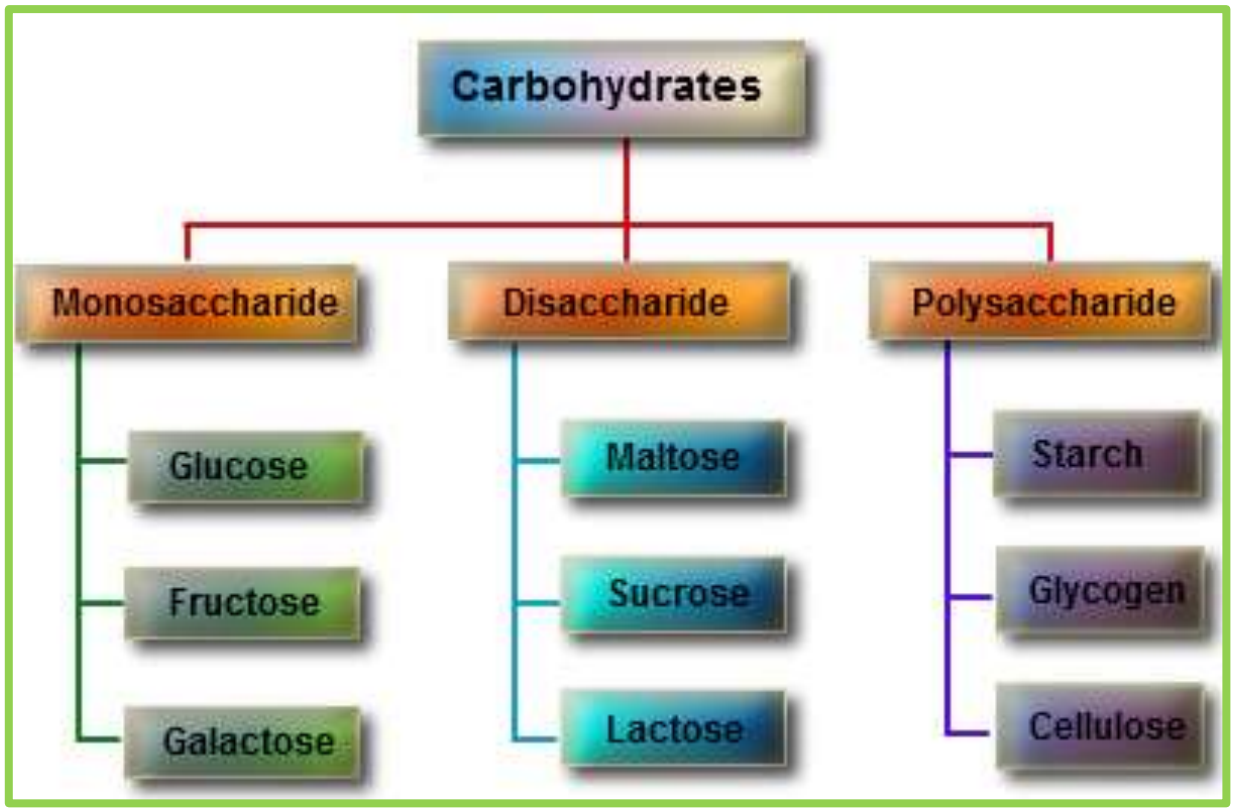
Carbohydrates-2nd part



Heteropolysaccharides !!!

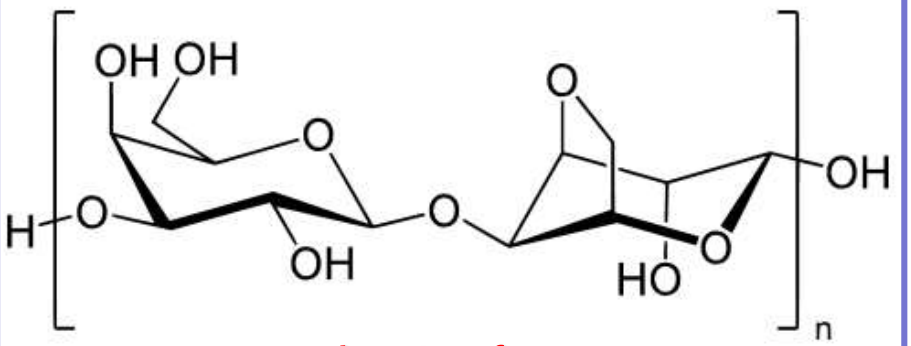
Hydrocolloids

- Substances having the property to swell and form gels
- They have application in microbiology, food and materials production, packaging materials (edible films) for protection against oxidation or microbial spoilage in meat, etc.]
  - ✓ Agar
  - ✓ Carrageenans
  - ✓ Alginic acid

Heteropolysaccharides

Hydrocolloids

Agar



Structural unit of agarose:
Agarobiose

- ✓ It is found in the cell walls of certain red algae of the genus *Gelidium*, *Gracilaria*, etc. (for commercial use it is isolated from the *Gelidium amansii*)
- ✓ Forms stable, transparent & elastic gels
- ✓ It is a complex mixture of polysaccharides, with two main polymers:
  - **Agarose** (2/3 of agar): β-D-1→3-galactan & α-L-1→4-(3,6)-anhydro-galactan
  - **Agaropectin**: β-D-1→3 & α-L-1→4-galactan partially esterified with sulphuric acid

Heteropolysaccharides !!

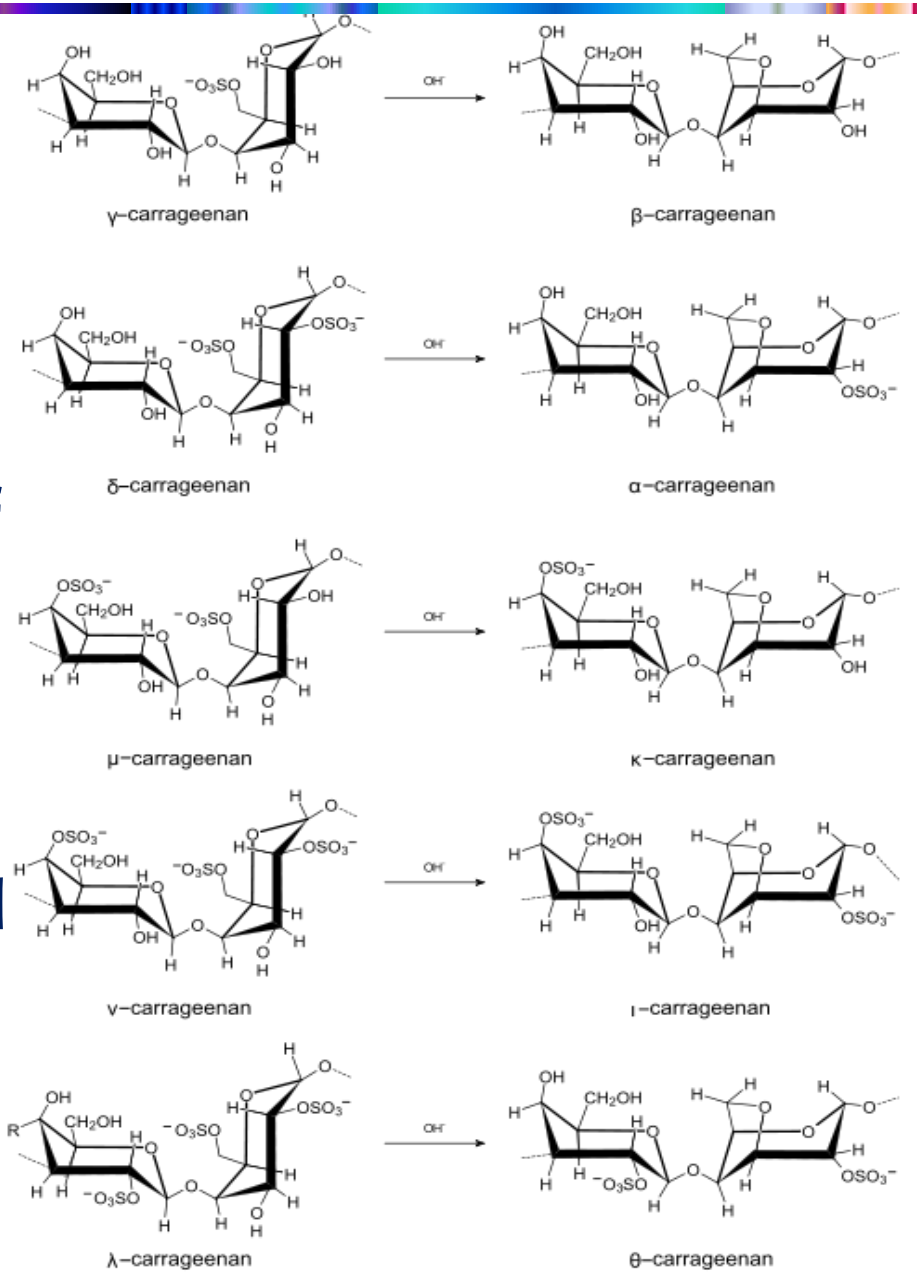
Hydrocolloids

- **Carrageenans**

✓ **Sulphated galactans like agar**

✓ **Used in in the preparation of chocolate milk (stabilisers), to improve the texture of cheese, in ice cream, etc.**

