CARBOHYDRATES-A BRIEF DELIBERATION WITH BIO-ASPECT

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Abstract

Carbohydrate is an organic molecule having carbon, hydrogen and oxygen as chief elements. It is mostly sugary in taste and categorized in three different types according to the presence of carbon numbers in the molecule. It bears two different functional groups i.e. aldehyde (-CHO) and ketone (>CO) with different spatial configuration, resulting different isomers. Amongst many of the roles, one of the most important is the formation of structural formation of RNA and DNA. Metabolic activities like glycolysis (pathway to convert glucose to pyruvate), citric acid cycle (final oxidative pathway for carbohydrate, fats and amino acids), gluconeogenesis (synthesis of glucose from non-carbohydrate precursors), glycogenesis (synthesis of glycogen from glucose in presence of ATP) and glycogenolysis (degradation of stored glycogen) are the major functions. Carbohydrate undergoes various mechanism by which necessary product are formed, as a result human body easily function and synthesize many compounds within the human body. Obesity, diabetes mellitus, hypoglycemia are some disease condition arose due to high level of carbohydrate concentration in the body.

Keywords: spatial configuration, glycolysis, RNA and DNA, metabolic activity, obesity

Initiation

Carbohydrates are the most abundant organic molecules, primarily composed of elements; carbon, hydrogen and oxygen. It may be defined as polyhydroxyaldehyde or ketones or compounds which produce them on hydrolysis. The term 'sugar' is applied to carbohydrates soluble to water and sweet to taste. The basic formula of carbohydrate is $(CH_2O)n$. However, there are some other non-carbohydrate compounds e.g. lactic acid, acetic acid which appear as hydrates of carbon. Carbohydrate are the ultimate source of our living, they are the basic necessities of life. Our daily consumption needs such as the foods, cloths, furniture, papers, etc. contain starch, cellulose and other forms of cellulose. It must be noted that the ultimate source of all carbohydrate is the plants that can build carbohydrate from carbohydrate (CO_2) and water (H_2O) by a process called photosynthesis. Carbohydrate are referred to as saccharides (sugar). [2,4,6]

Objectives

The scope of this paper is related to some typical description of the carbohydrates and its structure as well as few major reactions, also correlates with the biological concern i.e. human body.

Methodology

This article is mainly based on the well recognized numbers of books mentioned in work cited, some cases are overviewed from practical concerning phenomenon, also includes word diagrams which are searched from various sources: subject related websites, national and international publications.

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Categories of carbohydrate

On the basis of number of sugar units, carbohydrates are broadly classified into three major groups: monosaccharides, oligosaccharides and polysaccharides.

Monosaccharides are the simplest group of carbohydrates, often referred to as simple sugars and have general formula $C_n(H_2O)_n$. When the functional group is –CHO (aldehyde), they are referred as aldoses and when the functional group is –CO (keto), they are referred as ketoses. Based on number of carbon atoms, monosaccharides are regarded as trioses (3C), tetroses (4C), pentoses (5C), and nexoses (6C). Some examples of monosaccharides include glucose (dextrose), galactose and fructose (levulose). Monosaccharides show tautomerism in alkaline solution i.e. when glucose is kept in alkaline solution, it causes shifting of hydrogen atom from one carbon atom to another to form D-fructose and D-mannose which are highly reactive. Sugars have reducing property. The tests include Benedicts test, Fehling's test, Barfoed's test, etc. The terminal aldehyde or alcohol groups of carbohydrates get oxidized to form acid. The aldehyde or keto group of carbohydrate when treated with reducing agents, get reduced to alcohol. When monosaccharide are treated with concentrated sulfuric acid, they undergo dehydration with elimination of water molecules. Monosaccharides undergo esterification by enzymatic or non-enzymatic reactions.

Oligosaccharides contain 3-10 monosaccharides molecules which are liberated on hydrolysis. They can be disaccharides, trisaccharides on the basis of number of monosaccharides. A large number of oligosaccharides cab be prepared by partially breaking down more complex carbohydrate (polysaccharides). Most of the few naturally occurring oligosaccharides are found in plants. Maltotriose, a trisaccharide of glucose occurs in some plants and in the blood of certain arthropods. Raffinose, a trisaccharide found in many plants consist of melibiose (galactose and glucose) and fructose. Some examples of oligosaccharides are raffinose and stachyose. Disaccharides are the ones that yield two monosaccharides molecules on hydrolysis and their molecular formula is $C_{12}H_{22}O_{11}$. For example; sucrose, maltose, etc.

$C_{12}H_{22}O_{11} + H_2O$ $C_6H_{12}O_6$ + $C_6H_{12}O_6$
Sucrose Fructose Glucose

Trisaccharides are the ones that yield three monosaccharides molecules on hydrolysis and their molecular formula is $C_{18}H_{32}O_{16}$.

$C_{18}H_{32}O_{16} + H_2O$ $C_6H_{12}O_6 + C_6H_{12}O_6 + C_6H_{12}O_6$
Raffinose Fructose Glucose Galactose

Polysaccharides are high molecular weight compounds which are polymer of monosaccharides. They are also known as non-sugar because of absence of sugary taste. Its basic formula is $(C_6H_{12}O_6)_n$. They are of two types: homopolysaccharides and heteropolysaccharides. They are primarily concerned with two important functions i.e. structural and storage of energy. The occurrence of branches in polysaccharides is due to the glycosidic linkages formed at any one of the hydroxyl groups of a monosaccharides. The pentosans $(C_5H_8O_4)_n$, are not so widely distributed in nature. Some examples of polysaccharides includes starch, dextrins, dextrans, insulin, glycogen, cellulose. [4,6,9]

Stereochemistry of carbohydrates

Stereoisomers are the compounds having same structural formula but differ in spatial configuration. The simplest monosaccharide, glyceraldehyde has one asymmetric carbon atom and it has two stereoisomers; D-glyceraldehyde and L-glyceraldehyde. They are mirror images of each other. If the -OH group is on right side, the sugar is D-isomer and if it is on left side, it is L-isomer.

