Biochemistry

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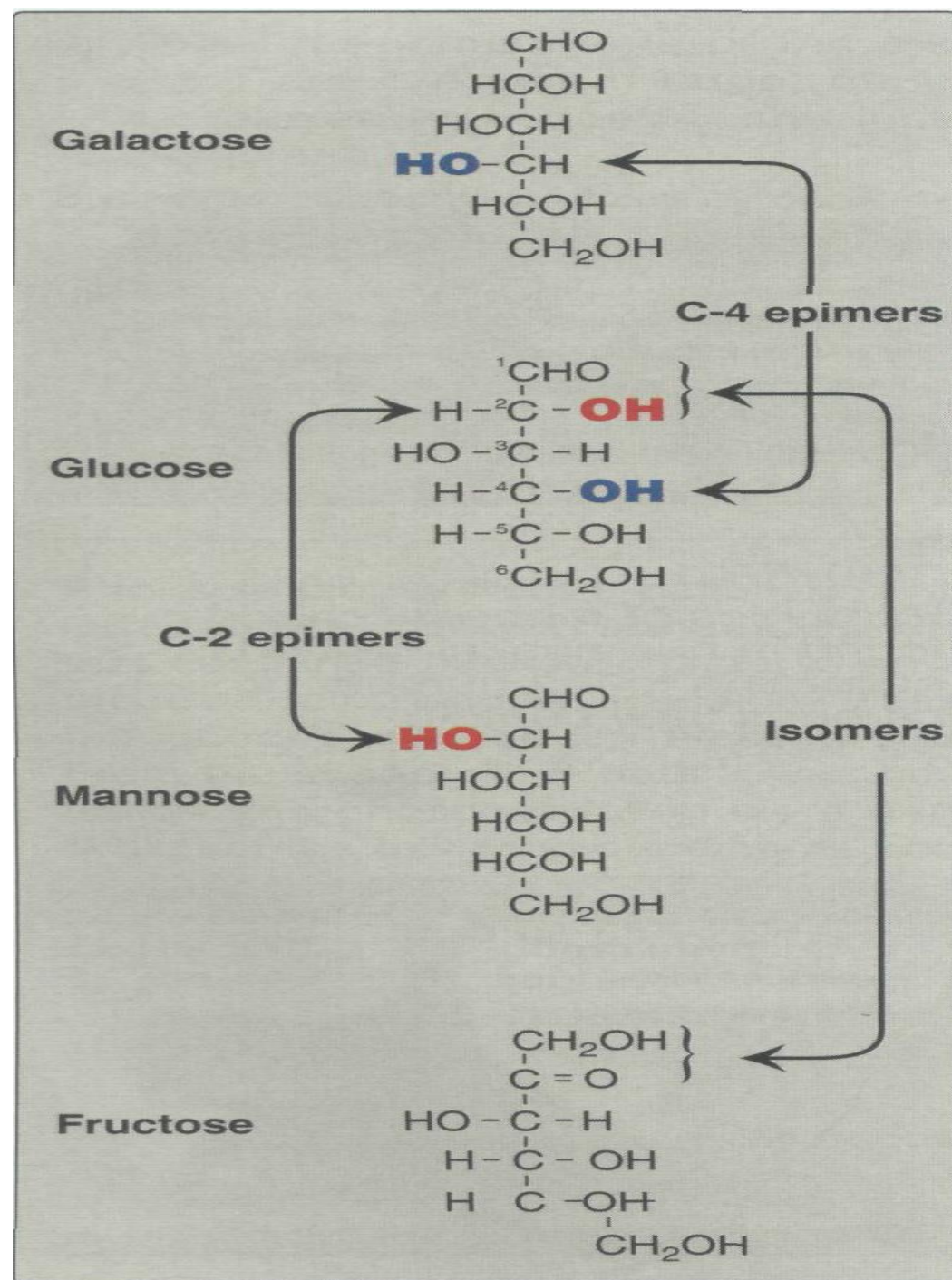
Introduction to carbohydrates