✓ **There are 3 main commercial types types, depending on the number and location of the sulphite ester groups:**



Heteropolysaccharides

Hydrocolloids

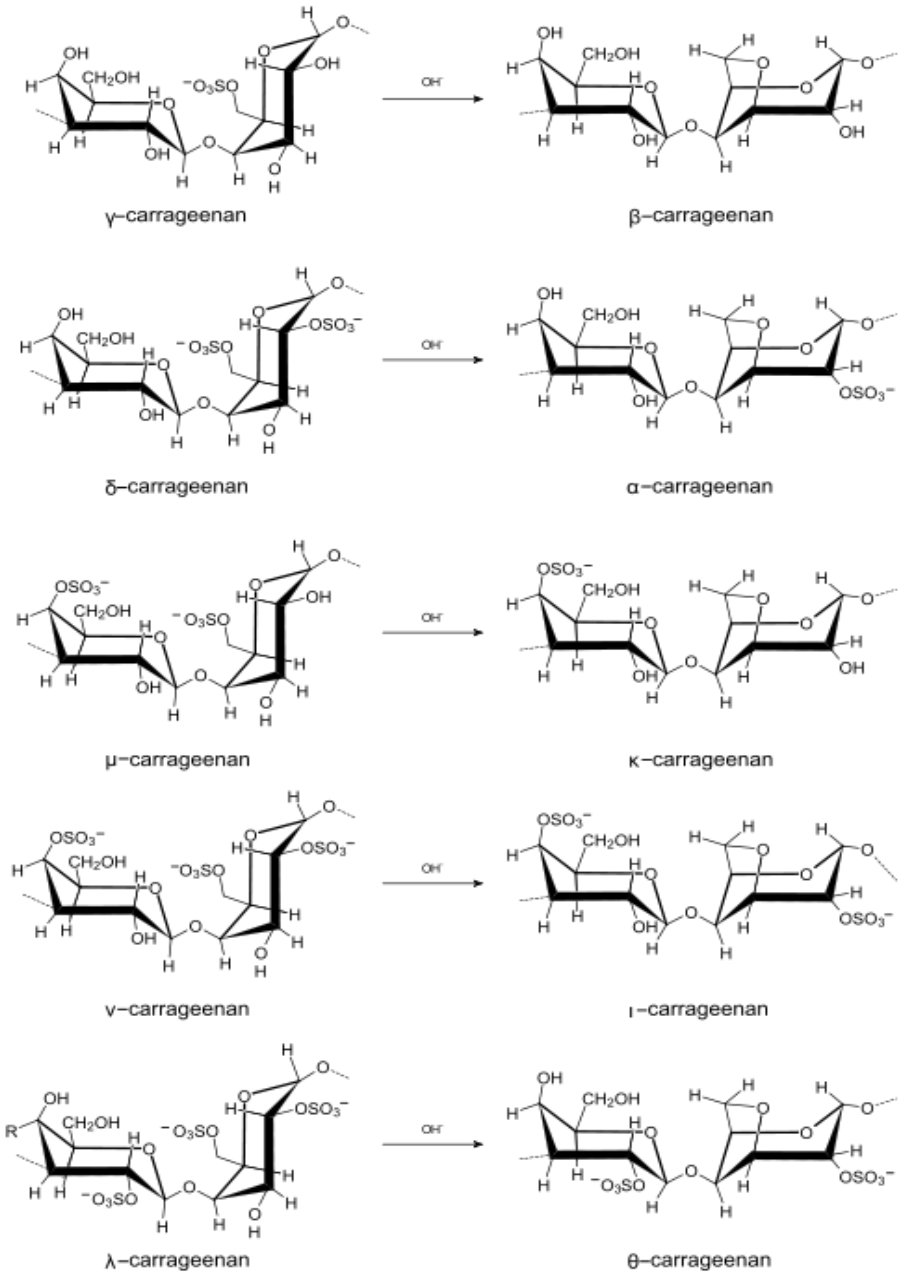
!!

- **Carrageenans**

✓ ***κ- Carrageenans***
form hard gels (gels) in the presence of K^+

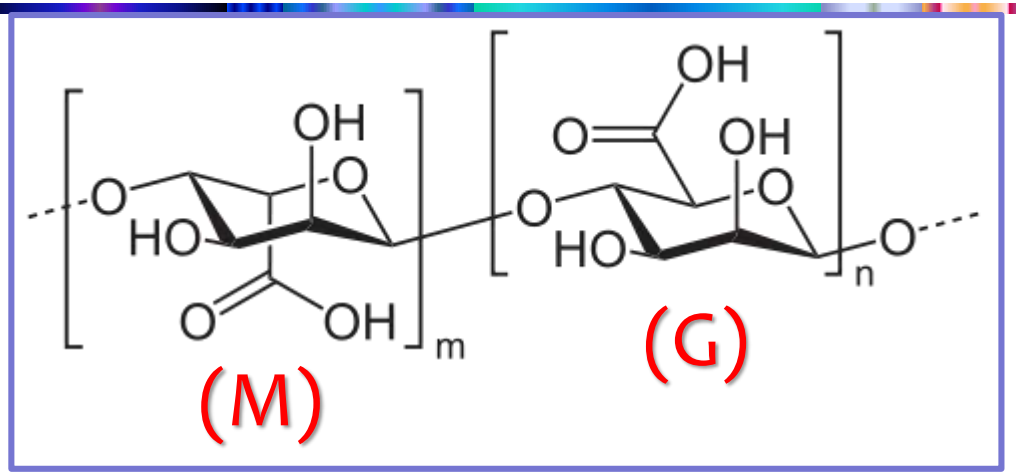
✓ ***ι-Carrageenans***
form soft gels gels in the presence of Ca^{+2}