H – C = O H – C = O

|	|
H – C – OH	OH – C – H
|	|
CH_2OH	CH_2OH
D-glyceraldehyde	L-glyceraldehyde

These compounds having asymmetric carbon atom shows optical activity i.e. when polarized light Is passed through a solution of optical isomer, it will rotate either right (dextrorotatory) or left (levo-rotatory). If both D-isomer and L-isomers are concentrated in equal amount, it is called racemic mixture. Glucose and galactose are C4-epimers as they differ from each other in their configuration around a single carbon atom.

Glucose is the most common naturally occurring monosaccharide. It exists in α and β cyclic forms, known as anomers, which differ in configuration only around C1 (anomeric carbon). They have different optical rotations. The interconversion of a α and β anomeric forms with change in optical rotation is called mutarotation. [3,6,10]

$$\underset{+\,112.2^{o}}{\alpha\text{-D-glucose}} \longleftrightarrow \underset{+\,52.7^{o}}{\text{Equilibrium mixture}} \longleftrightarrow \underset{+\,18.7^{o}}{\beta\text{-D-glucose}}$$

Role of carbohydrate

- Carbohydrate are the most abundant dietary source of energy (4 cal/g) for all organisms.
- They also serve as the storage source of energy (glycogen) to meet the immediate energy demands of the body.
- They are precursors for many organic compounds (fats, amino acids).
- They promote digestive functions in the body and also preserve muscle.
- Carbohydrates (as glycoproteins and glycolipids) participate in the structure of cell membrane and cellular functions such as cell growth, adhesion and fertilization.
- They are the structural component of many organisms. E.g. cellulose of plants, cell wall of microorganisms, exoskeleton of some insects.
- Carbohydrate aid in the regulation of nerve tissue and is the energy source for the brain.
- It helps in the formation of the structural framework of RNA and DNA (ribonucleic acid and deoxyribonucleic acid).
- Carbohydrate, which are rich in fiber content help to prevent constipation and also help in the modulation of the immune system.

Sources of carbohydrate

Carbohydrate are present in wide range of both healthy and unhealthy foods like bread, beans, milk, potatoes, cookies, soft drinks, corn. The most common and abundant forms are sugars, fibers and starches. Healthiest sources includes whole grains, vegetables, fruits, beans. An unhealthier sources of carbohydrate includes white bread, pastries, sodas and other highly processed or refined foods.

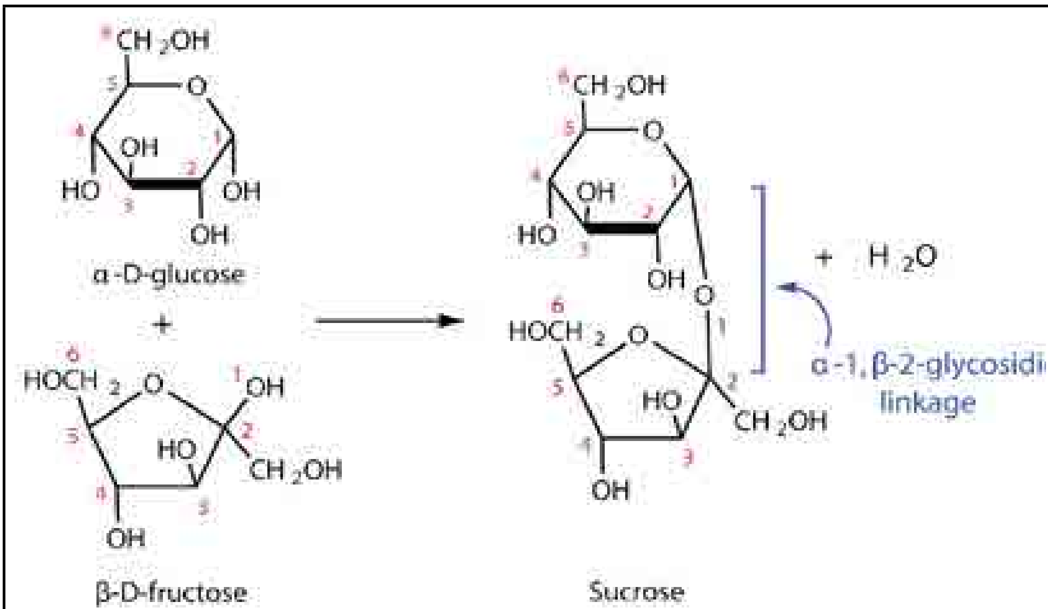
Simple and complex carbohydrates

Simple carbohydrates are sugars. They include white bread, sugars and candies. They consist of only one or two molecules. They provide a instant source of energy, but the consumer feels hungry again.

Complex carbohydrates consists of long chains of sugar molecules. It includes whole grains, fruits, vegetables, pulses. They provide energy for longer duration and contains more vitamins, minerals and fibers. The United States Dietary Guidelines 2015-2020 recommend obtaining 45 to 60 % of energy needs from carbohydrates and a maximum of 10 percent should come from simple carbohydrate (glucose and simple sugars). [1,6,9]

Glycosidic bond

A covalent bond formed between a carbohydrate molecule and another molecule (i.e. between two monosaccharides) is known as glycosidic bond. Monosaccharides can be joined together by glycosidic bonds to form disaccharides, oligosaccharides and polysaccharides. The glycosidic bonds are formed by enzymes known as glycosyltransferases that use nucleoside sugars sich as UDP-glucose as substrates. Glycosidic bonds (also known as glycosidic linakges) can be of the alpha or the beta type. Glycosidic bonds between sugars are named according to the numbers of the connected carbons and also with regard to the position of the anomeric hydroxyl group of the sugar involved in the bond. If this anomeric hydroxyl is in the α configuration, the linkage is as α bond. If it is in the β configuration, the linkage is known as β bond. For example; lactose have glycosidic bond between carbon 1 of β galactose and carbon 4 of glucose and the linkage is therefore a β (1 → 4) glycosidic bond. Important disaccharides include lactose (galactose + glucose), sucrose (glucose + fructose) and maltose (glucose + glucose). [4,6,9]