Carbohydrates are the most abundant organic molecules in nature. They have a wide range of functions, including providing a significant fraction of the energy in the diet of most organisms, acting as a storage form of energy in the body, and serving as cell membrane components that mediate some forms of intercellular communication. Carbohydrates also serve as a structural component of many organisms, including the cell walls of bacteria,

Generic names		Examples
3 carbons:	trioses	Glyceraldehyde
4 carbons:	tetroses	Erythrose
5 carbons:	pentoses	Ribose
6 carbons:	hexoses	Glucose
7 carbons:	heptoses	Sedoheptulose
9 carbons:	nonoses	Neuraminic acid

Isomers and epimers

Compounds that have the same chemical formula but have different structures are called isomers. For example, fructose, glucose, mannose, and galactose are all isomers of each other, having the same chemical formula $C_6H_{12}O_6$. If two monosaccharides differ in configuration around only one specific carbon, they are defined as epimers of each other. (Of course, they are also isomers) For example, glucose and galactose are C-4 epimers there structures differ only in the position of the -OH group at carbon 4. [Note: The carbons in sugars are numbered beginning at the end that contains the carbonyl carbon— that is, the aldehyde or keto group] Glucose and mannose are C-2 epimers.

However, galactose and mannose are **NOT** epimers they differ in the position of -OH groups at two carbons (2 and 4) and are, therefore, defined only as isomers .
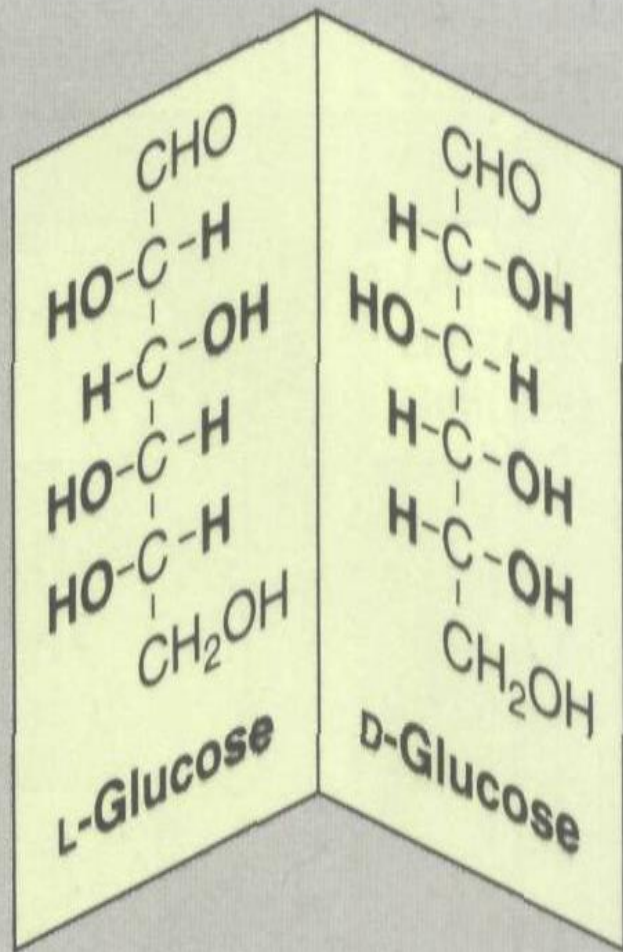
Galactose