✓ ***λ-Carrageenans***
do not form gels



Heteropolysaccharides

Hydrocolloids



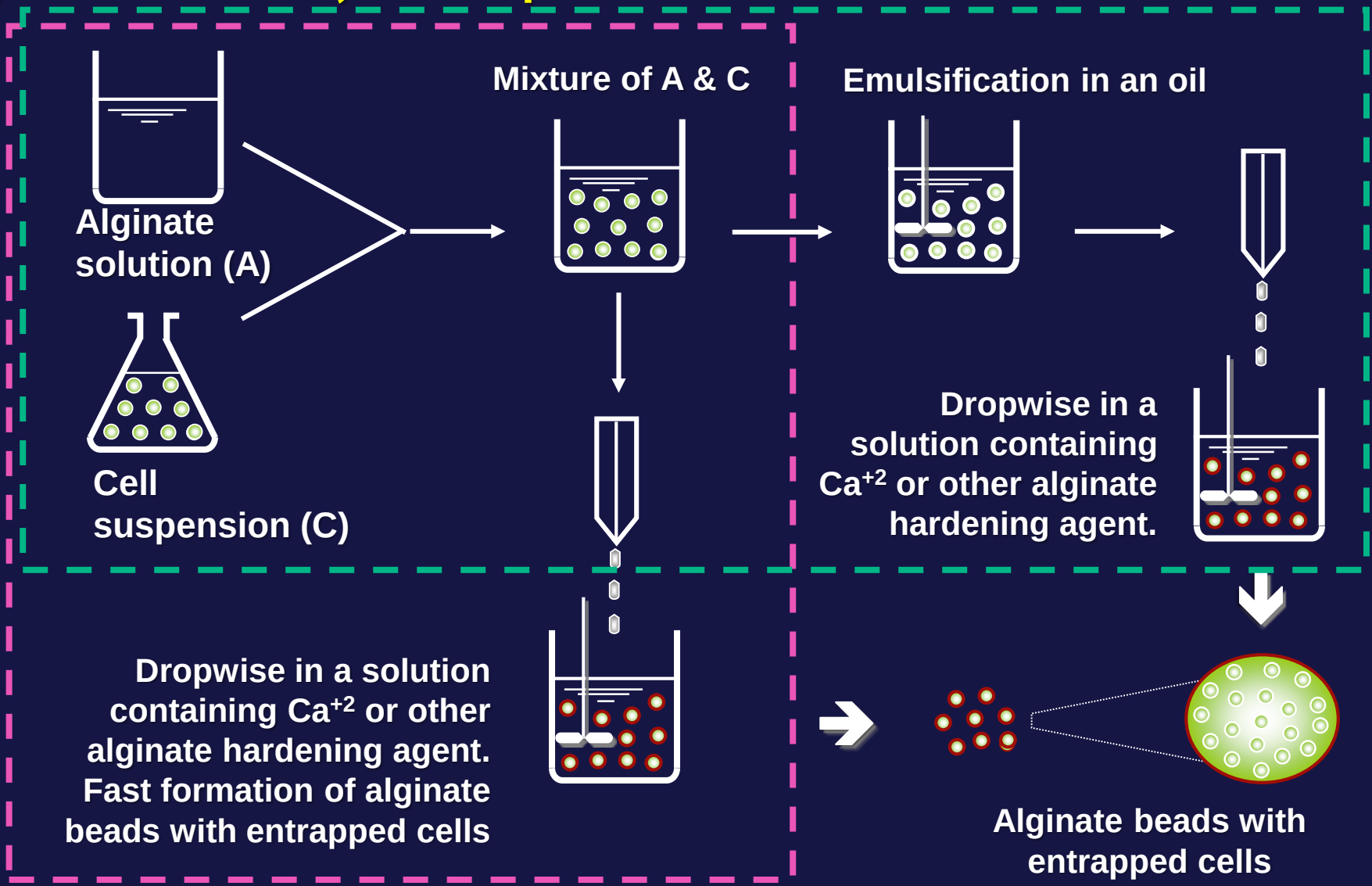
- **Alginate (alginic acid)**
- It is an anionic polysaccharide of algae such as: *Macrocystis pyrifera*, *Ascophyllum nodosum*, *Laminaria* sp., and some species *Pseudomonas* & *Azotobacter* bacteria
- It is a linear polymer consisting of 1->4 bound β-D-mannuronic acid (M) units, with alternating oligomeric or monomeric α-L-guluronic acid (G) in various proportions
- Rapidly absorbs water 200 - 300 times its weight
- Used (as salts with Fe^{+3}, Mg^{+2}, NH^{4+}, etc.) as thickener, gelling agent, stabilizer, and emulsifier, especially in ice cream.

Heteropolysaccharides

Hydrocolloids: Application as matrices in cell entrapment (immobilization) techniques

Extrusion

Emulsion



Heteropolysaccharides

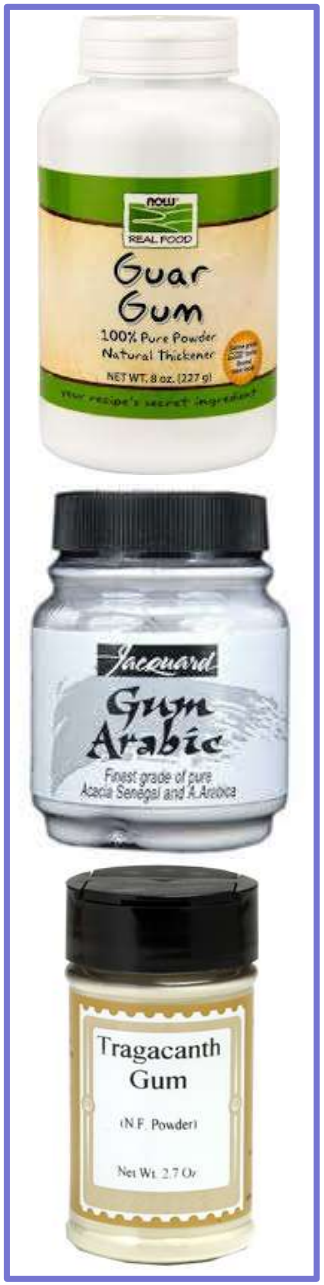
Hydrocolloids: Application for solidifying liquids in Molecular gastronomy techniques!

https://www.facebook.com/MoMixBarKerameikos/

Heteropolysaccharides !!

Natural gums

- Large class of hydrophilic substances with gummy texture
- Functional properties in food: Gelling agents, moisture retainers, emulsion stabilizers, foam stabilisers, clarifiers (e.g., in wines)
- The exact composition of many gums is not known
- Either they flow from tree trunks (e.g. Arabic gum, or Tragacanth gum) or are extracted from seeds (e.g. Guar gum, Carob gum, etc.)

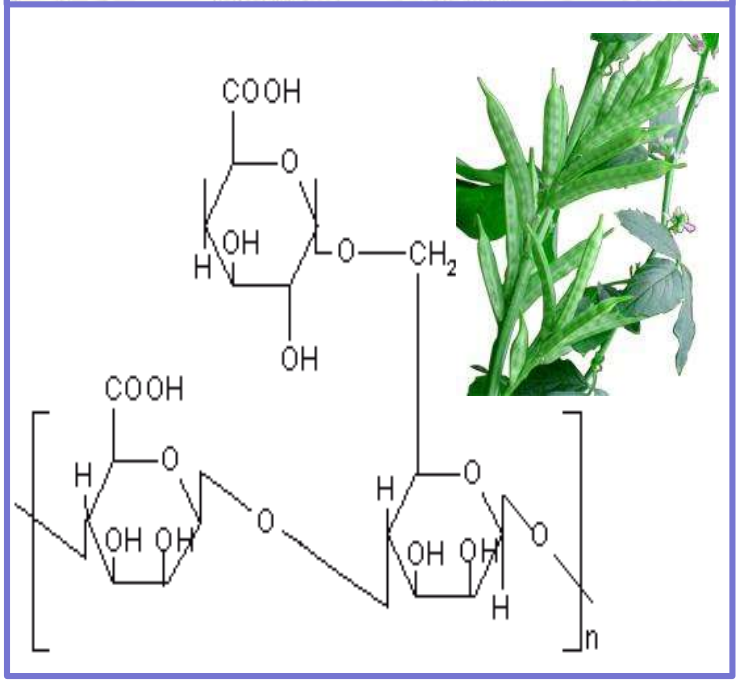


Heteropolysaccharides

Natural gums

!

