Carbohydrates

Carbohydrates are universal constituents of living organisms.

They are organic compounds with carbonyl (aldehyde or ketone) and multiple hydroxyl functions

Oxidized or reduced derivatives such as; uronic acids, polyalcohols and their esters, ethers and amine derivatives (aminosugars) are also present

Classified as

. Monosaccharides: the general formula Cn(H2O)n, characterized by the presence of an aldehyde or ketone carbonyl function and n-1 hydroxyl functions. The number of carbon atoms range from three to nine

.Oligomeric and polymeric saccharides:

Resulting from the combination, through glycosidic, of several monosaccharide molecules

.Glycosides:

they result from the establishment of a bond between a sugar and non-sugarmolecule (aglycone)

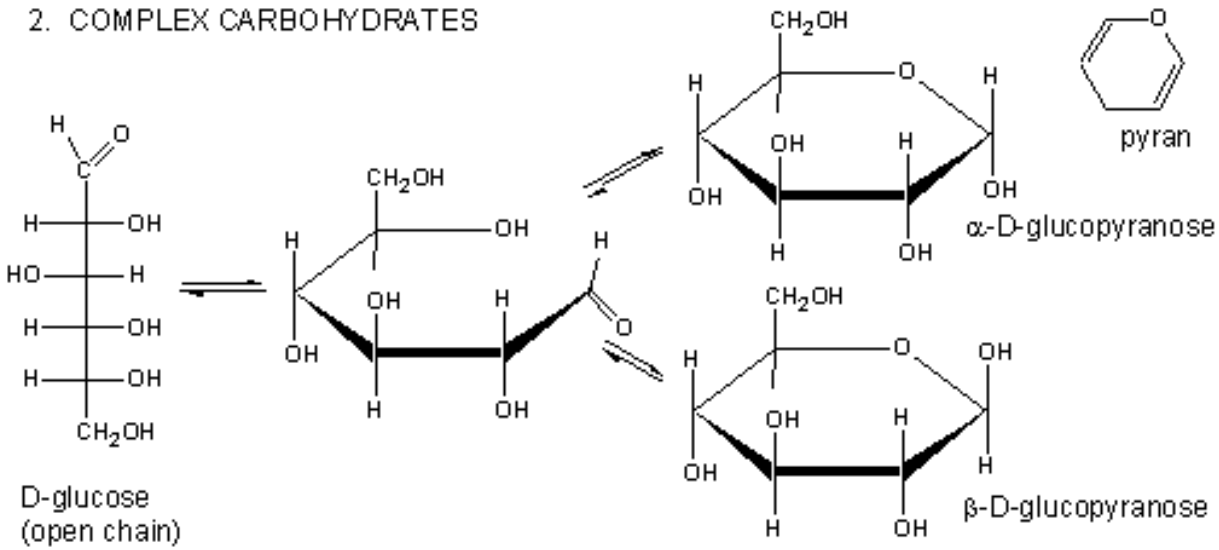
Monosaccharides

- Naming of monosaccharides is based on the number of oxygen atoms in the molecule; triose, tetrose, pentose,hexose
- and the nature of their carbonyl function such as; aldoses, D-ribose, D-xylose; ketoses, D-ribulose, D-fructose

- Monosaccharides have asymmetric carbon atoms and they have enantiomers (*R*) and (*S*). Enantiomer numbers can be calculated by 2^n
- Optical isomers can be formed which are strucurally identical but are mirror images of each other.
- They can sign as d and l, means rotate the plane of polarised light

- The enantiomer is known (+) form rotates the plane of polarisation in a clockwise direction
- The enantiomer is known (-) form rotates the plane of polarisation in a anti-clockwise direction

