

2.2: Sugars and Polysaccharides

François Baneyx

Department of Chemical Engineering, University of Washington

baneyx@u.washington.edu

Carbohydrates or saccharides are abundant compounds that play regulatory and structural roles and serve as cellular fuel and energy storage. Carbohydrates have for general formula $(\text{CH}_2\text{O})_n$, where $n \geq 3$. They are synthesized from atmospheric CO_2 and H_2O via photosynthesis and polymerized into more complex polysaccharides such as starch, glycogen and cellulose.

The simplest carbohydrates are monosaccharides. These simple sugars contain three to nine carbon atoms and are classified as aldoses or ketoses depending on whether their carbonyl group is an aldehyde or a ketone. The smallest monosaccharides are trioses that only contain three carbon atoms. Those sugars containing four, five, six, etc, carbon atoms are called tetroses, pentoses, hexoses, etc, respectively. Table 1 shows the chemical structure of common monosaccharides. A particularly important monosaccharide is glucose which is used to power many cellular processes and serves as a precursor for the synthesis of more complex carbohydrates. Fig. 1 shows that carbons 2-to-5 of D-glucose are chiral, leading to $2^4 = 16$ possible stereoisomers that correspond to all possible aldohexoses (four of which are shown in Table 1). While glucose can be found in both L and D forms, the L form is less abundant in Nature and L-glucose only plays a minor role in biological systems. In solution, D-glucose adopts a ring structure (known as pyranose for a 6-membered ring) that results from the reaction of its carbonyl group and alcohol groups (Fig. 1). The α denomination refers to the location of the OH substituent on carbon 1 of the ring. If the hydroxyl were located on the same side of the ring as the CH_2OH group, the resulting molecule would be called β -D-glucose.

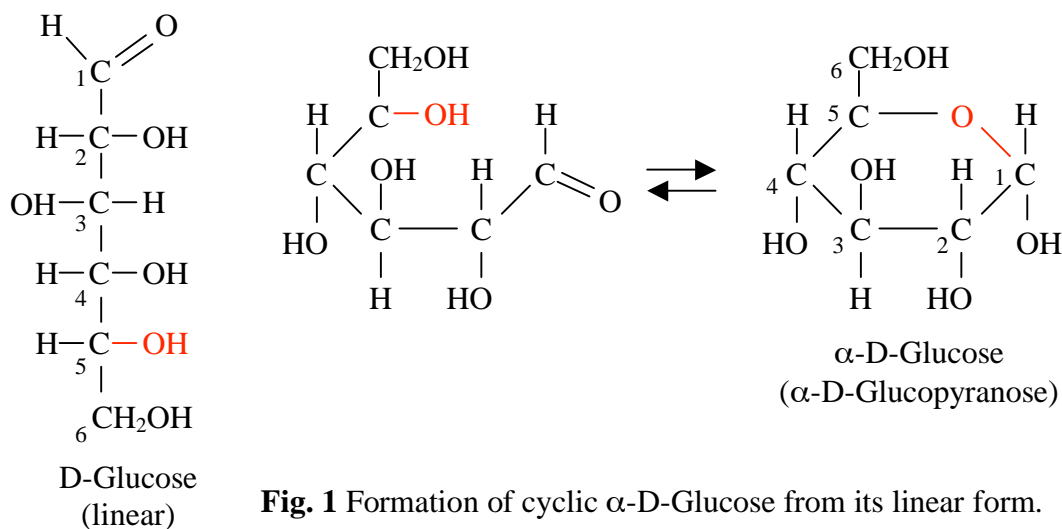
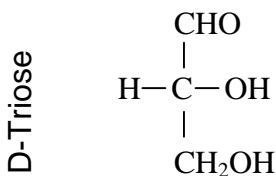
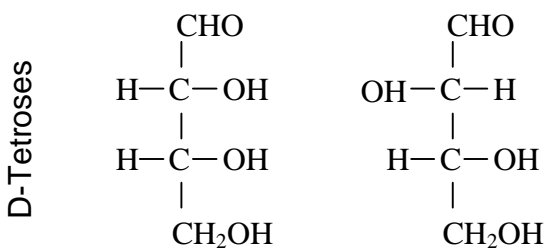