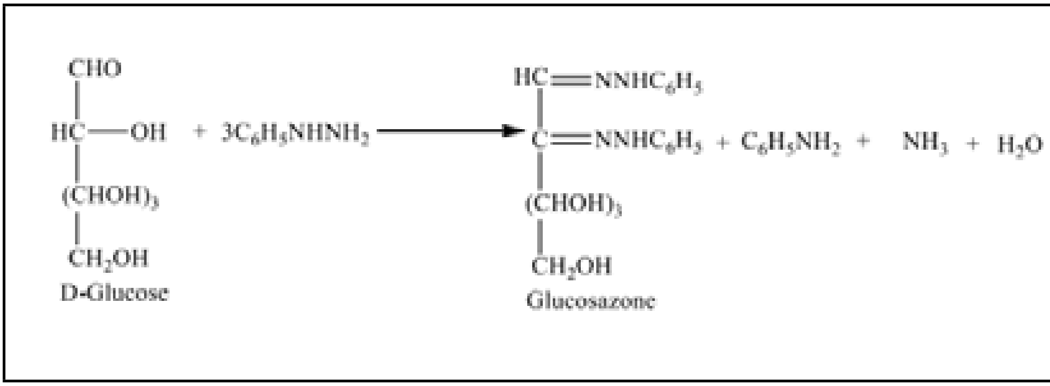
Good carbohydrate and bad carbohydrate

Good carbohydrate contains high fiber, are slowly digested (take several hours) and gradually increase the blood sugar level. It includes unprocessed foods like whole grain breads, beans, cereals and products made from whole wheat flour, fruits and vegetables. These foods keep our digestive system healthy, prevents obesity and reduce the risk of diabetes and heart disease.

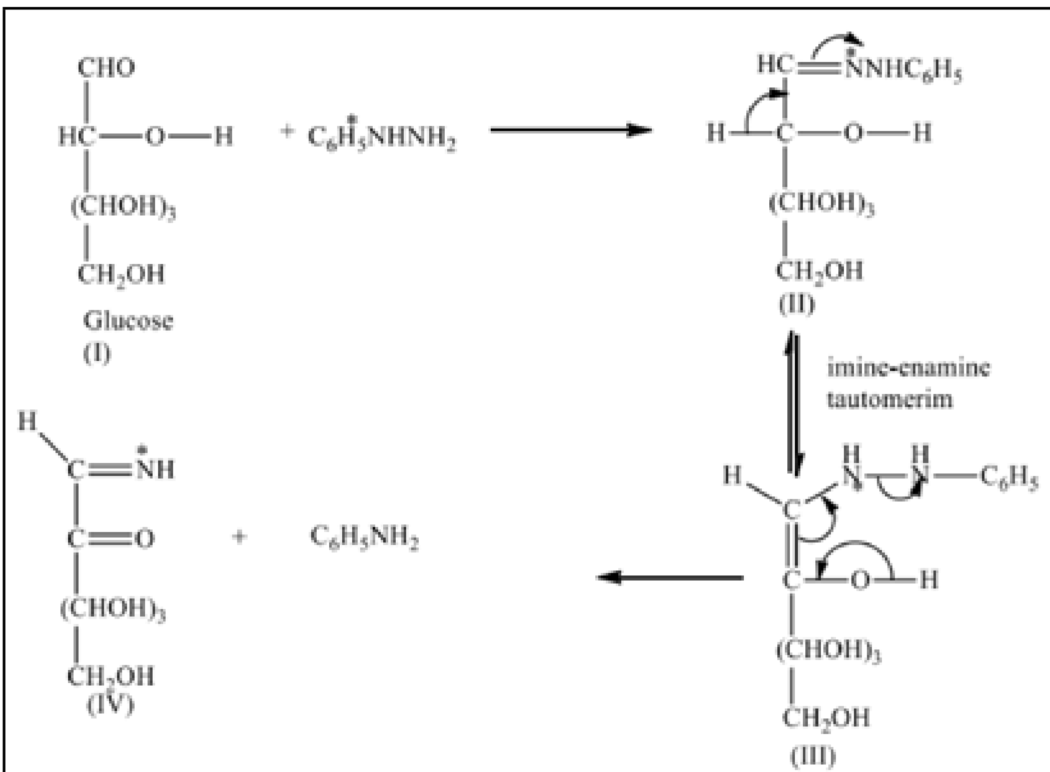
Bad carbohydrate contains low fiber and are rapidly digested. It includes processed foods like cakes, cookies, bakery items, processed rice and some cereals. The natural ingredients of food are removed during the process of making it. These foods increases obesity and risk of diabetes and heart diseases. [3,6,11]

Osazone formation

Glucose and fructose react with one equivalent of phenylhydrazine, resulting in formation of phenylhydrazone. In contrast, α-hydroxy carbonyl compounds react with three equivalents of phenylhydrazine to form bis-phenylhydrazones, known as osazone.



The first equivalent of phenylhydrazine forms phenylhydrazone with the aldehyde of ketone group. Phenylhydrazone undergoes the rearrangement, known as Amadori rearrangement to give α-iminoketone (IV) with the loss of aniline.