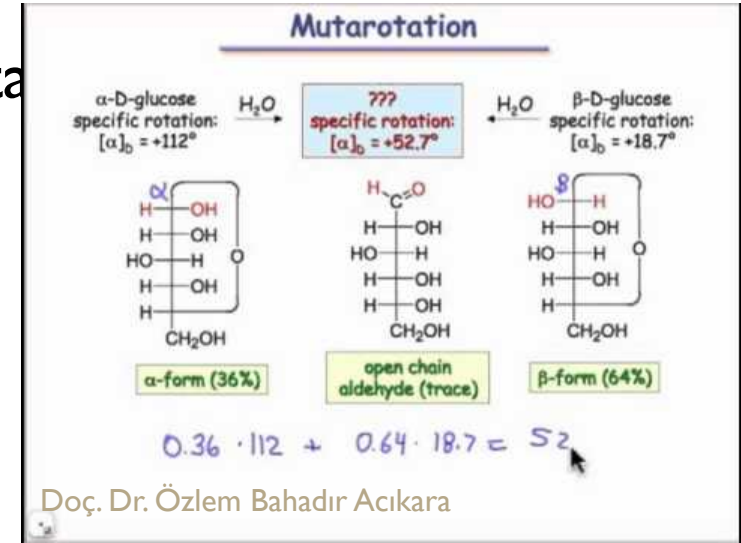
- The particular chemical behaviour of monosaccharides has led to the postulate that they exist in a cyclic form involving the carbonyl group and one hydroxyl group;
- Depending on the nature of the bridge (1-4 or 1-5) the cycle is either furan or pyran
- Generally aldohexoses form pyranose rings and ketohexoses form furanose rings



- Cyclization leads to two isomeric hemiacetals, α and β, called anomers. The configuration of the anomeric carbon is α when the hemiacetal hydroxyl group is in the same orientation as the secondary hydroxyl group. In the opposite case the configuration is β.

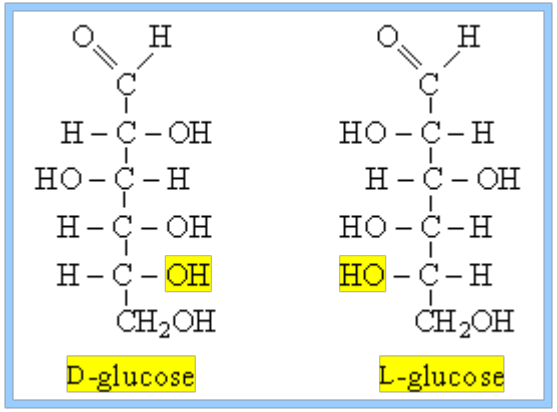
Mutarotation

- Both isomers(anomers) α and β are found in same solution; **the value of the specific rotation changes over time, eventually reaching the same value (for glucose +52.5°)**
- The alpha (α) anomer of D-glucose has a specific rotation of +112 degrees in water.
- The beta (β) anomer of D-glucose has a specific rotation of +19 degrees. (18.7 actually, but rounding up to 19).
- This behaviour is known as mutarota

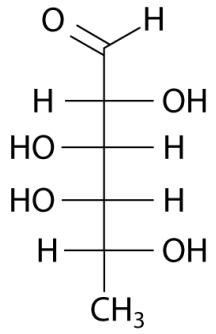


D and L isomerization

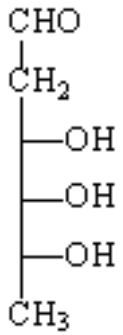
- Orientation of the hydroxyl group most distant from the carbonyl group determines if a monosaccharide belongs to the D or to the L series.



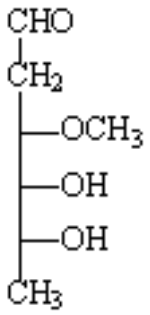
- Hexose and pentose are found widely in the nature.
- 6 deoxyhexoses, Methyl pentoses contains 6 carbon and 5 oxygen (L-rhamnose, D-fucose)



- 2,6 deoxyhexoses (D-digitoxose, D-cymarose)