$$CHO$$
$$HCOH$$
$$HOCH$$
$$HO-CH$$
$$HCOH$$
$$CH_2OH$$

C-4 epimers

Glucose

$$^1CHO$$
$$H-^2C-OH$$
$$HO-^3C-H$$
$$H-^4C-OH$$
$$H-^5C-OH$$
$$^6CH_2OH$$

C-2 epimers

Mannose

$$CHO$$
$$HO-CH$$
$$HOCH$$
$$HCOH$$
$$HCOH$$
$$CH_2OH$$

Isomers

Fructose

$$CH_2OH$$
$$C=O$$
$$HO-C-H$$
$$H-C-OH$$
$$H\ C-OH$$
$$CH_2OH$$

Enantiomers

A special type of isomerism is found in the pairs of structures that are mirror images of each other. These mirror images are called **enantiomers,** and the two members of the pair are designated as a D- and an L-sugar . The vast majority of the sugars in humans are D-sugars.
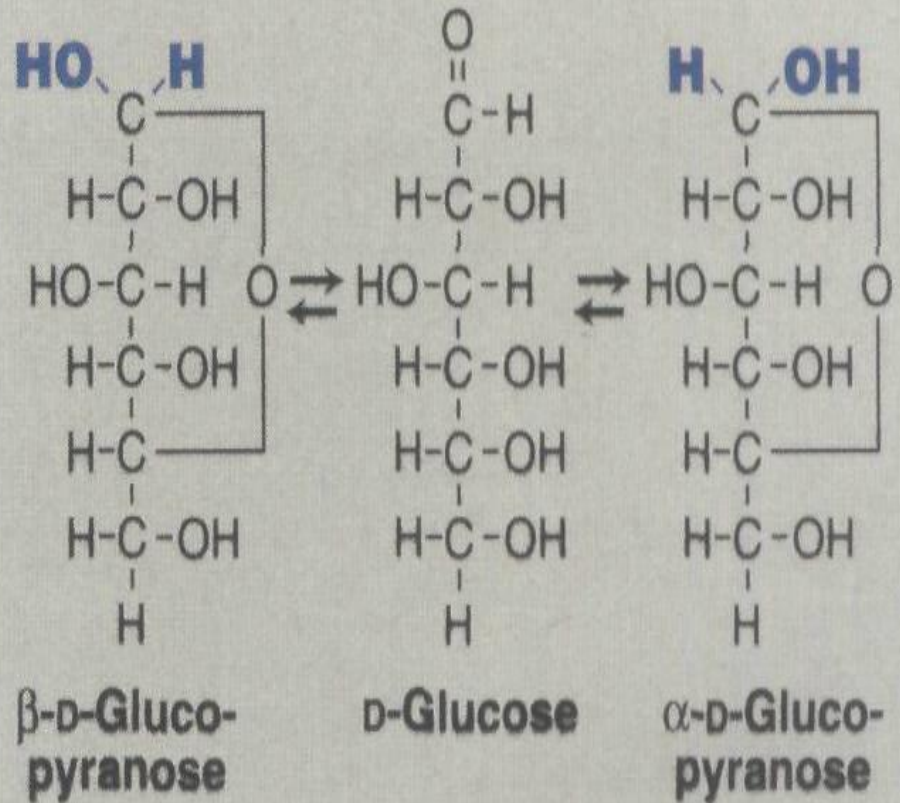
Cyclization of monosaccharides

Less than one percent of each of the monosaccharides with five or more carbons exists in the open-chain (acyclic) form. Rather, they are predominantly found in a ring form, in which the aldehyde (or ketone) group has reacted with an alcohol group on the same sugar.

Figure 7.5
Enantiomers (mirror images) of glucose.

Figure 7.6
The interconversion of the α and β anomeric forms of glucose (mutarotation).