Table 1 Structure of some common monosaccharides

Aldoses

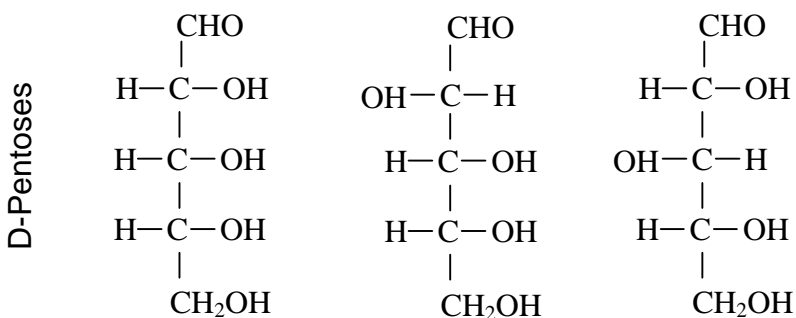


D-Glyceraldehyde



D-Erythrose

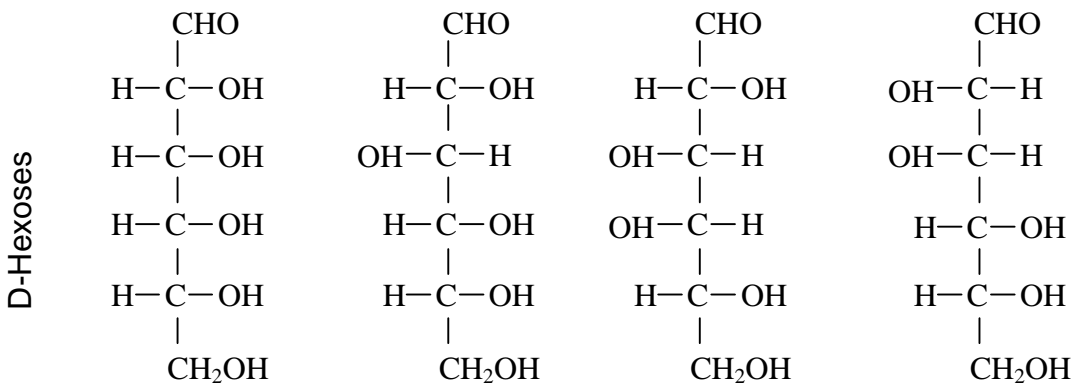
D-Threose



D-Ribose

D-Arabinose

D-Xylose



D-Allose

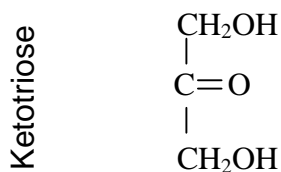
D-Glucose

D-Galactose

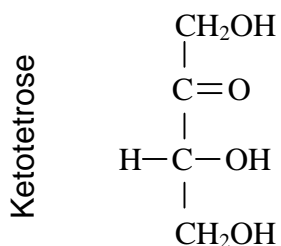
D-Mannose

Table 1 (Continued)