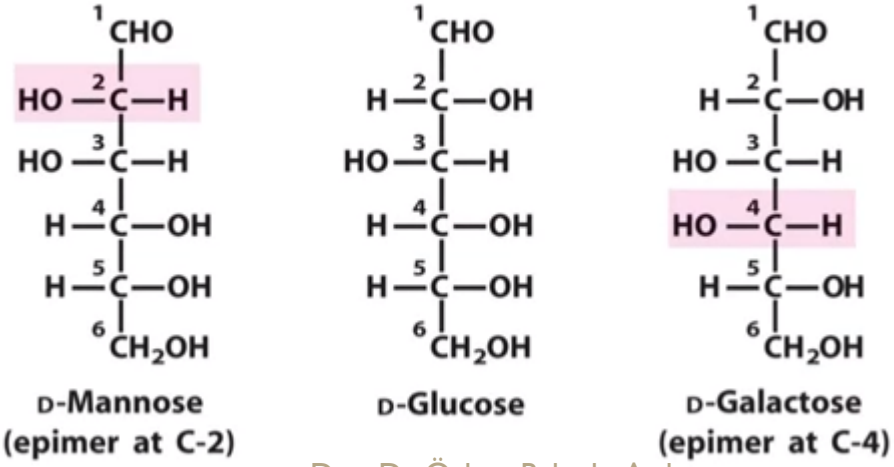


D-digitoxose

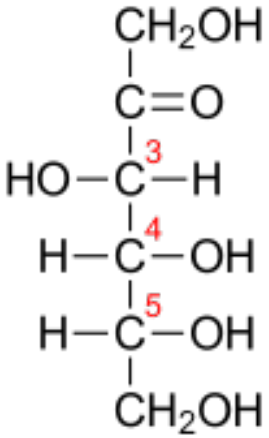


D-cymarose

- Aldohexoses: D-glucose, D-mannose, (2-epimer of D-glucose) D-galactose (4-epimer of D-glucose) are widely distributed in nature. Glucose is commonly free, as well as combined into polysaccharide structures (starch, cellulose and other glucans). 2- and 4-epimers are almost exclusively known as polymers (for example mannans, gluco and galactomannans

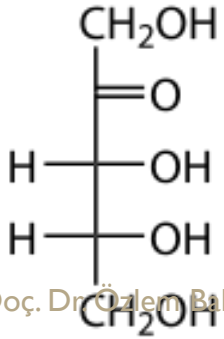


- Ketohexose; D-fructose commonly found in fruits in the free state, it is just as common as a dissaccharide (sucrose)
- It also occurs in oligosaccharides

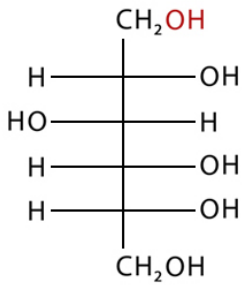


D-Fructose

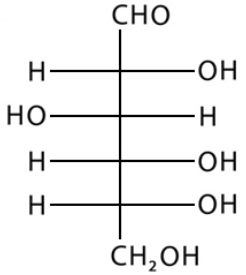
- D-ribulose, ketopentose



- Polyalcohols; polyalcohols result from the reduction of the carbonyl function of monosaccharides (glycerol, sorbitol, mannitol)

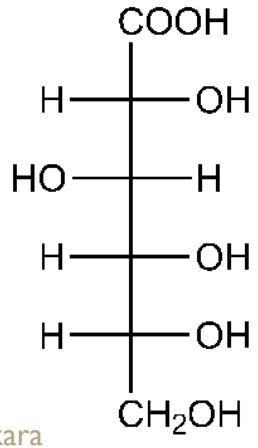


Sorbitol

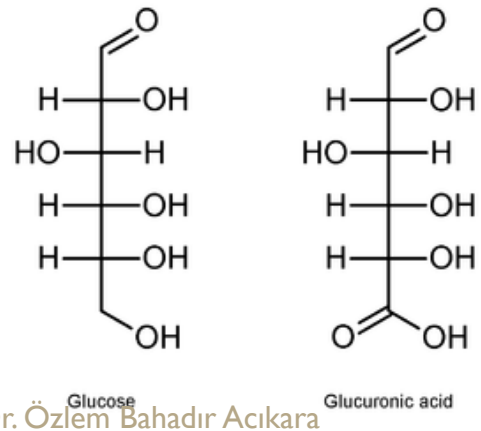


Glucose

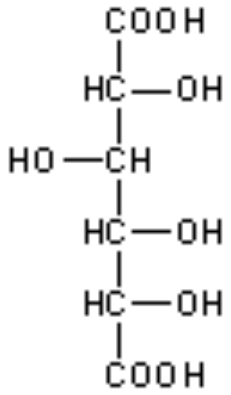
- Onic acids; result from the oxidation of the carbonyl function of the monosaccharides (D-gluconic acid)



- Uronic acids; uronic acids are the products of hexose oxidation by specific dehydrogenases in which the primary alcohol function is oxidized to a carboxylic acid
- D-glucuronic acid and galacturonic acid are normal consituents of parietal polysaccharides such as pectin and mucilages. Other acids are less frequent but are also constituents of polymers.