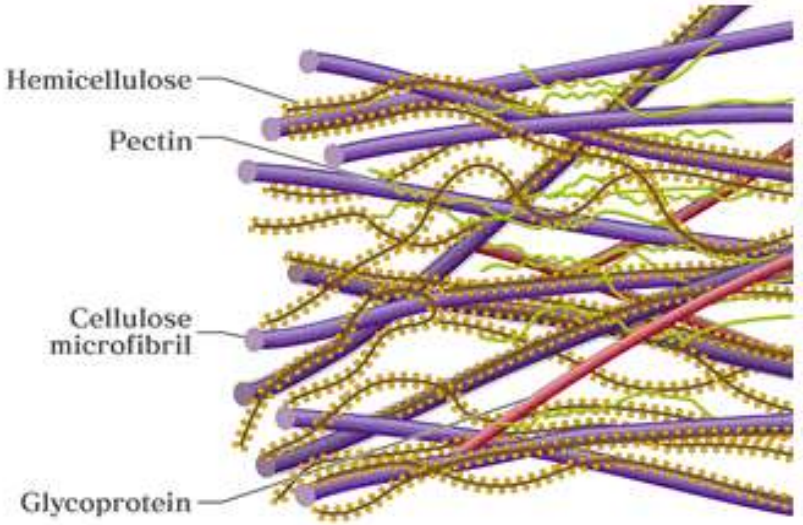
- **Gum Arabic**
- A complex mixture of glycoproteins and polysaccharides with a high percentage of glucuronic acid
- On hydrolysis it yields, in addition to the acid, D-galactose, L-arabinose, L-rhamnose



- **Guar gum**
- Polysaccharide of galactose and mannose (linear chain β-1→4- bound mannose units with side chains of galactose linked by 1→6 bonds

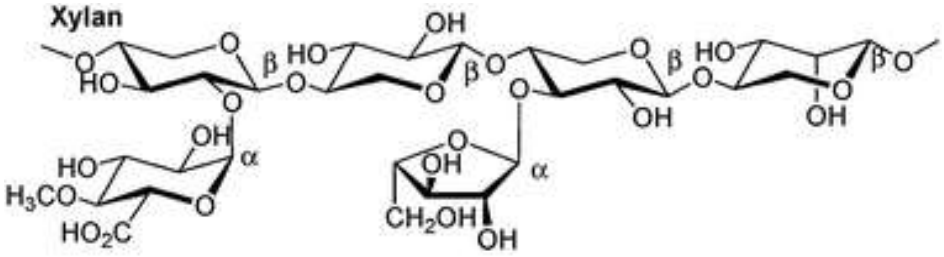
Heteropolysaccharides

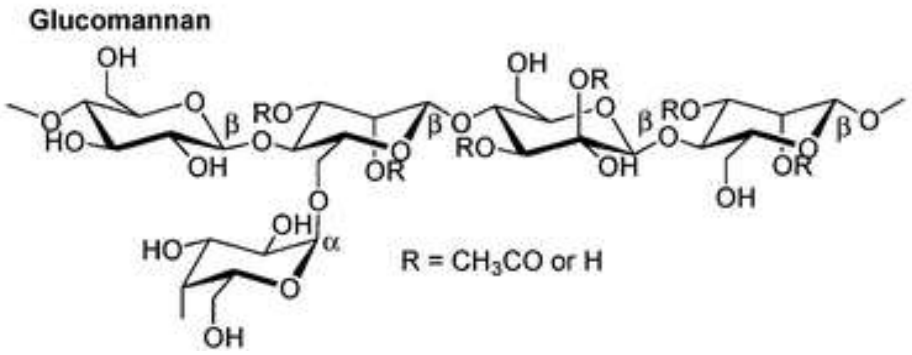
Hemicelluloses & pentosans !!



- They are compounds found in plant cell walls bound to other polymers such as lignin and cellulose

- They consist of units hexuronic acids (mainly D-glucuronate) and pentose or hexose units (xylose, glucose, mannose, galactose, rhamnose)



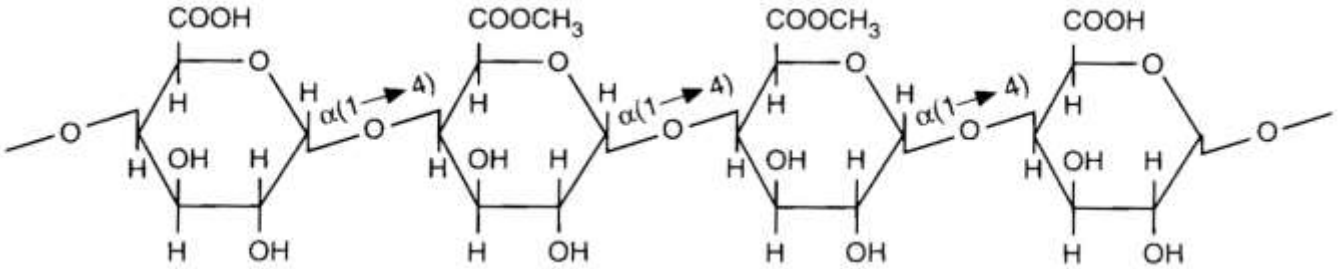


Heteropolysaccharides

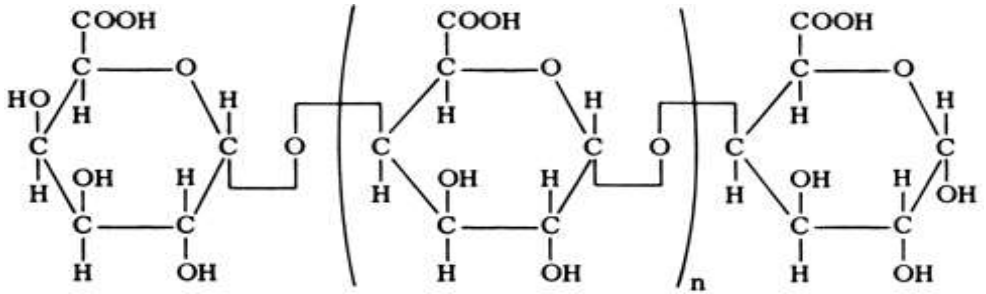
Pectins

!!!!

- ✓ Complex colloidal derivatives of carbohydrates, components of plant cell walls
- ✓ They contain in high proportion: Galacturonic acid units (a-1→4 bound), with their carboxyl groups partially esterified as methyl esters



Pectin



Pectic acid

Heteropolysaccharides

Pectins

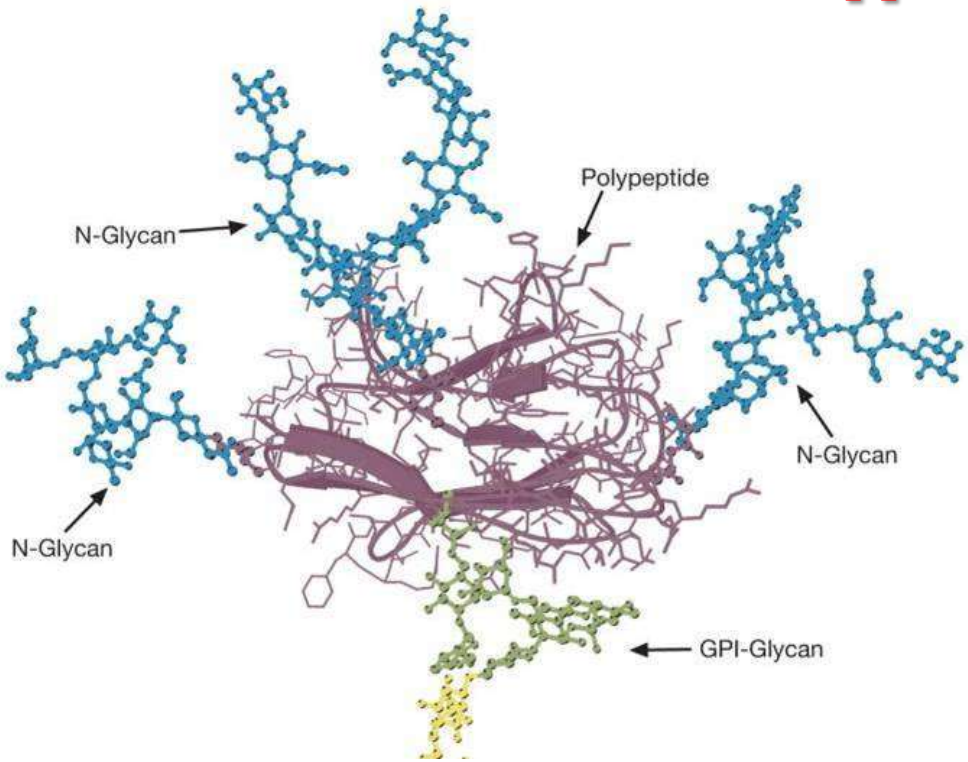
!!!!