Subsequent attack of two moles of phenylhydrazine on the iminoketone or on the ketoaldehyde results in the formation of osazone accompanied by the elimination of ammonia. The given mechanism is supported by the observation that phenyl hydrazine prepared by the reaction of glucose with N15 (N*) labeled phenylhydrazine is treated with ordinary phenylhydrazine, unlabeled osazone is obtained accompanied by the explusion of labelled ammonia. [1,4]

Reducing property of sugar

If the oxygen on the anomeric carbon of a sugar is not attached to any other structure, that sugar can act as a reducing agent and is termed as reducing sugar. The reducing property is mainly due to the ability of these sugars to reduce metal ions such as copper or silver to form insoluble cuprous oxide, under alkaline condition. The aldehyde group of aldoses is oxidized to carboxylic acid. Reducing sugar can react with chromogenic agents (Benedict's reagent) and can cause the reagent to be reduced and colored, with the anomeric carbon of the sugar becoming oxidized. All the monosaccharides are reducing whereas in the case of oligosaccharides, if the molecule possesses a free aldehyde or ketone group, it belongs to reducing sugar (e.g. maltose and lactose). If the reducing groups are involved in the formation of glycosidic linkage, the sugar belongs to the non-reducing group (e.g. sucrose, raffinose). [6,9,10]

Specific reaction of carbohydrate

Chemical reaction of glucose

A. Reaction due to aldehyde group:

I. Reduction: Monosaccharides can be reduced by reducing agents such as sodium amalgam or by hydrogen under high pressure in the presence of catalysts. On reduction, they yield alcohols.

$$CH_2OH(CHOH)_4CHO + 2[H] \xrightarrow{Na/Hg} CH_2OH(CHOH)_4CH_2OH$$

Glucose Sorbitol

II. Oxidation: When glucose is treated with bromine water, the aldehyde group is oxidized to carboxylic group resulting in formation of gluconic acid.

$$CH_2OH(CHOH)_4CHO \xrightarrow{Br_2, H_2O} CH_2OH(CHOH)_4COOH$$

Glucose Gluconic acid

III. Reaction with HCN: like aldehydes, glucose reacts with HCN to form cyanohydrins.

IV. Reaction with hydroxylamine: glucose forms glucose oxime.

B. Reaction due to hydroxyl group:

I. Reaction with methanol: Glucose reacts with methanol in the presence of HCl and to form methyl glucoside (α and β glucoside).

$$C_6H_{11}O_5OH + HOCH_3 \xrightarrow{HCl} C_6H_{11}O_5OCH_3 + H_2O$$

Glucose Methyl glycoside

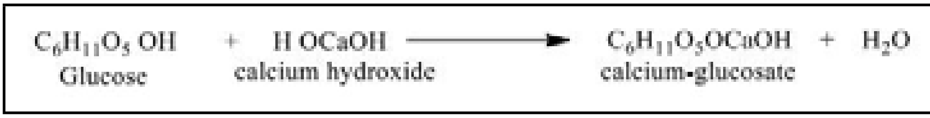
II. Reaction with acetic anhydride: Glucose forms penta acetate with acetic anhydride of acetyl chloride.

$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 + 5(CH_3CO)_2O \\ | \end{array} \xrightarrow{ZnCl_2} \begin{array}{l} CHO \\ | \\ (CHOCOCH_3)_4 + 5CH_3COOH \\ | \end{array}$$

CH_2OH CH_2OCOCH_3

Glucose Acetic anhydride Glucose penta-acetate

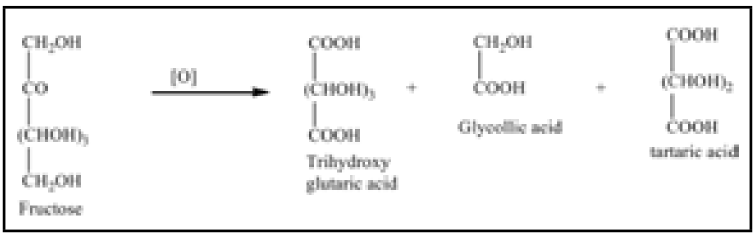
III. Reaction with metallic hydroxides: Glucose reacts with calcium hydroxide to form calcium glucosate that is water soluble.



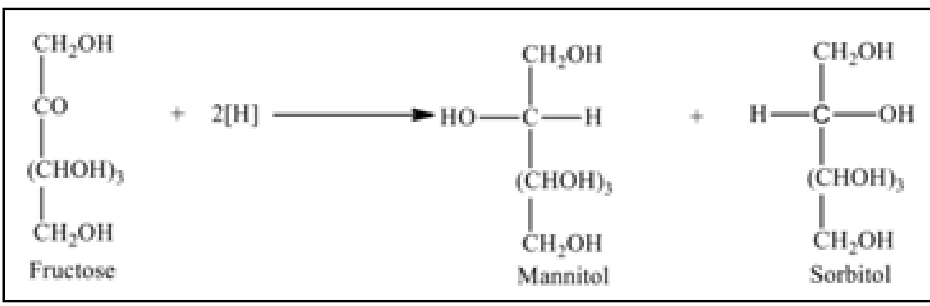
Chemical reaction of fructose

A. Reaction due to ketone group

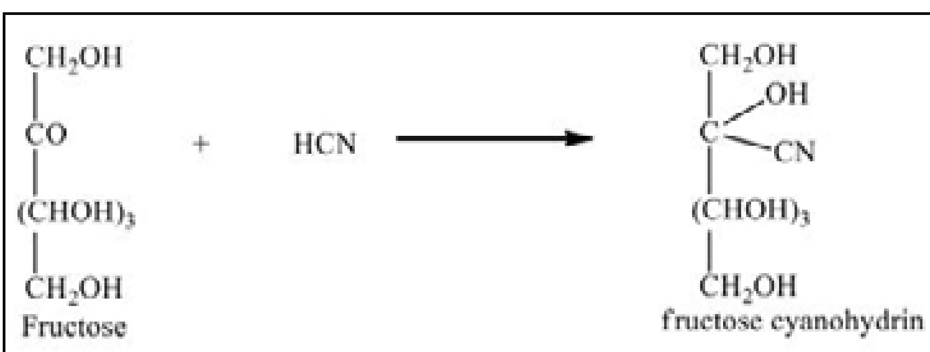
I. Oxidation: Fructose gets oxidized by strong oxidizing agents like nitric acid into a mixture of trihydroyl glutaric, glycolic and tartaric acids.