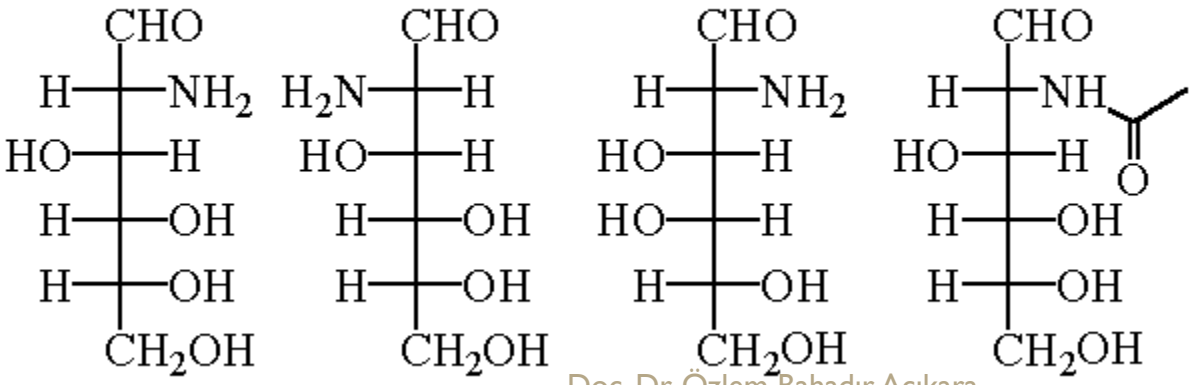


- Saccharic acid is derived from glucose in which both aldehyde and primary alcohol group are oxidized to carboxylic acid groups



- Aminosugars; aminosugars are fundamental constituents of bacterial polysaccharides.
- One or more hydroxyl groups of the monosaccharides are replaced by amino groups

Amino Sugars



- Ester of sugars; these are esters of sugars and acids such as phosphoric acid, sulphiric acid, acetic acid
- Acetyl digitoxose
- Fucoidin
- Ester of mesoinositol

- They have usually sweet taste
- They can soluble in aqueous solutions because of their hydroxyl groups
- Their solutions are optically active
- Crystallization of the sugars is hard
- Furfural formation occurs by heating acids which leds to the identification of the sugars

- Seliwanoff's test is given positive by ketohexoses so it is answered by fructose. This test distinguishes between glucose and fructose
- Fehling test is a chemical test to detect reducing sugars and uronic acids
- Osazone test is also used for the identification of sugars. It involves the reaction of monosaccharide with phenyl hydrazine, a crystalline compound. Each osazone crystal has a spesific shape, structure and crystallization time

- Identification of the pentose; sugar solution is heated by acid leads to furfural formation and adding phloroglucinol cyrstalin;
- Red colour shows pentose,
- Violet colour shows uronic acid

Quantitation of sugars

- Titrimetric method
- A. Fehling method: Suitable for monosaccharides in high amounts
- B. Bertrand method: Suitable for monosaccharides in low amount. This method is based on permanganometric titration.

- Sugar solution + $CuSO_4$..... Cu_2O
- Cu_2O + $Fe_2(SO4)_3$+ H_2SO_4 ..... $2FeSO_4$+ 2 $CuSO_4$ + H_2O
- (KMnO4 is used for $FeSO_4$ titration)
- 10 $FeSO_4$ + 8 H_2SO_4 + 2 $KMnO_4$..... 5 $Fe(SO_4)_3$ + K_2SO_4 + 2 MnSO4 + 8 H2O

- Iodometric titration

- **Sugar solution + $CuSO_4$ Cu_2O**
- **Cu_2O + 3 KI + KIO_3 + 4 H_2SO_4 $2I_2$+ 2$CuSO_4$+ 4 H_2O**
- **$Na_2S_2O_3$ is used for titration of I_2**

- Polarimetric method

If there are only one monosaccharide

$[\alpha]^{20}_{D=}$ 100. α/ l.d.C

- Colorimetric method

- **Reducing sugars are chromatographed by paper chromatograhy**
- **Alkaline triphenyltetrazolium reactive is used for determination of reducin sugars by red spots**
- **Red spots are eluted with HCl- pyridin (%10) solution.**
- **Pyridin solution was measured**

Quantition of sugar mixtures

- **Aldose (Gl.) + Ketose (Fr.) + Diholoside (Fr.+Gl.) + Triholoside (Gl. +Fr.+Gl.)**
- **Mineral acids and enzymes are used for hydrolysis of holosides which led to the formation of reducing sugars and they are used for quantition**
- **I) Aldose.....Iodometric method (G)**
- **2) Fehling method.....Reducing sugars Fr. + Gl. Mixture (R_I)**