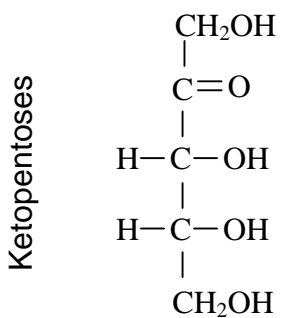
Ketoses



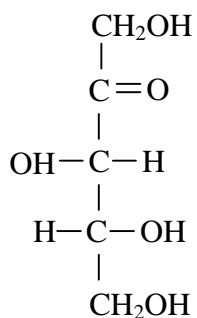
Dihydroxyacetone



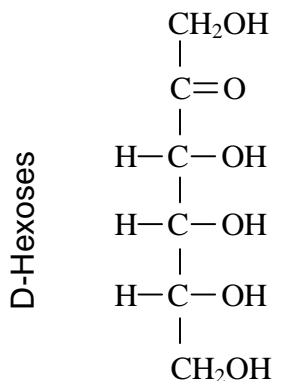
D-Erythrulose



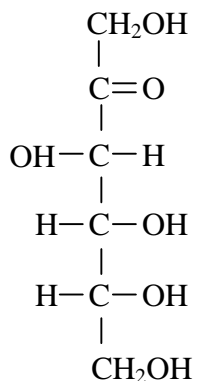
D-Ribulose



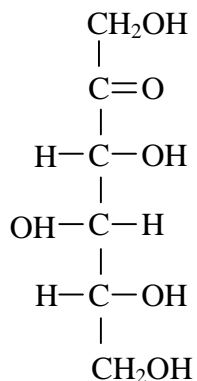
D-Xylulose



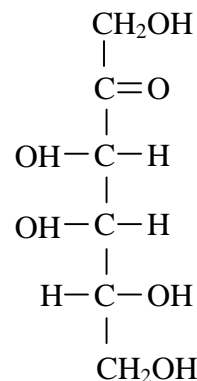
D-Psicose



D-Fructose



D-Sorbose



D-Togotose

D-ribose and D-deoxyribose are two other important monosaccharides that are structural components of RNA and DNA, respectively. The structure of these five carbon ring sugars is shown in Fig. 2.

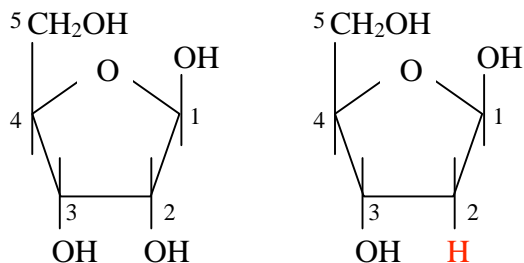


Fig. 2 Structures of D-ribose (left) and D-deoxyribose (right). The two molecules differ by the presence or absence of a hydroxyl group on carbon 2. Not all hydrogen atoms are shown.

Monosaccharides can polymerize via condensation reactions to yield polysaccharides. The simplest case involves two simple sugars and the generation of a disaccharide. Depending on whether the reaction proceeds with the α or β form of the sugar, an α -1,4 or β -1,4 glycosidic bond is generated, giving rise to different disaccharides as illustrated in the case of D-glucose in Fig. 3.