Types of pectins

- ✓ **Pectins:** Polygalacturonic acids with a varying ratio of methyl ester groups, but capable of forming gels
- ✓ **Pectinic acids:** Polygalacturonic acids with almost negligible proportion of methyl ester groups
- ✓ **Pectic acids:** Polygalacturonic acids free of methyl ester groups

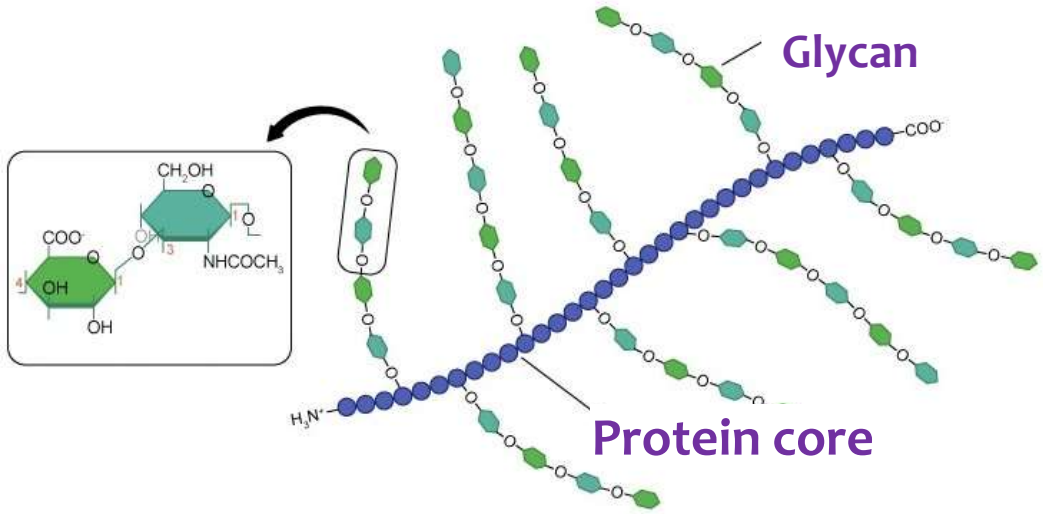
Heteropolysaccharides !!

Glycoproteins & proteoglycans



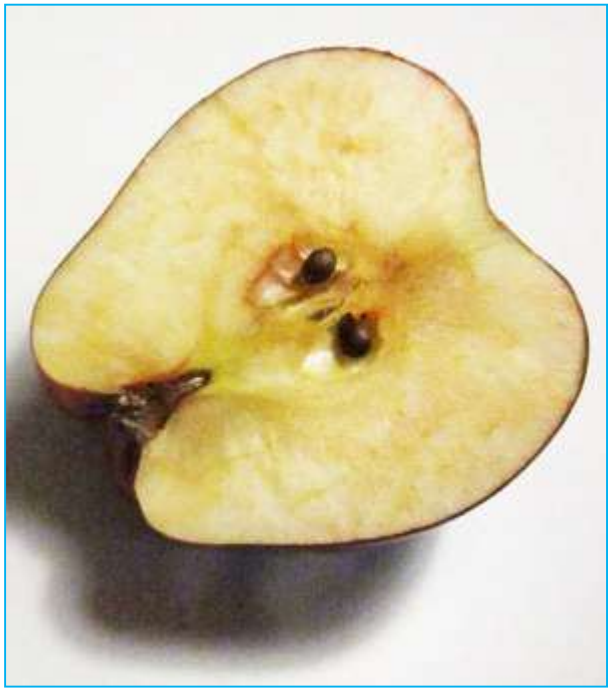
✓ **Glycoproteins:**
proteins of large biological importance covalently linked to oligosaccharides (globulins, hormones, transferins, etc.)

✓ **Proteoglycans:**
polysaccharides chemically bound to proteins (mainly components of the connective tissue, etc.)



!!! Browning reactions of carbohydrates

Oxidative or non-oxidative browning



Browning of fruit or vegetables after slicing and contact with air and enzymes

- The browning reactions of food are divided into oxidative, non-oxidative and enzymatic or non-enzymatic, depending on their initial stages
- **Oxidative browning**

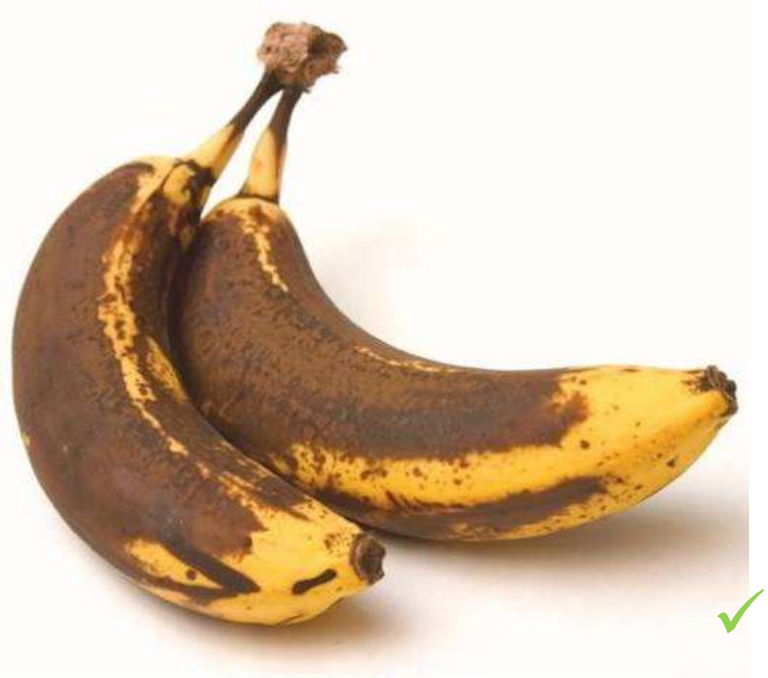
✓ Can be initiated **enzymatically or not** (e.g. by radiation)

✓ It includes transformations such as:

- Aldoses → aldonic acids → 2-ketoaldonic acids → smaller products
- Ascorbic acid → dehydroascorbic acid
- Formation of red/chestnut pigments by reaction with amino acids

!!! Browning reactions of carbohydrates

Oxidative or non-oxidative browning



Browning of fruit or vegetables due to natural decay

- **Non-Oxidative browning**

✓ Can be initiated **enzymatically or not**, e.g. enzymes (**hydrolases**) release reducing monosaccharides that through enol formation, cleavage, dehydration, etc., may give compounds which react with other components (e.g. **amines** & **amino acids**) to form brown-coloured compounds (e.g. polymeric **melanoidins**)

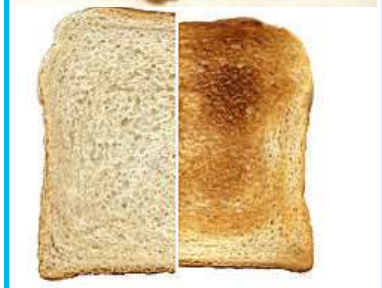
✓ It contributes to colour development and taste in foods such as honey, syrups, dates, etc.

✓ It is part of the natural decay of plants

!!! Browning reactions of carbohydrates

Caramelization






- Complex transformation of sugars caused by heating and leading to the formation of hundreds of products with dark colours and bitter flavours
- It includes:
  - ✓ Balance between anomeric-cyclic structures
  - ✓ Inverting sucrose into fructose & glucose
  - ✓ Condensations
  - ✓ Incompletions
  - ✓ Intermolecular bond formation
  - ✓ Isomerisation of aldoses into ketoses
  - ✓ Dehydrations
  - ✓ Protein oxidation
  - ✓ cis-trans isomerizations
  - ✓ etc.