II. Reduction: Fructose in presence of Na-Hg and water or catalytic hydrogenation gives a mixture of sorbitol and mannitol on reduction.

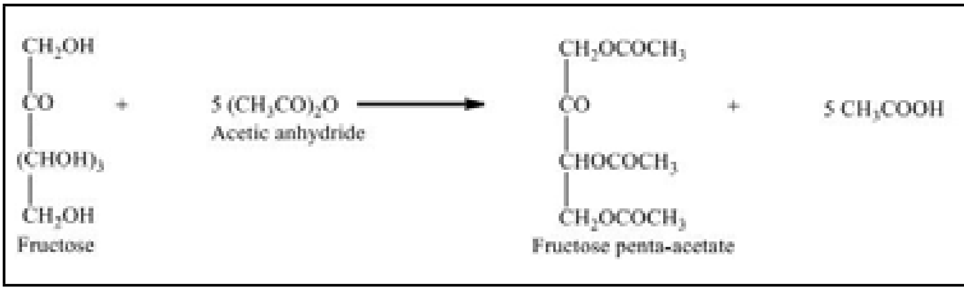


III. Reaction with HCN: fructose reacts with HCN to form cyanohydrins.



B. Reaction due to alcoholic group

I. Acetylation: Fructose in presence of acetic anhydride, forms penta-acetate.



II. Reaction with methyl alcohol: fructose reacts with methyl alcohol to form methyl fructoside in presence of HCl gas.

$$\underset{\text{Fructose}}{C_6H_{11}O_5\,OH} + H\,OCH_3 \xrightarrow{\text{Dry HCl}} \underset{\text{Methyl fructoside}}{C_6H_{11}O_5OCH_3} + H_2O$$

III. Reaction with metallic hydroxides: Fructose reacts with calcium hydroxide to form calcium-fructosate.

$$\underset{\text{Fructose}}{C_6H_{11}O_5\,OH} + \underset{\text{calcium hydroxide}}{H\,OCaOH} \longrightarrow \underset{\text{calcium-fructosate}}{C_6H_{11}O_5OCaOH} + H_2O$$

Metabolism of carbohydrates

The normal fasting blood glucose level in an individual is 70-100 mg/dl. Liver plays an important role in maintaining blood glucose level. Carbohydrates undergo various pathways of metabolism. [2,3,5,8]

a) Glycolysis:

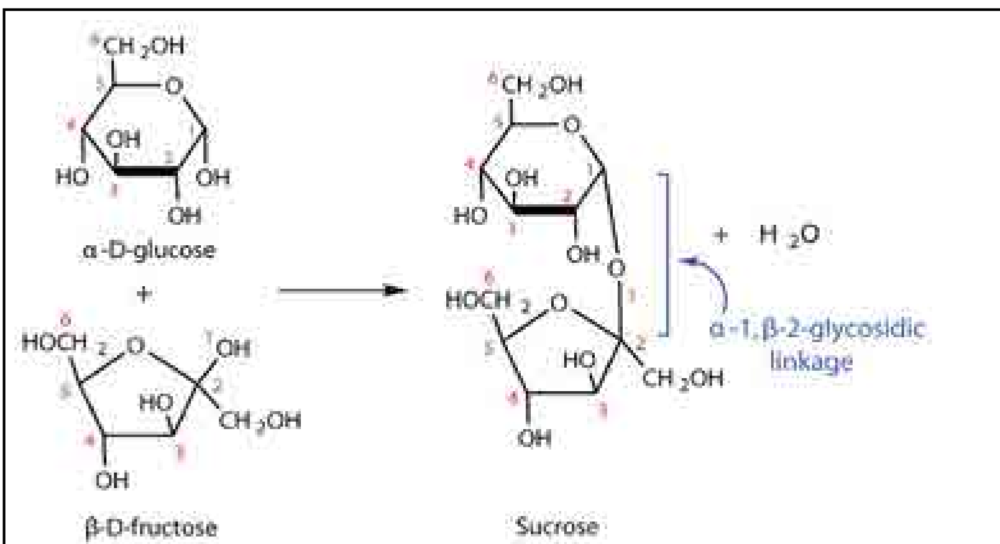


Figure: Glycolysis pathway
Source: miro.medium.com

It is the pathway to convert glucose to pyruvate or lactate with the production of ATP. It occurs in cytoplasm of cell. It involves three phases: energy investment phase (glucose is converted to fructose-1,6-biphosphate), splitting phase (fructose-1,6-biphosphate is converted to glyceraldehyde-3-phosphate) and energy generation phase (glyceraldehyde-3-phosphate is converted to lactate or pyruvate). Pyruvate is then converted to acetyl CoA by oxidative decarboxylation by multi-enzyme found in mitochondria.

b) Citric acid cycle (Krebs cycle):

