$ linkages connect the units


Gram positive bacterium, *Staphylococcus aureus*

Gram-negative bacterium *Escherichia coli*

**Glycan moiety of peptidoglycan**

MurNAc found only in bacteria and consists of GlcNAc connected at C-3 by an ether linkage to lactate.
Fig. 8.16 A schematic representation of the peptidoglycan in *Staphylococcus aureus* (Gram positive).

Yellow: polysaccharide
Red: tetrapeptide
Blue: pentaglycine

Structure of the peptidoglycan of *Staphylococcus aureus* (gram positive bacteria cell wall peptidoglycan)

(a) Repeating disaccharide unit, (b) Cross-linking of the peptidoglycan macromolecule

(to tetrapeptide, next slide)

Review section pgs. 138-140, Chapter 8
Fig. 8.17 The formation of cross-links in *S. aureus* peptidoglycan.

Fig. 8.18 A transpeptidation reaction. An acyl-enzyme intermediate is formed in the transpeptidation reaction leading to cross-link formation.
Penicillin inhibits a transpeptidase involved in bacterial cell wall formation

- Structures of penicillin and -D-Ala-D-Ala
- Penicillin structure resembling -D-Ala-D-Ala is shown in red

Review section pgs. 138-140, Chapter 8

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- Proteoglycans
- Lipo-oligosaccharides
- Glycoproteins
Proteoglycans

- ____________ – glycosaminoglycan (~95%)-carbohydrate-protein conjugates. Often found in ECM (extracellular matrix). Function as lubricants, cell-cell adhesion, messengers, & give tensile strength & elasticity to soft tissues

- _________________ (GAGs)- unbranched heteroglycans of repeating disaccharides (many sulfated hydroxyl and amino groups)

- Disaccharide components include:
  1. amino sugar (D-galactosamine or D-glucosamine),
  2. an alduronic acid

---

**Fig. 10.18**

The only GAG that is NOT part of a proteoglycan
Repeating disaccharide of hyaluronic acid

- GlcUA = D-glucuronate
- GlcNAc = N-acetylglucosamine

Hyaluronic acid is GAG not attached to protein

Types of GAGs

1. Not covalently attached to protein
   * Hyaluronic acid

2. Covalently attached to proteins (i.e. present in proteoglycans)
   * Heparin (and heparan sulfate)
   * Keratan sulfate
   * Chondroitin sulfate
   * Dermatan sulfate
**Supramolecular Proteoglycan aggregate in cartilage ~150 GAGs:protein (Aggrecan) interacting with hyaluronic acid**

**Fig. 10.21, pg 179-180**

Proteoglycans (core proteins with glycosaminoglycan chains attached) and Central strand of hyaluronic acid interact noncovalently.

- Chondroitin sulfate
- Keratan sulfate
- Link proteins
- Noncovalent attachment

2 other GAGs not in this aggregate: heparan sulfate; heparin

---

**Figure 10.21.** Structure of proteoglycan in cartilage.
Lipo-oligosaccharides and oligosaccharides can serve as signal molecules

Specific lipo-oligosaccharides are produced by nitrogen-fixing bacteria (e.g. Rhizobia) that interact specifically with certain plants (i.e. legumes) to form root nodules. These lipo-oligosaccharides resemble chitin oligomers with specific modifications.

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Glycoproteins

- Proteins that contain covalently-bound oligosaccharides
- O-Glycosidic and N-glycosidic linkages
- Oligosaccharide chains exhibit great variability in sugar sequence and composition
- ______________ - proteins with identical amino acid sequences but different oligosaccharide chain composition

Four subclasses of ______________ linkages

1. GalNAc-Ser/Thr (most common)
2. 5-Hydroxylysine (Hyl) to D-galactose (unique to collagen)
4. GlcNAc to a single serine or threonine
**O-Glycosidic**
(Common linkage to proteins in O-linked glycoproteins)

see Fig. 10.15

---

Four subclasses of **O-glycosidic linkages**

(a)  
NeuNAc α-(2 → 3) GalNAc β-(1 → 3) GalNAc — Ser/Thr
    NeuNAc α-(2 → 6)

(b)  
— Gal — Hyl

(c)  
— Gal — Gal — Xyl — Ser

(d)  
GlcNAc — Ser/Thr

see Fig. 10.23
**N-glycosidic**

*(N-glycosidic linkage in N-linked glycoproteins)*

**Consensus sequence for N-glycosylation:**

Asn-X-Ser/Thr

---

**Synthesis of dolichol-P-P-GlcNAc₂Man₉Glc₃ as part of N-glycosylation pathway**

---

*Essentials of Glycobiology*

Second Edition

Chapter 8, Figure 3

46
**Structures of N-linked oligosaccharides**

You must KNOW the pentasaccharide core structure in ALL N-linked glycoproteins

(a) \[ \text{Man } \alpha(1 \rightarrow 2) \text{ Man } \alpha(1 \rightarrow 4) \text{ Man } \alpha(1 \rightarrow 3) \]
\[ \text{Man } \alpha(1 \rightarrow 2) \text{ Man } \alpha(1 \rightarrow 3) \text{ Man } \alpha(1 \rightarrow 6) \]
\[ \text{Man } \alpha(1 \rightarrow 2) \text{ Man } \alpha(1 \rightarrow 6) \]

(b) \[ \text{SA } \alpha(2 \rightarrow 3,6) \text{ Gal } \beta(1 \rightarrow 4) \text{ GlcNAc } \beta(1 \rightarrow 2) \text{ Man } \alpha(1 \rightarrow 3) \]
\[ \text{Man } \beta(1 \rightarrow 4) \text{ GlcNAc } \beta(1 \rightarrow 4) \text{ GlcNAc } \rightarrow \text{ Am} \]
\[ \text{SA } \alpha(2 \rightarrow 3,6) \text{ Gal } \beta(1 \rightarrow 4) \text{ GlcNAc } \beta(1 \rightarrow 2) \text{ Man } \alpha(1 \rightarrow 6) \]

see Fig. 10.16

(continued)

(c) \[ \text{Gal } \beta(1 \rightarrow 4) \text{ GlcNAc } \beta(1 \rightarrow 2) \text{ Man } \alpha(1 \rightarrow 3) \]
\[ \text{Man } \alpha(1 \rightarrow 3) \]
\[ \text{Man } \alpha(1 \rightarrow 6) \]

The oligosaccharides attached to proteins may alter physical properties such as size, shape, solubility, or stability, may effect folding, and/or may have biological roles including signaling and binding

see Fig. 10.16
Why do blood transfusions sometimes cause death?

Reason discovered by Karl Landsteiner at University of Vienna in 1901.

All humans and many primates have **A, B, AB or O types** of oligosaccharides on the *N*-linked and *O*-linked oligosaccharides on the surface of their red blood cells (includes glycoproteins and glycolipids).

see Fig. 10.24

http://www.steve.gb.com/images/science/abo_glycolipids.png