  R_I – G= Fr. (F) (Ketose)

- Sugar mixture hydrolysis with invertase) .....Diholoside (Sucrose)… Gl.+Fr. Again reducing sugar quantition(R_2)
- **R_2 -R_1= Reducing sugar (Gl.+Fr.) (i)**
- i x 0.95= sucrose quantition
- 4) Hydrolysis with emulsin or HCl and reducing sugar quantition (R_3)

- **R_3 – R_2= M (triholoside) (melezitose)**
- **M x 0.93 = Melezitose quantition**

Usage of sugars and derivatives

- **Nutrient**
- **Fructose and sorbitol are used for diabetic patients**
- **Ca-gluconate, risckets**
- **Mannitole, laxative**
- **Sorbitol, colagog (cholecystokinetic properties)**
- **Inositol, growth factor**

- Xylose and mannitol and in microbiology
- Fermentation products of glucose are used in pharmaceutical industry
- Lactic acid
- Ethanol
- Sitric acid
- Vinum
- Tartaric acid

GLUCOSUM (TF) GLUKOZ, DEXTROSUM, $C_6H_{12}O_6.H_2O$

- *Vitis vinifera* and some other fruits contain naturally
- **"GLUCOSUM ANHYDRICUM"** is an official form of glucose
- The percentage of the glucose in *Vitis vinifera* fruits is % 20-30, however this is not used as a source for glucose
- Honey is also rich source for glucose as well as fructose
- Glucose naturally found in starch and cellulose .α and β pyranose forms (maltose and starch contain α –GL.; while cellulose β-GL.

- Glucose is prepared by enzymatic hydrolysis of starch
- Potato starch is used in America hydrolysis with %1 HCl or H_2SO_4 by heating 45^0C. Then under pressure they are leaving for one hour at 120^0C.
- %1 HCl or H_2SO_4 removed by evaporation and Na_2CO_3 is used for neutralization, activated carbon is used for decoloring and evaporation under vacuum to obtain glucose syrup

- This product is known as glucose syrup **% 30-40 GL.and holosides**

- **Crystallization is hard for this product and if the conditions are changed such as high temperature is used for hydrolysis in long time glucose can be obtained as a crystalline product**

- Glucose found in plant and animal tissue naturally
- In human blood approximately 100 mg
- In urine should be in little amount
- In diabetes mellitus concentration of the glucose in blood and in urine is high
- Sweet taste of glucose is lower than succrose, can be absorb easily from intestine and have more calories

Usage

- %5 solution of glucose is used for parenteral administration in coma and in cases where oral nutrition is not available

- 2) Treatment of dehydration %0.9 NaCl and %5 GL. solution

- 3) %5-20 solution in treatment of **ANGINA PECTORİS** or cardiac insufficiency

- %33-50 solution is anti-edema
- High concentration solutions in pomade are used as antiseptic
- FERMENTATION industry for obtaining ethanol
- In food industry for preventing crystallization
- "GLUCOSI INJECTIO" as nutrition and liquid supplementation which is recorded in Turkish Pharmacopoeia

DEXTROSE INJ.

ALCOHOL+ DEXTROSE INJ.

NaCl + DEXTROSE INJ.

NaCl + DEXTROSE TABLETLERİ

DOPAMIN. HCl + DEXTROSE INJ.

LİDOKAİN. HCl + DEXTROSE INJ.

KCl + DEXTROSE INJ.

- "GLUCOSUM PRO INFUSIONE" is recorded in some pharmacopoeia

In TP;

" Glucosum injectio" **as nutrition and liquid supplementation**

"Glucosum et Natrii Chloridi injectio" **as nutrition and electrolyte supplementation**

EUROPEAN PHARMACOPOEIA;

- "**Dextrosum Anhydricum ad usum Parenterale**".... D (+) glucopyranose, white, scentless, crystalline, sweet and solubile in water
- "**Dextrosum Monohydricum ad usum Parenterale**"

Honey

- **Prepared by *Apis mellifera* (Apidae)**
- Honey is a sweet product made from flower nectar, combined with an enzyme secreted by honey bees, then concentrated by reducing moisture in the honeycomb cells.
- **Honey obtained from honeycomb by pressing or heating or centifugation**
- **gl.+fr.+ carbohydrate+essential oil+ pigments+ polen is found in honey**
- **%62-83 reducing sugar**
- **%1-10 sucrose, dextrin, protein, aa, organic acids, asetyl cholin, mineral salts, antibacterial compounds, antioxidant compounds**