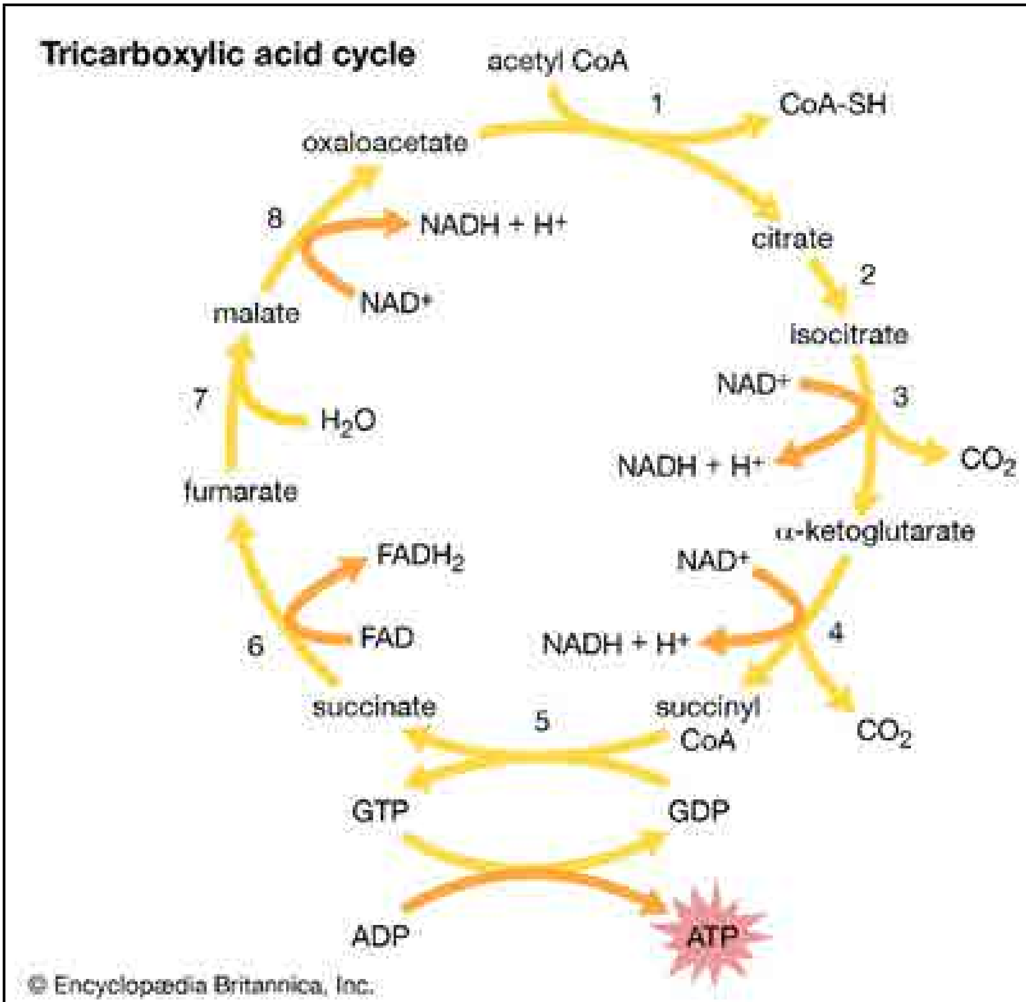


Figure: Citric acid cycle

Source: cdn.britannica.com

This cycle involves oxidation of acetyl CoA to CO_2 and H_2O. It is the final oxidative pathway for carbohydrates, fats and amino acids. It occurs in mitochondria. The two carbon compound acetyl CoA condenses with four carbon compound, oxaloacetate to yield citric acid, a six-carbon carboxylic acid. It then releases two molecules of carbondioxide in successive decarboxylation which yields high-energy electrons. Following this, oxaloacetate is regenerated which initiates another cycle. Thus, this cycle removes electron from acetyl CoA which is used to reduce NAD^+ and FAD to form NADH and $FADH_2$. Vitamin complexes, thiamine, rivoflavin, niacin and pantothenic acid plays a role in energy generation. The three enzymes namely citrate synthase, isocitrate dehydrogenase and α-ketoglutarate dehydrogenase are important for regulation of rate of citric acid cycle. Krebs cycle is amphibolic in nature i.e. it has both catabolic and anabolic nature as it provides intermediates for synthesis of many compounds in body.

c) Gluconeogenesis:

