WEEK SEVEN

Isomerism

The total number of possible stereoisomers of one compound (n) is dependent on the number of stereogenic centers (c) in the molecule. The upper limit for the number of possible stereoisomers is $n = 2^{c}$. The only monosaccharide without an isomer is <u>dihydroxyacetone</u> or DHA.

Monosaccharides are classified according to their <u>molecular configuration</u> at the chiral carbon furthest removed from the aldehyde or ketone group. The chirality at this carbon is compared to the chirality of carbon 2 on <u>glyceraldehyde</u> or the penultimate chiral carbon of any monosaccharide. If it is the OH of the penultimate carbon rotate to the right equivalent to Dglyceraldehyde's C2, the sugar is D; if it is equivalent to L-glyceraldehyde's C2, the sugar is L. Due to the chirality of the sugar molecules, an aqueous solution of a D or L saccharides will rotate light. D-glyceraldehyde causes polarized light to rotate clockwise (<u>dextrorotary</u>); Lglyceraldehyde causes polarized light to rotate counterclockwise (<u>levorotary</u>). Unlike glyceraldehyde, D/L designation on more complex sugars is not associated with their direction of light rotation. Since more complex sugars contain multiple chiral carbons, the direction of light rotation cannot be predicted by the chirality of the carbon that defines D/L nomenclature.



Sugar Ring Structures

When sugars cyclize, they typically form **furanose or pyranose** structures. These are molecules with fivemembered or six-membered rings, respectively. Cyclization creates a carbon with two possible orientations of the hydroxyl around it. Cyclization of an aldose occurs by intramolecular reaction with the aldehyde and alcohol groups to form a **hemiacetal**. Cyclization of a ketose occurs by intramolecular reaction with the ketone and alcohol groups to form a **hemiketal**. In either case, a new asymmetric carbon is created by the reaction and we refer to the carbon as the **anomeric carbon** and the two possible configurations as **anomers**. The two possible configurations of the hydroxyl group are called **alpha** and **beta**, which correspond to the hydroxyl being in the "down" and "up" positions, respectively, in standard projections. Anomers are capable of interconverting between alpha and beta positions in a process are called mutarotation IF the hydroxyl group of the hemiacetal or hemiketal is unaltered.









Epimers: They are a special case of diastereoisomerism where there is a difference for one and only one asymmetric center. e.g. D-glucose and D-mannose; D-glucose and D-galactose are epimers.

epimer, is used to designate diastereomers that differ in configuration at only one chiral center. Thus, ribose and arabinose are epimers at C-2, and arabinose and lyxose are epimers at C-3. However, arabinose and xylose are not epimers, since their configurations differ at both C-2 and C-3.



Four Diastereomeric C₅H₁₀O₅ Aldopentoses

Amino Sugars - made by replacing a hydroxyl of a sugar with an amine group. Two common examples are **beta-D-glucosamine** and **beta-D-galactosamine**. Common molecules derived from these include beta-D-N-acetylglucosamine, muramic acid, N-acetylmuramic acid, -D-N-acetylgalactosamine, and **N-acetyl-neuraminic acid** (also called sialic acid). Amino sugars are often found in oligosaccharides and polysaccharides. It is significant in several biological systems. It is part of a biopolymer in the bacterial <u>cell wall</u>, GlcNAc is the monomeric unit of the polymer <u>chitin</u>, which forms the outer coverings of <u>insects</u> and <u>crustaceans</u>. GlcNAc is also of note in <u>neurotransmission</u>, where it is thought to be an atypical <u>neurotransmitter</u> functioning in nocioceptive (<u>pain</u>) pathways. It has been proposed as a treatment for <u>autoimmune</u> diseases.