!!! Browning reactions of carbohydrates

Reactions with amino-compounds:

Maillard reaction

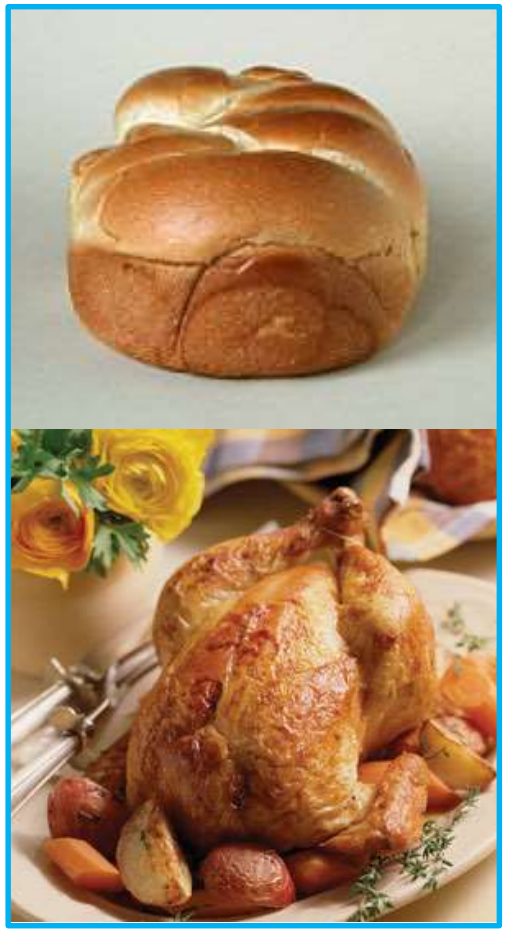
Reaction of the active carbonyl group of a reducing sugar with the amino group of an amino acid to produce interesting but poorly studied products with characteristic aroma & taste

- It requires heating like caramelization
- It is a kind of "non-enzymatic browning" of food
- It accelerates in alkaline environment where the amino acids are undissociated

!!! Browning reactions of carbohydrates

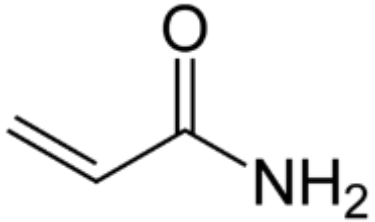
Reactions with amino-compounds:

Maillard reaction



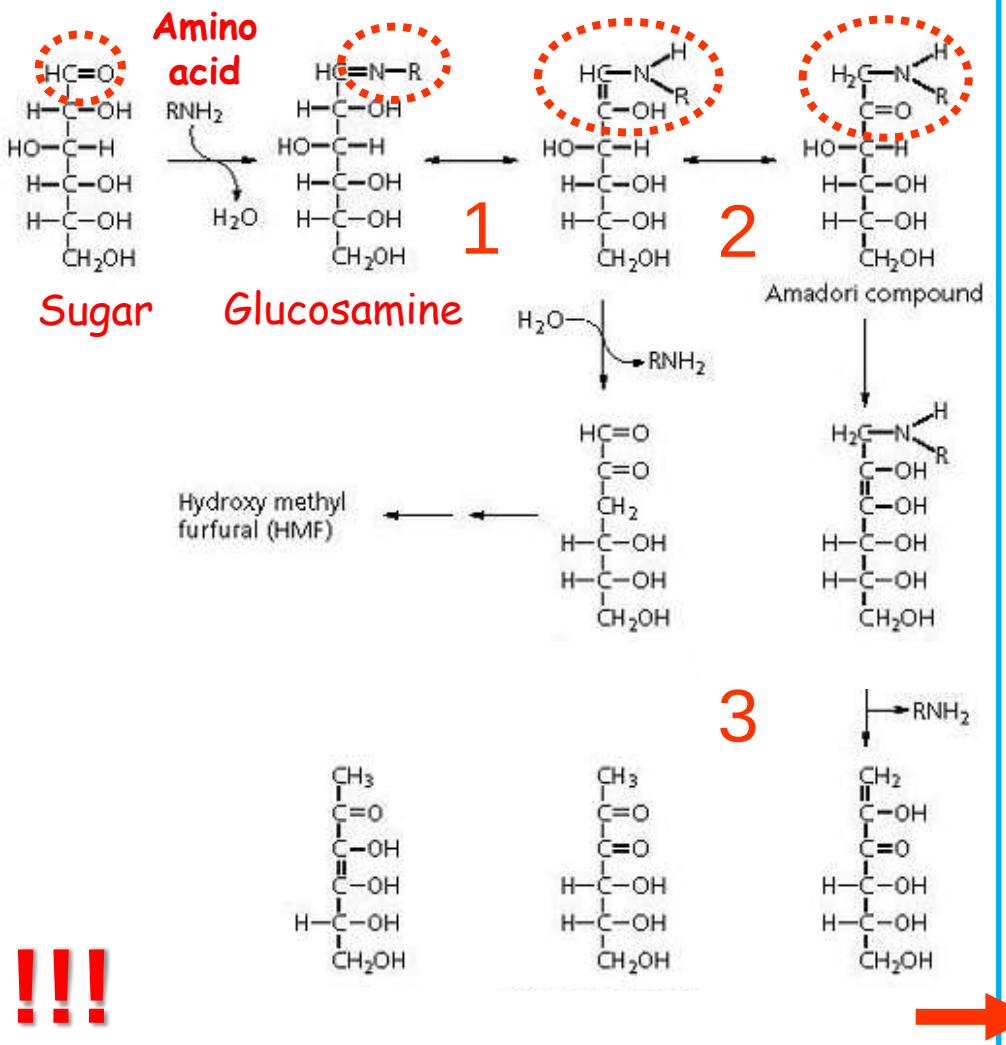
Effect in food:

- Colour production
- Production of aroma
- Production of antioxidants
- Nutrients destruction (e.g. lysine & vit. C are destroyed)
- Production of toxic ingredients such as Acrylamide ($CH_2=CHCNH_2$):



Browning reactions of carbohydrates

Maillard reaction



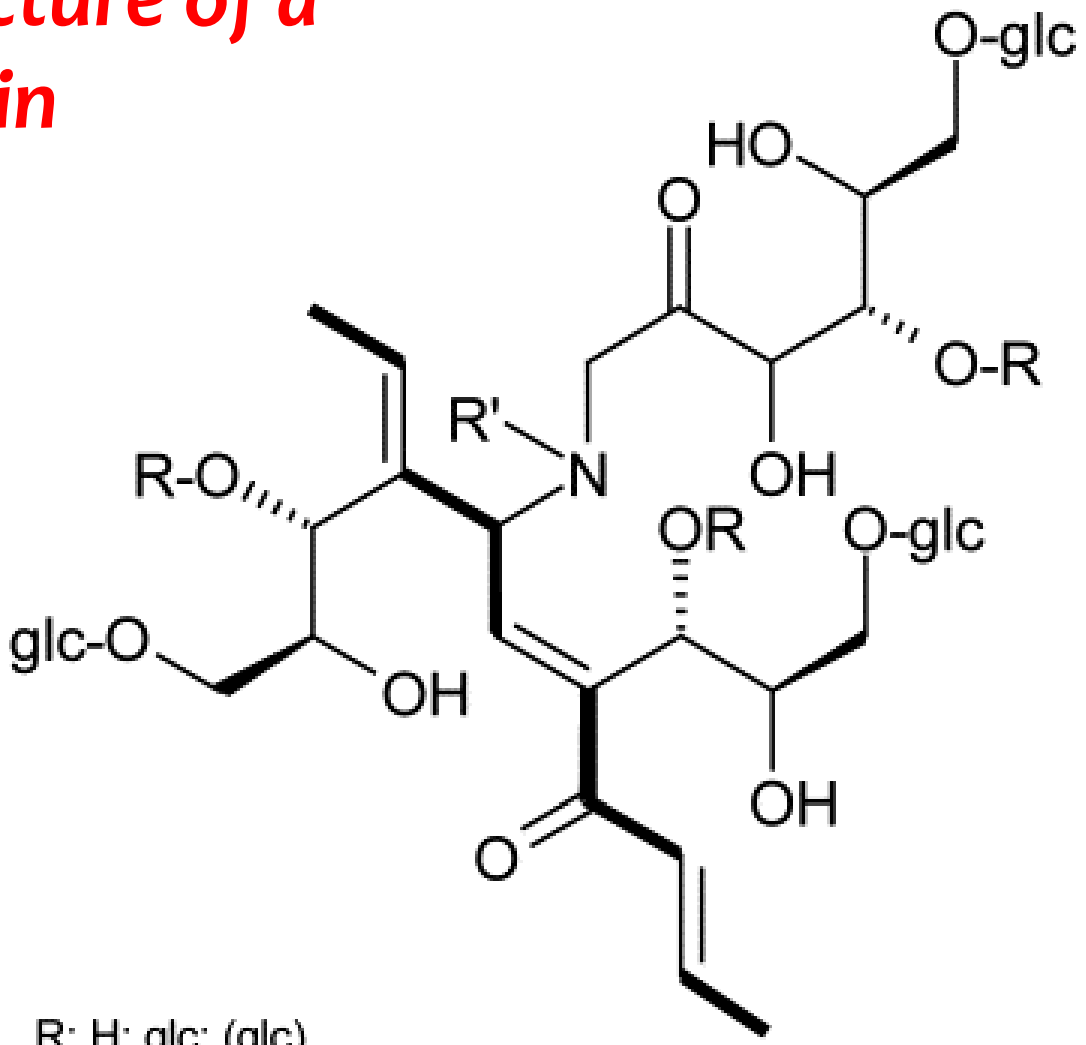
1. The carbonyl group of a sugar reacts with the amino group of the amino acid to a N-substituted glucosamine & water