Anomeric carbon: Formation of a ring results in the creation of an anomeric carbon at carbon 1 of an aldose or at carbon 2 of a ketose. These structures are designated the **alpha or Beta configurations** of the sugar, for example, alpha D-glucose and B D-glucose . These two sugars are both glucose, but they are anomers of each other. Enzymes are able to distinguish between these two structures and use one or the other preferentially. For example, glycogen is synthesized from a- D-glucopyranose whereas cellulose is synthesized from B -D-glucopyranose . The cyclic a and B anomers of a sugar in solution are in equilibrium with each other, and can be spontaneously interconverted (a process called mutarotation).
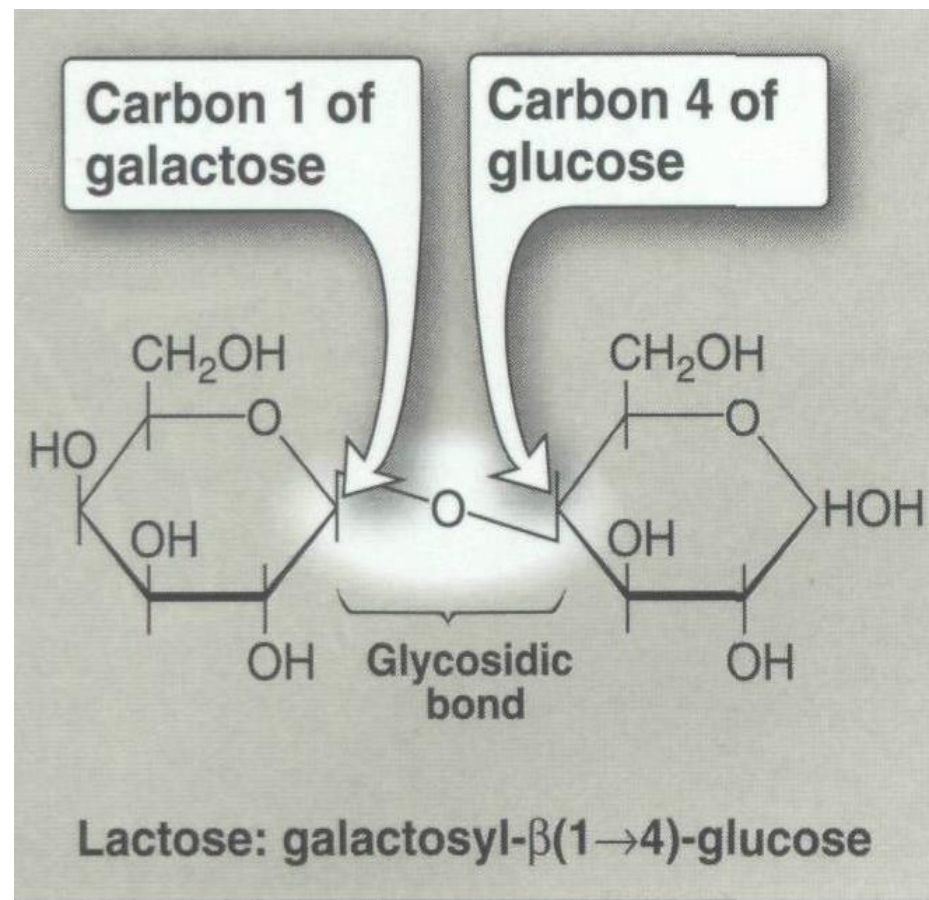
Reducing sugars:

If the oxygen on the anomeric carbon (the carbonyl group) of a sugar is not attached to any other structure, that sugar is a reducing sugar. A reducing sugar can react with chemical reagents (for example, Benedict's solution) and reduce the reactive component, with the **anomeric carbon** becoming oxidized. [Note: Only the state of the oxygen on the anomeric carbon determines if the sugar is reducing or nonreducing the other hydroxyl groups on the molecule are not involved.]

Complex carbohydrates

Carbohydrates can be attached by glycosidic bonds to non-carbohydrate structures, including purines and pyrimidines

(found in nucleic acids), aromatic rings (such as those found in steroids and bilirubin), proteins (found in glycoproteins and lipids (found in glycolipids). The aldose, the carbon 1 of which (or ketose, the carbon 2 of which) participates in the glycosidic link, is called a **glycosyl residue.** For example, if the anomeric carbon of glucose participates in such a bond, that sugar is called a **glucosyl residue;** thus, the disaccharide lactose .

Lactose: galactosyl-β(1→4)-glucose

Figure 7.3
A glycosidic bond between two hexoses producing a disaccharide.