- The colour of the honey can be changed according to its origin from yellow to red, contents can be changed according to geographical origins
- Honey is clear when it is fresh then it becomes opaque
- Nutritious, energizing and demulsan
- Honey is used for its treatment effects from ancient times in folk medicine
- 50-100 g laxative
- Wound healing, treating effects in stomach diseases, preventing micoorganisms proliferation
- Borax+honey mixture is used in mouth wounds as well as aphtae
- Sweetener in infusions

- Anzer Honey is obtained from Rize-İkizdere, Anzer plateau
- Smell and other features differences originated from the plant ***Rhododendron caucasicum*** (Beyaz Komar) which is growing widely in this area.
- **This honey is used for wound healing externally**

- **Honey of the Turkey were investigated for thier antibacterial activities. The activities were determined that they have higher antibacterial activities than German Honey.**
- **Honey is laxative in children and because of its sugar and vitamin contents has nutritional value**
- **Its reducing property ıron salts can be prepared**
- Its useful in cardiovascular diseases and cold

- **MEL DEPURATUM (TK)**
- **Cleared honey**
- **40 part honey+ 60 part water + HCl. Then mixed with 3 part white clay and heated. Filtered when its hot and concentrated to fix its density as1.34**

Toxic Honey

- **ZEHİRLİ BAL, DELİ BAL**
- **North East of the Anatolia (Doğu Karadeniz)**
- **B.C. 400 Greek Army and 1461 Fatih Sultan Mehmet soldiers were poisoned from this honey**
- **Nausea, lack of appetite, weakness and diarrhea were observed as symptoms**
- **Poisoning affects are observed at 50-100 g dosage and disappear easily however in higher dosage reslted in death**

- Toxicity of the honey is resulted from **ANDROMEDOTOXIN**
- Andromedotoxin is found in *Rhododendron* species from Ericaceae family
  - *Rhododendron* (orman gülü)
  - *R. ponticum* (Komar) (with red flower)
  - *R. luteum* (zifin, sarı ağu) (yellow flower)
  - *R. caucasicum* (white flower)

- ***Andromedo*** **and** ***Kalmia*** **species**
- ***Aesculus hippocastanum*** **and** ***Sambucus nigra*** **plants are also suggested to poisoning**
- **Especially fresh honey is poisoning, old or boiled honey is not poisoning**
- **Toxic honey can be detected easily by pollen of *Rhododendron***
- **Andromedotoxin can be also identified chemically.**

Royal jelly (La Gelée Royale)

- Royal jelly is a sticky substance produced by worker bees for queen bees and their larvae. Worker bees produced from 6th to 10-12th days of their active lifes.
- **Equipment to collect of royal jelly should be sterile in other case microorganisms can be proliferated easily.**
- **100-250 mg royal jelly can be obtained from one cell**

- 170-200 g royal jelly is produced by one beehive.
- Like a concentrated milk, asidic, characteristic smell, easily darken in open air
- %12 sugar, protein, lipid, minerals (Ca,S,P,Mg,Zn,Cu,F), vitamins (especially B complex)

- **Enhancing anabolism and lipotropic**
- **Mixed with honey at %1 percentage and is used for increase growth and rejuvenation**
- **Used in cosmetic industry for cream and pomade**
- **Lyophilize preparations can be used as I.V.**

Pulpa Tamarindorum (Tamarind)

- ***Tamarindus indica*** **L. (Leguminosae) furits pulp.**
- **Pulp is reddish-brown, has a mild sweet taste**
- **Contents; %10-20 organic acids (tartaric, citric, malic acid)**
- **%30-40 monosaccharides**
- **Pectin**

- Laxative in children
- It can be used together with other laxatives
- 20-60 g laxative, used for symptomatic treatment of constipation.
- Paste can be prepared by mixing chamomile, senna and sugar

- "**Pulpa Tamarindorum cruda**" and "**Pulpa Tamarindurum depurata**" is recorded in Turkish Codex
- "**Pulpa Tamarindurum depurata**" is prepared by soften pulps with hot water and filtered to remove solid parts and then concentrated to obtain this product
- Sugar is added to this product in 1/5 ratio