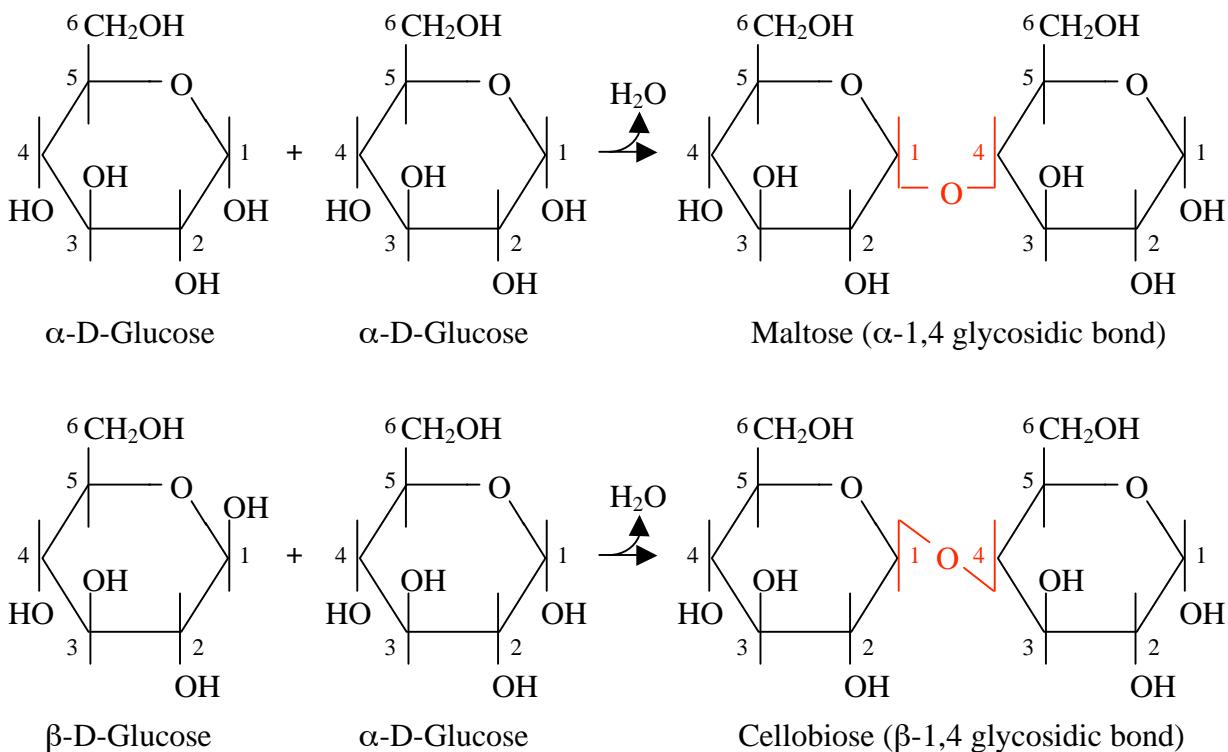


Fig. 3 Maltose and cellobiose both result from the condensation of two D-glucose molecules. However, whereas maltose contains an α -1,4 glycosidic bond, cellobiose contains a β -1,4 bond.

In addition to reacting with carbon 4, the hydroxyl group of carbon 1 in one sugar may also react with carbon 6 of the second sugar, leading to the formation of an α -1,6 glycosidic bond (Fig. 4). Such bonds act as branch points in more complex polysaccharides.

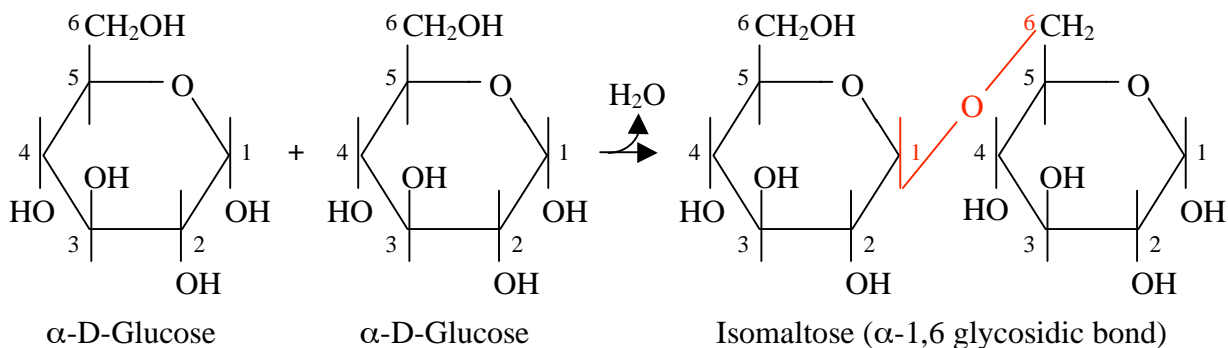


Fig. 4 Formation of an α -1,6 glycosidic bond between two α -D-Glucose molecules.