Monosaccharides

Glucose found have mild sweet flavor, known as blood sugar essential energy source found in every disaccharide and polysaccharide

Fructose :sweetest sugar, found in fruits and honey,added to soft drinks, cereals.

Galactose hardly tastes sweet, rarely found naturally as a single sugar .

Disaccharides:

Maltose, a cleavage product of starch (e.g., amylose), is a disaccharide with an $\alpha(1\rightarrow 4)$ glycosidic link between C1 - C4 OH of 2 glucoses. It is the α anomer (C1 O points down).

Sucrose, common table sugar, has a glycosidic bond linking the anomeric hydroxyls of glucose & fructose. tastes sweet, fruit, vegetables, grains table sugar is refined sugar cane and sugar beets, brown, white, powdered.

Lactose, milk sugar, is composed of galactose & glucose :main carbohydrate in milk known as milk sugar.

Polysaccharides: Plants store glucose as **amylose** or **amylopectin**, glucose polymers collectively called starch. Glucose storage in **polymeric** form **minimizes osmotic effects**. The end of the polysaccharide with an anomeric C1 not involved in a glycosidic bond is called the **reducing end**.

Cellulose, a major constituent of plant cell walls, consists of long linear chains of glucose with β(1→4) linkages. **Every other glucose is flipped over**, due to β linkages. This promotes intra-chain and inter-chain H-bonds and van der Waals interactions, that cause cellulose chains to be straight & rigid, and pack with a crystalline arrangement in thick bundles - microfibrils. These microfibrils are very strong.

The role of cellulose is to impart strength and rigidity to plant cell walls, which can withstand high hydrostatic pressure gradients. Osmotic swelling is prevented.

Schematic of arrangement of cellulose chains in a microfibril.

DIGESTION OF CARBOHYDRATES

Digestion of carbohydrates begins in the mouth

The major dietary polysaccharides are of animal (glycogen) and plant origin (starch, composed of amylose and amylopectin). During mastication, salivary α-amylase acts briefly on dietary starch in a random manner, breaking some α(1-4) bonds. [Note: There are both α(1-4) and B(1-4) glucosidases in nature, but humans do not produce and secrete the latter in digestive juices. Therefore, they are unable to digest cellulose a carbohydrate of plant origin containing B(1-4) glycosidic bonds between glucose residues.]

Because branched amylopectin and glycogen also contain α (1-6) bonds, the digest resulting from the action of α-amylase contains a mixture of smaller, branched oligosaccharide molecules. Carbohydrate digestion halts temporarily in the stomach, because the high acidity inactivates the salivary α-amylase.

Further digestion of carbohydrates by pancreatic enzymes occurs in the small intestine