2. The unstable glucosamine undergoes Amadori rearrangement to form ketosamines (Amadori compounds)

3. Ketozamines react further with various ways producing various products and eventually producing various brown colour nitrogenous polymers, the **melanoidins**

Browning reactions of carbohydrates

Basic structure of a melanoidin



R: H; glc; $(glc)_n$

Browning reactions of carbohydrates

Reactions with amino-compounds: Strecker reaction

!!! Intermediate stage of the Maillard reaction: Reactions between alpha-dicarbonyl compounds (Maillard intermediates) and amines

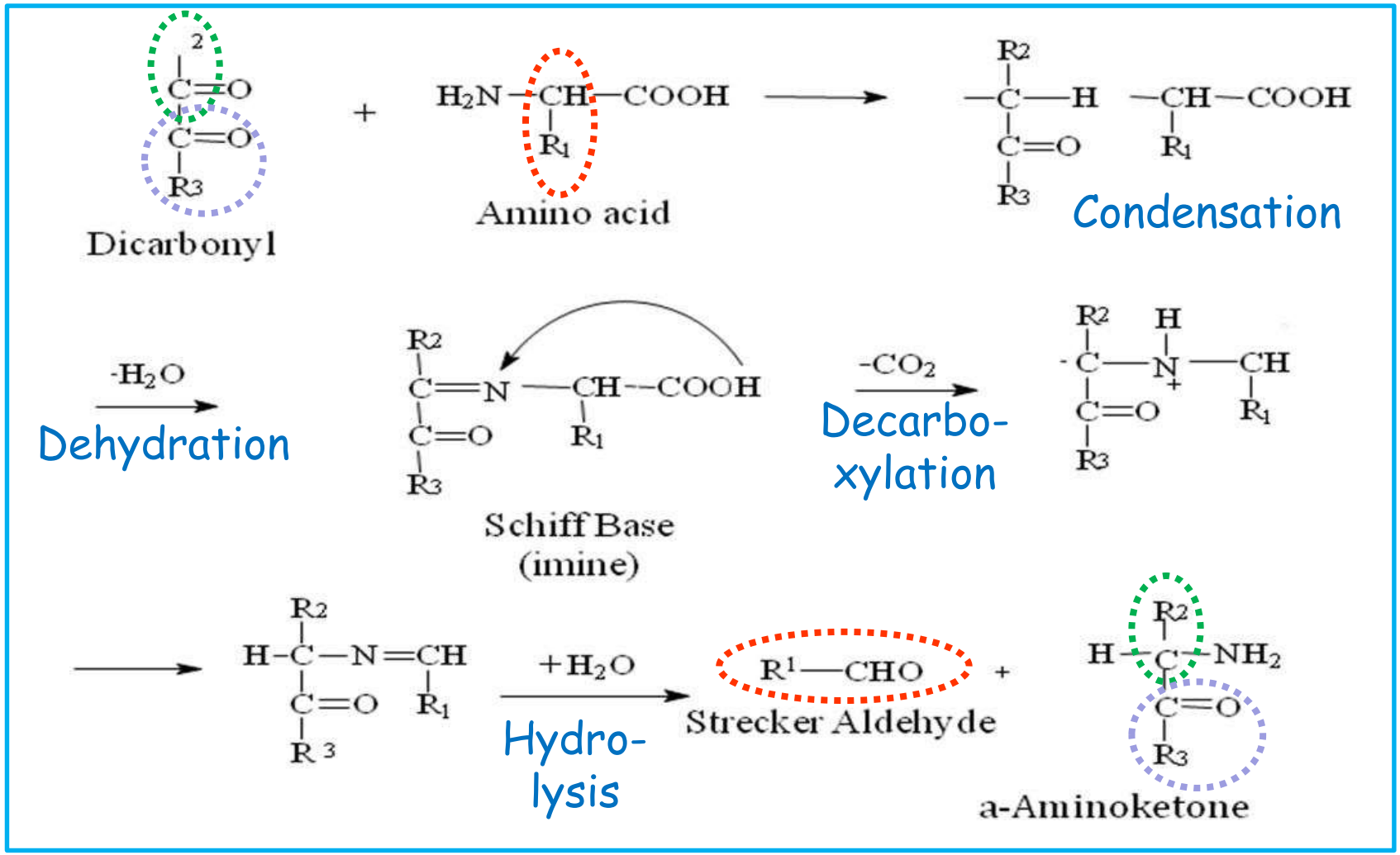
- Amino ketones & aldehydes (Strecker aldehydes) that provide strong odors to food
- Common Strecker aldehydes: acetaldehyde (fruity flavour), methylpropanal (malt flavour), 2-phenyl acetaldehyde (flower/honey flavour)
- Condensation of two amino ketones can give pyrazine derivatives which also have strong odours

Browning reactions of carbohydrates

Reactions with amino-compounds:

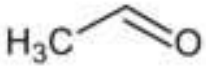
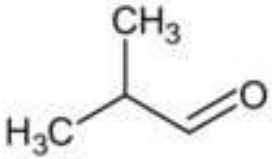
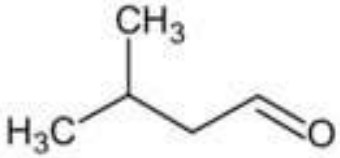
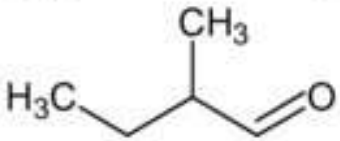
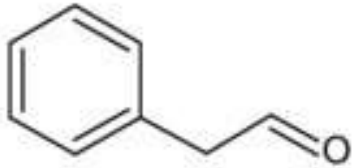
Strecker reaction

!!!!



Browning reactions of carbohydrates

Reactions with amino-compounds: Strecker reaction !!