Cellulose, the major structural constituent of plants cell wall is one of the most abundant molecules on earth, accounting for more than half the carbon in the biosphere. Cellulose is a linear polymer of up to 15,000 D-glucose monomers linked through β -1,4 glycosidic bonds (Fig. 5a). The length of the polymer is variable and cellulose molecular mass typically varies between 50-kDa and 1-MDa. In wood, cellulose fibers are embedded in a matrix consisting of other polysaccharides and lignin (a phenolic polymer), yielding a composite material that exhibits remarkable mechanical properties. Because it is tightly packed and hydrogen-bonded, cellulose is difficult to degrade into its constituent sugars. In herbivores, this slow process is catalyzed by cellulases produced by symbiotic organisms living in the animal intestinal tract. A related compound, chitin, is the main structural component of invertebrates exoskeleton although it is also found in the cell wall of fungi and certain algae. Chitin is a linear polymer of N-acetyl-D-glucosamine residues linked by β -1,4 glycosidic bonds (Fig. 5b).

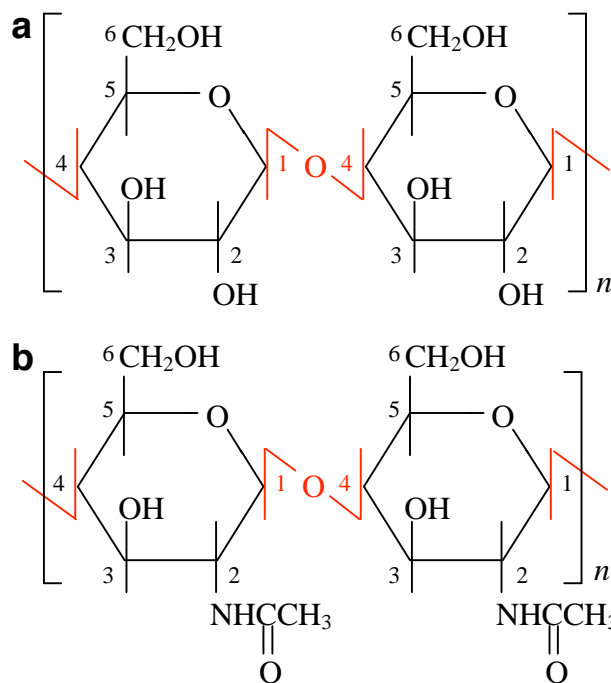


Fig. 5 Structures of cellulose (a) and chitin (b).

In addition to playing a structural role, polysaccharides may also serve as nutritional reservoirs. Starch, which is synthesized as insoluble granules by plants, is composed of a mixture of α -amylose (a linear polymer of thousands of α -D-glucose molecules linked to each other through α -1,4 glycosidic bonds) and amylopectin (which consists of α -1,4-linked glucose chains branching every 25-to-30 residues via α -1,6 glycosidic bonds).