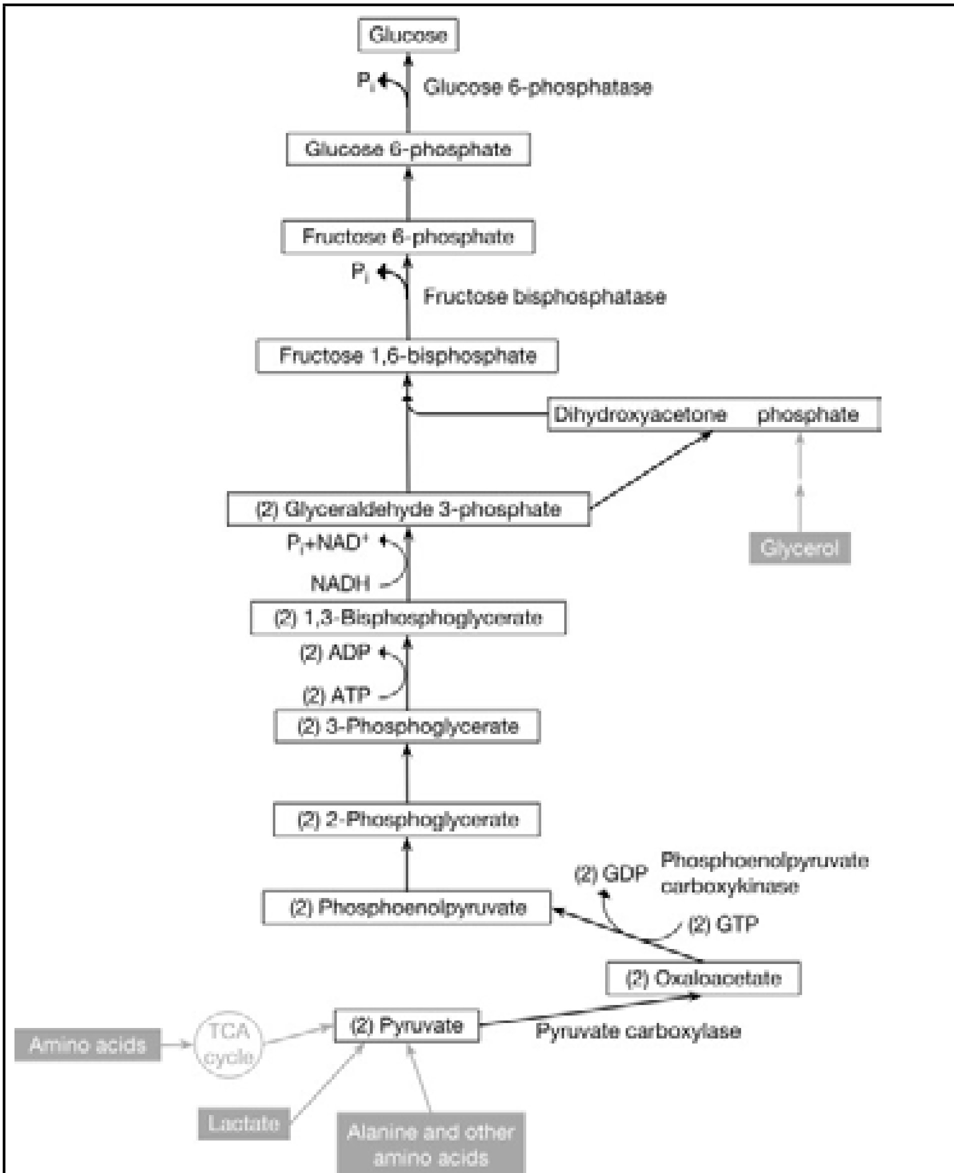


Figure: Gluconeogenesis

Source: sciencedirect.com

It involves synthesis of glucose from non-carbohydrate precursors. The major precursor includes lactate, pyruvate, amino acids and glycerol. As glucose needs its continuous supply for various functions in body, this cycle plays a crucial role. Moreover, brain of typical adult human being requires 120 mg of glucose which is out of 160 mg needed for whole body. Gluconeogenesis is essential for longer period of fasting to meet the basic requirement of body and also to maintain energy during anaerobic conditions. The metabolites like lactate, glycerol accumulated in body are cleared from blood by this mechanism. Gluconeogenesis is not a reversal of glycolysis although pyruvate is converted to glucose. It differs in three irreversible steps of glycolysis which are catalyzed by enzymes, hexokinase, phosphofructokinase and pyruvate kinase. The first step is the conversion of pyruvate into phosphoenolpyruvate with the formation of oxaloacetate in presence of ATP and CO_2, catalyzed by pyruvate carboxylase. Phosphoenolpyruvate undergoes reversal of glycolysis until fructose-1,6-biphosphate is produced. The second step follows conversion of fructose-1,6-biphosphate to fructose-6-phosphate catalyzed by fructose-1,6-biphosphate and Mg^{2+} ions. Then, glucose-6-phosphatase catalyzes the conversion of glucose-6-phosphate to glucose. The summary of gluconeogenesis is:

2 pyruvate + 4 ATP + 2 GTP Glucose + 2 NAD^+ + 4 ADP

+ 2 NADH + $2H^+$ + $6H_2O$ + 2 GDP + 6 Pi + $6H^+$

d) Glycogenesis:

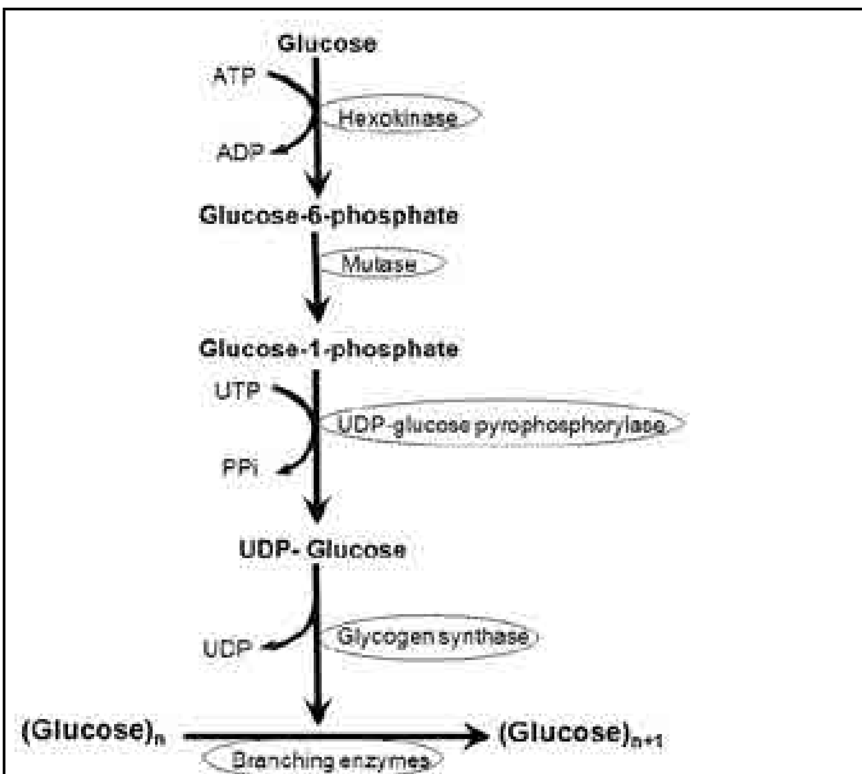


Figure: Glycogenesis

Source: laboratoryinfo.com

It refers to synthesis of glycogen from glucose in presence of ATP. Glucose is converted to UDP-glucose catalyzed by enzyme glucokinase and subsequently UDP-glucose phosphorylase. However, a primer is required to initiate glycogenesis where the pre-existing glucogen acts as a primer. Glucogen synthase is responsible for formation of 1-4-glycosidic linkages, thereby forming non-reducing end of glycogen. Since, glycogen is a branched tree-like structure, these branches are formed by enzyme, glycosyl α-4-6 transferase resulting to further elongation of glycogen.