Strecker aldehyde	Structure	Amino acid precursor	Odour threshold
ethanal = acetaldehyde		α-alanine/cysteine	25
propanal		α-aminobutyric	-
2-methylpropanal		valine	2
3-methylbutanal		leucine	3
2-methylbutanal		isoleucine	4
methional		methionine	0.2
2-phenyletanal = phenylacetaldehyde		phenylalanine	4

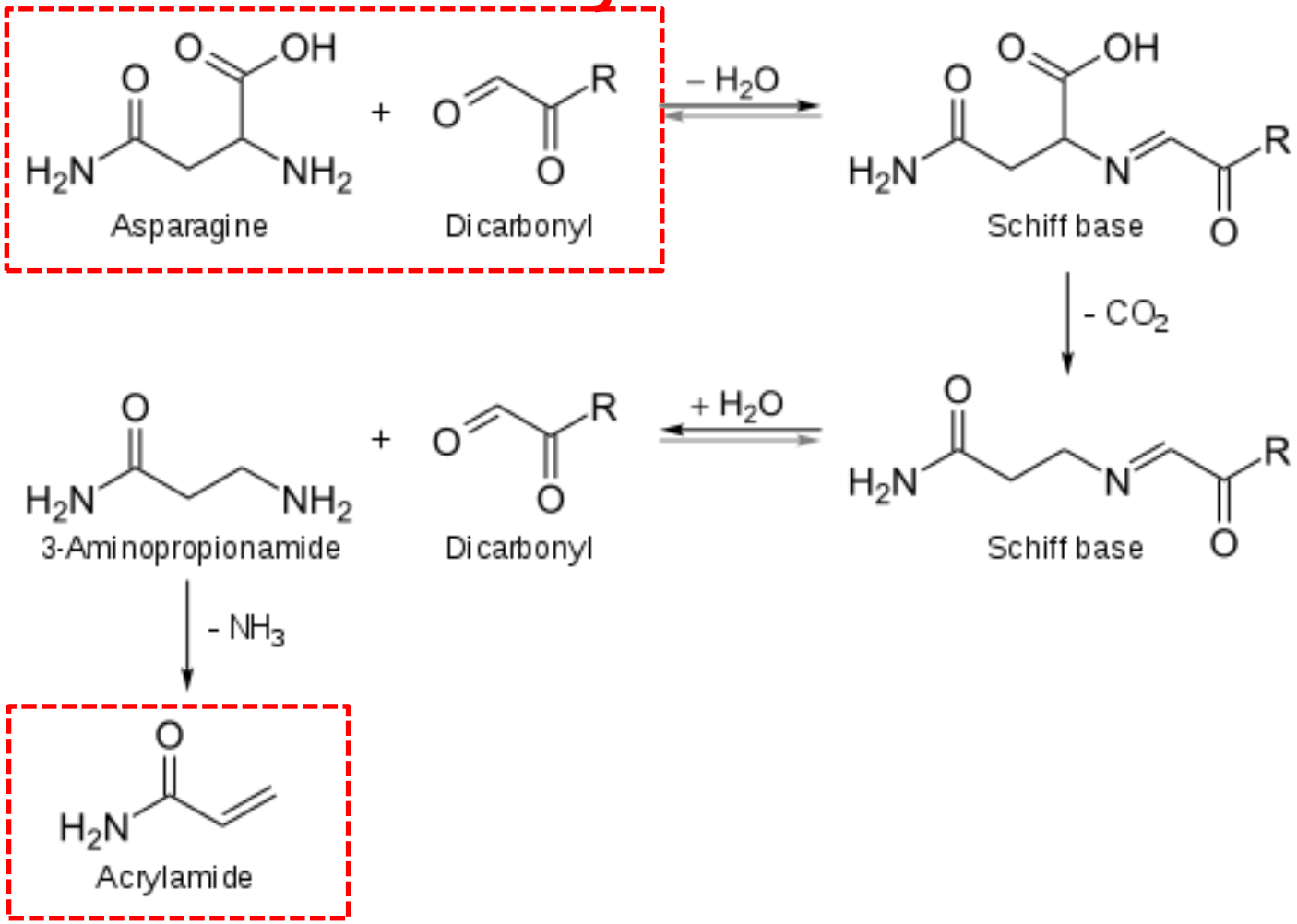
[a] [31,59,61,62]; [b] In µg/L, determined in water [15].

https://www.researchgate.net/publication/237095101_The_Development_of_Aromas_in_Ruminant_Meat/figures?lo=1

Browning reactions of carbohydrates

Reactions with amino-compounds: Strecker & Maillard reactions – toxic products

- Production of **acrylamide**



Possible exam questions on carbohydrates

1. **alpha & beta structures in sugars. Fisher and Haworth projection of α-D-glucose.**
2. **Layne-Eynon reaction and Fiehe test of sugars. Applications;**
3. **What is starch and what is its importance for food technology (both as an ingredient and as an additive).**
4. **Define from a chemical point of view the compounds: pectins / lactose / starch / anthocyanins / hydrocolloids / proteoglycans / glycoproteins / inulin / homopolysaccharides / heteropolysaccharides / melanoidins / gums / agar / carrageenans / alginic acid / cellulose / hemicelluloses / etc.**
5. **Briefly describe what the following terms mean in food: Caramelization / Browning / Gelatinization**
6. **What carbohydrate browning reactions occur in food?**

Possible exam questions on carbohydrates

7. What is the Maillard reaction and/or Strecker reaction and what is their importance for technology food?

8. What can happen during food heating containing carbohydrates with or without the presence of amino acids?

9. What are the main sugars present in the sugar fruits / milk / flour / flour / yeast flour / molasses and so on.

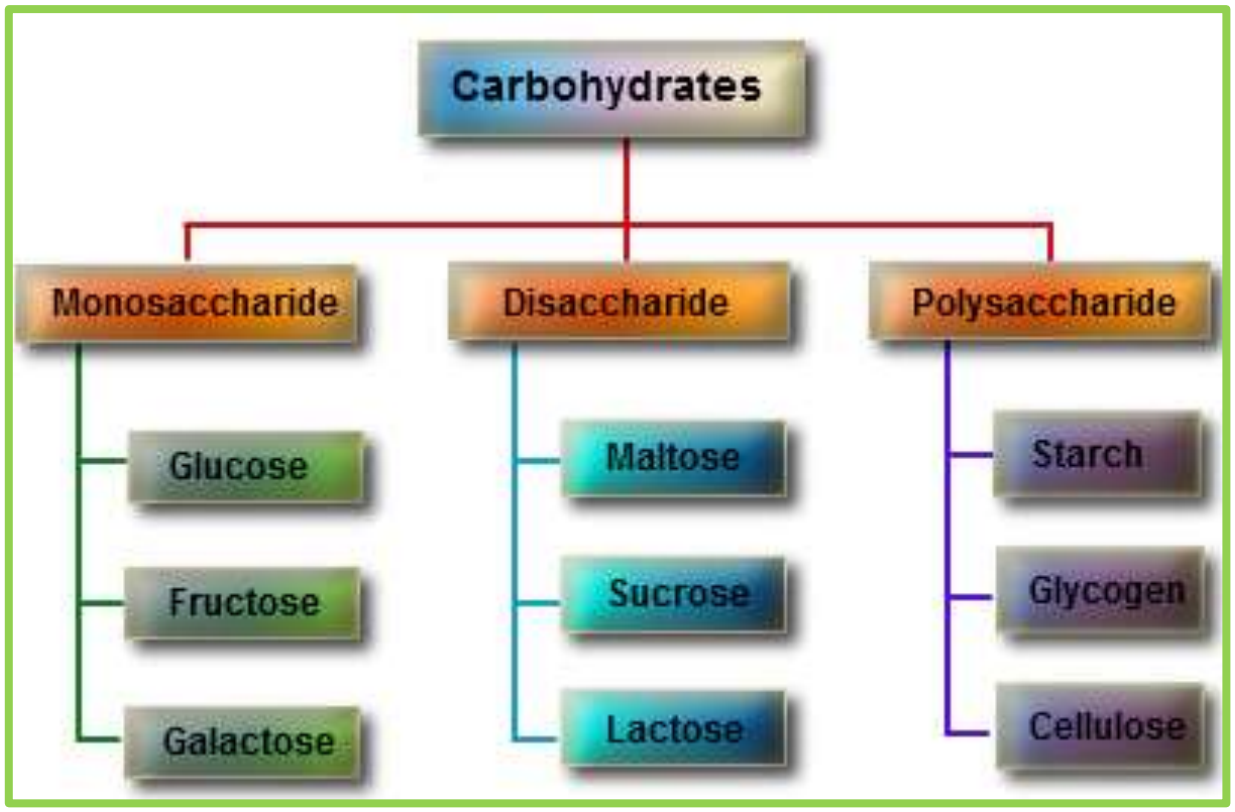
10. Give a description of the chemical structure of a compound (e.g. for mannose the answer is: a monosaccharide, a hexose, an aldose).

11. What are the main disaccharides in food? What are their structural components, what enzymes hydrolyze them and in which foods are they found?

12. What are the effects of alkali (or acids) on sugars? Applications/importance of the above reactions?

13. Why some sugars have reducing properties and others don't?

Carbohydrates-2nd part



Thank you!