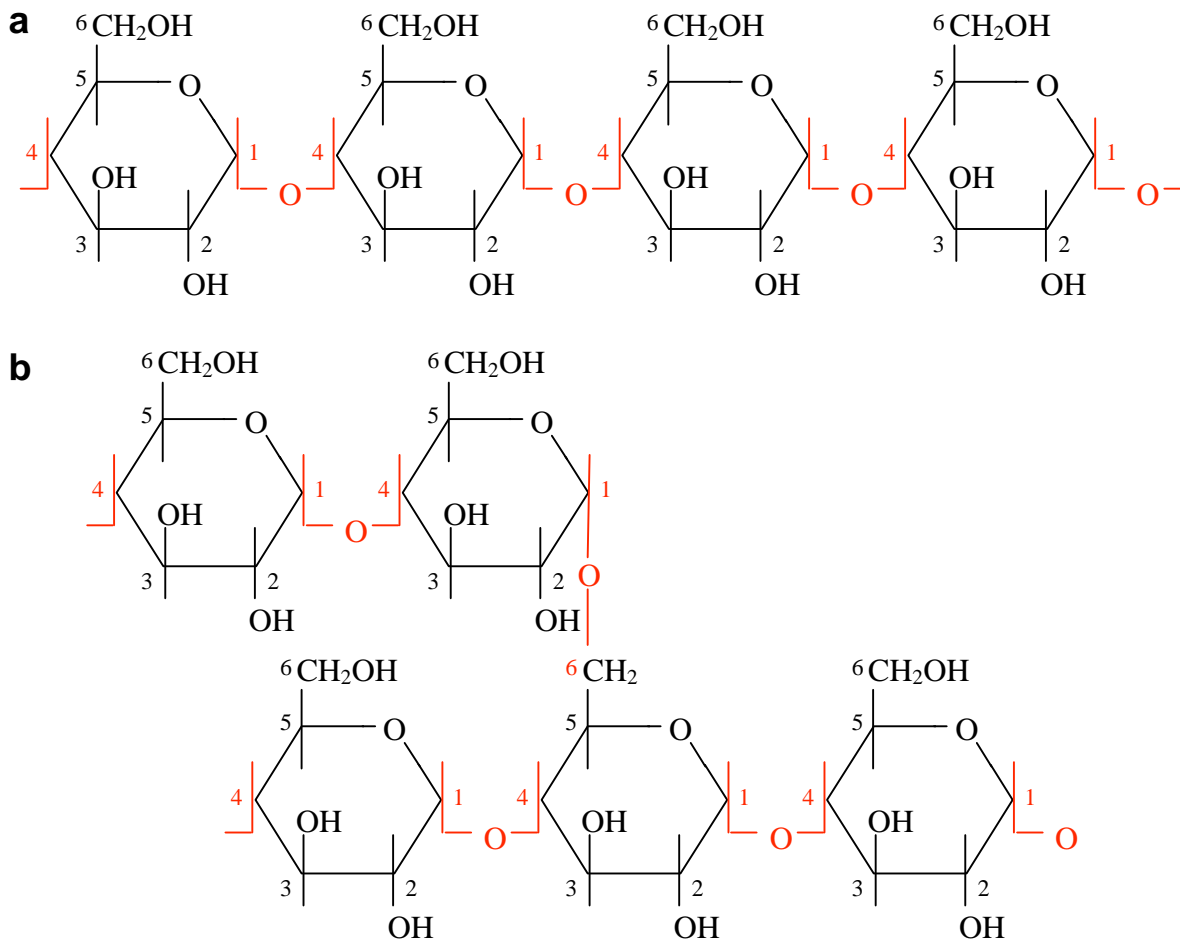


Fig. 6 Structures of amylose (a) and amylopectin (b). Although both are polymers of glucose joined through α -1,4 glycosidic bonds, amylopectin branches through α -1,6 glycosidic bonds.

The molecular mass of amylose, which makes up about 20% of starch, varies between a few thousands Da to 500-kDa (Fig. 6a). Amylopectin, one of the largest molecules in Nature, has a molecular mass that ranges from 1- to 2-MDa (Fig. 6b). In animals, the corresponding storage polysaccharide is glycogen which is chemically similar to amylopectin but much more highly branched (every 8-to-12 glucose residues on the average; Fig. 7b). In contrast to cellulose, amylose, amylopectin and glycogen adopt a

more amorphous structure because the α -1,4 glycosidic bonds do not cause successive glucose residues to flip 180° with respect to each other as β -1,4 glycosidic bonds do. Thus, all these compounds can be easily digested allowing for a rapid infusion of glucose in times of metabolic need (Fig. 7).