When the acidic stomach contents reach the small intestine, they - are neutralized by bicarbonate secreted by the pancreas, and pancreatic α-amylase continues the process of starch digestion.
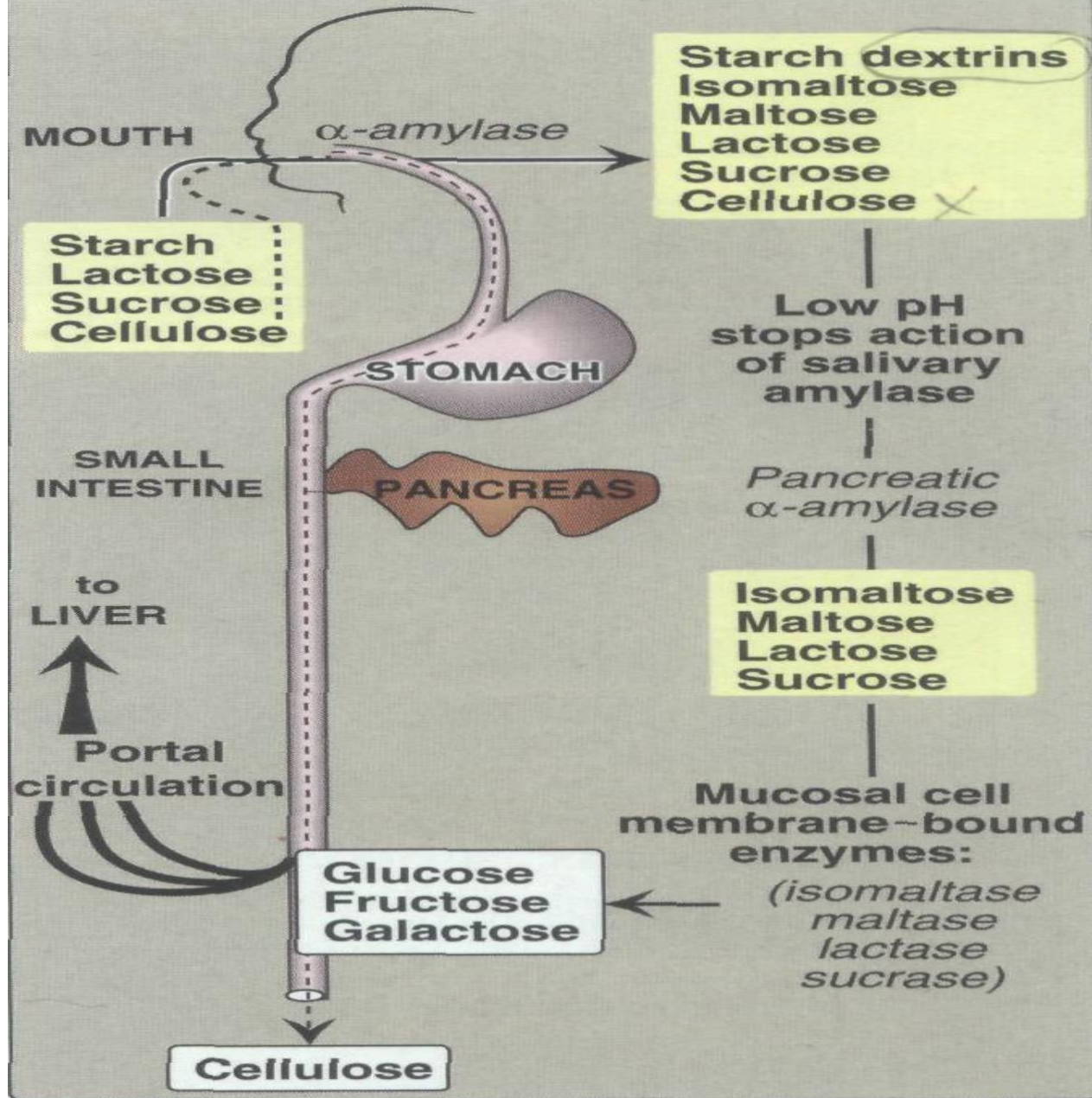
Final carbohydrate digestion by enzymes synthesized by the intestinal mucosal cells

The final digestive processes occur at the mucosal lining of upper jejunum, declining as they proceed down the small intestine, For example isomaltase, cleaves the α (1-6) bond in isomaltose and maltase cleaves maltose, both producing glucose, sucrase cleaves sucrose producing glucose and fructose, and lactase (β-galactosidase) cleaves lactose producing galactose and glucose. These enzymes are secreted through, and remain associated with, the luminal side of the brush border membranes of the intestinal mucosal cells.

Absorption of monosaccharides by intestinal mucosal cells

The duodenum and upper jejunum absorb the bulk of the dietary sugars. Insulin is not required for the uptake of glucose by intestinal cells. However, different sugars have different mechanisms of absorption. For example, galactose and glucose are transported into the mucosal cells by an active, energy-requiring process that involves a specific transport protein and requires a concurrent uptake of sodium ions. Fructose uptake requires a sodium-independent monosaccharide transporter (GLUT-5) for its absorption. All three monosaccharides are transported from the intestinal mucosal cell into the portal circulation by yet another transporter, GLUT-2.

Figure 7.10
Digestion of carbohydrates.