$(\text{Glucose})_n$ + Glucose + 2 ATP $(\text{Glucose})_{n+1}$ + 2 ADP + Pi

e) Glycogenolysis

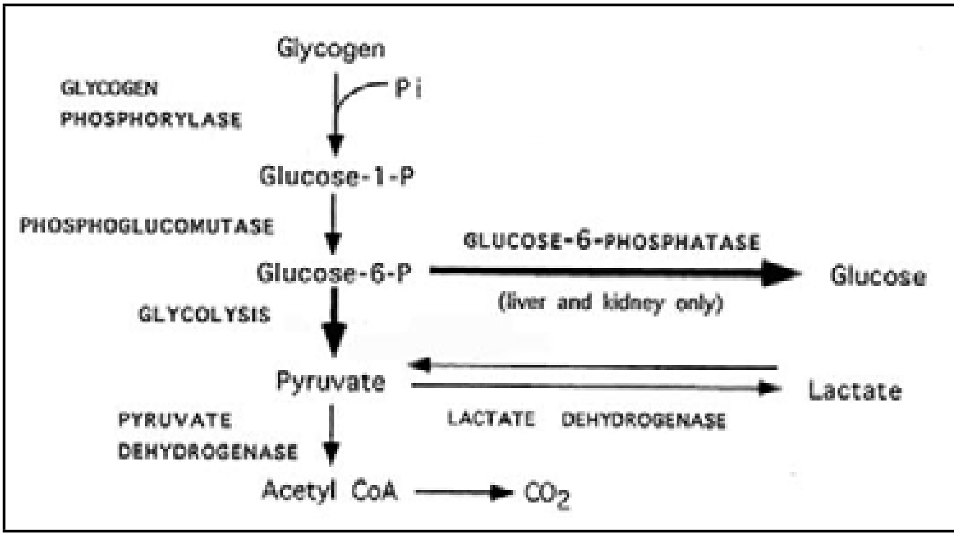


Figure: Glycogenolysis

Source: biochemden.com

Glycogenolysis indicates degradation of stored glycogen in liver and muscle. The initial step is catalyzed by enzyme, glycogen phosphorylase resulting to limit dextrin which cannot be further degraded by phosphorylase. The debranching enzyme then cleaves the branches of glycogen. Further, glycogen phosphorylase and debranching enzyme forms glycose-6-phosphate which is then converted to glucose in presence of glucose-6-phosphatase.

High carbohydrate level

Obesity

High intake of carbohydrate may lead to obesity. Though reduction in physical activity, rise in living standard leads to obesity. Higher consumption of junk food, food additives such as coloring, taste enhancers, artificial emulsifiers also contribute to obesity. Excessive amount of body weight is associated with various diseases and conditions, particularly cardiovascular diseases, diabetes mellitus type 2, obstructive sleep apnea, certain types of cancer, osteoarthritis and asthma. At an individual level, combination of excessive food energy intake and lack of physical activity is thought to explain the major causes of obesity. Other cases are due to primarily genetics, medical reasons or psychiatric illness.

The main treatment of obesity consists of reducing body weight by dieting and physical exercise.

Dieting produces sustained weight loss. Intense behavioral interventions combining both dietary changes and exercise are also recommended. In short-term, low carbohydrate diets appear better than low fat diets for weight loss. In long-term, all types of low carbohydrate and low fat diets are equally beneficial. Decreased intake of sweet drinks is also related to weight loss. Intense behavioral counselling is recommended in those who are both obese and have other risk factors for heart disease. [2,3,5,7]

Diabetes mellitus

Carbohydrates after consumption are broken down to glucose. This glucose enters the blood and raise blood glucose level. Diabetes mellitus is a clinical syndrome characterized by increase in blood glucose level. The major types, type 1 which is autoimmune in cause, mainly due to destruction of insulin producing cells and type 2 is characterized by resistance to insulin. Type 1 diabetes is autoimmune disease, where genetic factors accounts for one-third of disease and is more focused on human leucocyte antigen (HLA) region within the major histocompatibility complex, designated as IDDM (Insulin Dependent Diabetes Mellitus).

In Type 2 diabetes mellitus, the pancreatic B-cells are not able to sustain insulin demand resulting to insulin deficiency. Type 2 diabetes mellitus is associated with triad of obesity, overeating and underactivity. The suspected individual may be asymptomatic, or presents polyuria, polydipsia, nocturia, polyphagia, weight loss despite increased appetite. Some of them may have recurrent urinary tract infections and other fungal infections. Laboratory examination includes testing the urine for glucose, ketones, proteins and testing the blood glucose, glycated hemoglobin. Glycated hemoglobin provides an accurate glycemic level over a period of weeks to months. Diabetes is confirmed in increase in fasting plasma glucose >126 mg/dl and post-prandial plasma glucose >200 mg/dl. The objective of management is to improve symptoms of hyperglycemia and reduce the risk of vascular complications. Treatment includes dietary modification, lifestyle change and medication with oral anti-diabetic drugs. Diabetic ketoacidosis is a metabolic emergency due to insulin deficiency in which hyperglycemia is associated with metabolic acidosis due to formation of excess of ketones in the blood. [5,8,12]

Hypoglycemia

In diabetic patient, hypoglycemia results from missed or delayed meals, overdose of insulin or oral hypoglycemic drug, renal cause causing decreased clearance of insulin. Hypoglycemia in non-diabetic people is called spontaneous hypoglycemia. It may be caused due to prolonged fasting, heavy alcohol consumption, liver diseases (acute hepatic failure), endocrine disease (hypopituitarism, addison's disease, some drugs and toxins like ethanol, quinine, insulinomas, sepsis). The individual clinically presents with sweating, trembling, hunger, confusion, drowsiness, nausea, tiredness, headache, inability to concentrate. The treatment of hypoglycemia depends on severity of hypoglycemia and the patient condition. Oral carbohydrates is supplied if the patient is conscious otherwise parenteral therapy is required. Carbohydrate in junk and processed foods and drinks causes a person to rapidly utilize energy and feel hungry thus increasing the glucose level and insulin production rapidly. [7,8,12]

Conclusion

Basic empirical formula of carbohydrate is $(CH_2O)_n$, if n is equivalent with 6, is a lowest monomer. Carbohydrate shows stereoisomer and the two monomers are joined together by glycosidic bond. Anabolic and catabolic mechanism of carbohydrate keeps the body balancing producing different energy levels as well as converts them into appropriate compounds. Various body functions may be harmed or abnormalities may arise when the level of carbohydrate is increased or decreased in the body.

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