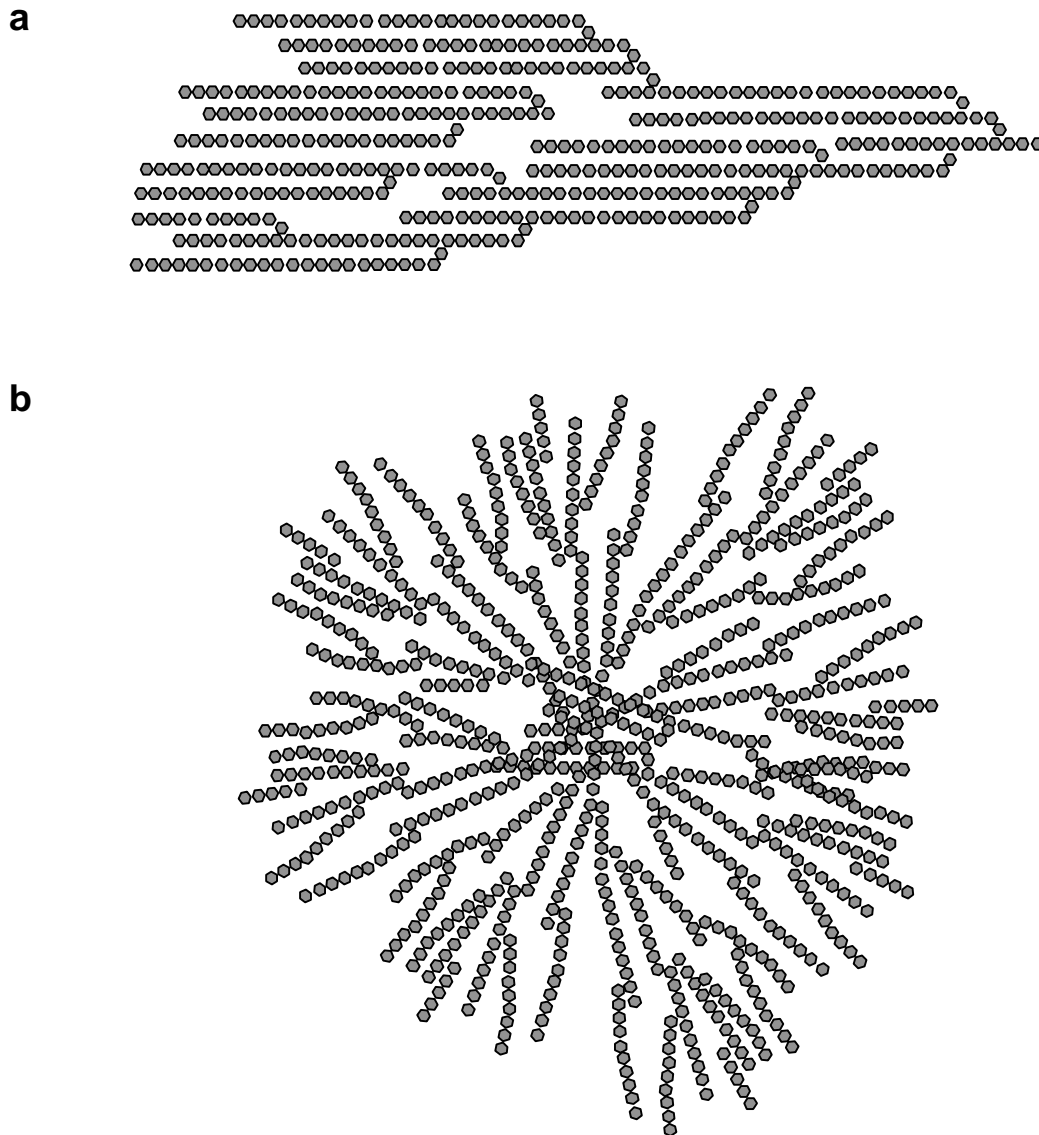


Fig. 7. Schematic representation of the structural organization of amylopectin (a) and glycogen (b). In amylopectin, side branches are clustered while glycogen adopts a tree-like structure.