Useful books: 1st & last online textbooks on syallabus
the last print books.

2013-10-1

* Reading textbook is a waste of time, ~~to~~ make sure you understand lecture notes! (∵ textbook will talk about other information, and it may talk differently).

Week 4:

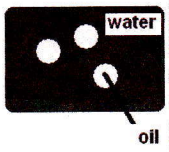
Carbohydrate I

Reading Assignment:

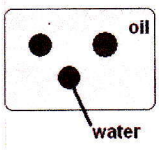
Role of protein and ferulic acid in the emulsification properties of sugar beet pectin

Emulsions are discrete particles dispersed in a continuous phase

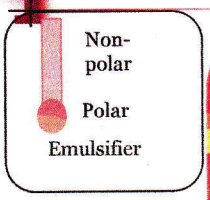
- O/W (oil in water emulsion)
  - Discrete particle= dispersed phase = oil
  - Continuous phase is water

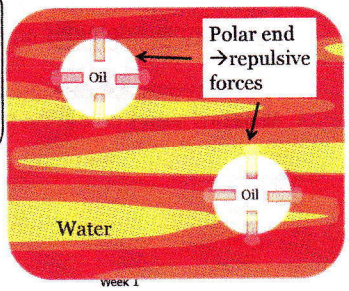


- W/O (water in oil emulsion)
  - Discrete particle = dispersed phase = water
  - Continuous phase is oil



Emulsions are stabilized by emulsifiers





Paper discusses the role of a polysaccharide as an emulsifying agent

Table 4. Static Surface Tension Measurements of the Sugar Beet Pectin and Gum Arabic Samples Compared to Some Nonbeet Pectin Samples and SDS

sample		surface tension, mN/cm
water		71.1
SBP1	Protein and ferulic acid present	54.5
SBP2		56.1
SBP3		n/d*
GA		57.1
high-methoxyl citrus pectin	No protein or ferulic acid	62.7
low-methoxyl amidated apple pectin		69.2
high-methoxyl apple pectin		66.9
sodium dodecyl sulfate (SDS)		37.9

* n/d: not determined.

have some emulsified property

not as good as SDS, but better than polar

still close to 71.1

Highly Polar

emulsified agent can drop surface tension.

reagent: help to dissolve cellular protein, membrane.

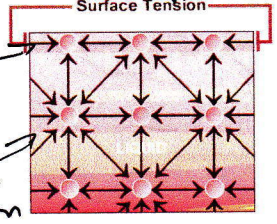
Surface tension & emulsions

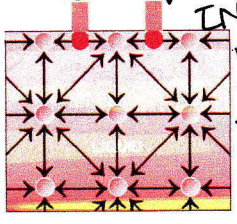
Cohesive forces at the surface of water

water walker

Surface Tension and Emulsifiers

Non-polar
Polar





unbalance forces between molecules

forces from all direction

get in water molecule and reduce forces [NO oil in it] mimic the function of emulsified agent in oil.

Source: http://www.ramehart.com/surface_tension.htm

not a single molecule, a complex

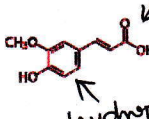
form ester linkage in sugar...

Table 2. Amino Acid Profiles of the Sugar Beet Pectin Samples

amino acid	SBP1	SBP2	SBP3
	% of total protein		
hydroxyproline	0.47	0.52	0.76
aspartic acid	0.16	0.17	0.17
threonine	0.17	0.20	0.24
serine	0.17	0.19	0.23
glutamic acid	0.26	0.27	0.29
proline	0.16	0.18	0.21
glycine	0.10	0.11	0.14
alanine	0.12	0.13	0.14
cystine	0.01	0.02	0.00
valine	0.19	0.22	0.26
methionine	0.00	0.01	0.01
isoleucine	0.06	0.07	0.08
leucine	0.10	0.12	0.13
tyrosine	0.16	0.17	0.23
phenylalanine	0.07	0.09	0.08
histidine	0.16	0.17	0.24
tryptophan*	n/d	n/d	n/d
lysine	0.21	0.24	0.36
arginine	0.11	0.13	0.12
total protein, %	2.87	3.01	3.69

* Tryptophan usually suffers complete loss during acid hydrolysis and was therefore not quantified in the analysis. n/d: not determined.

Various, sugar backbone, protein



Polar carboxyl group.

Hydrophobic

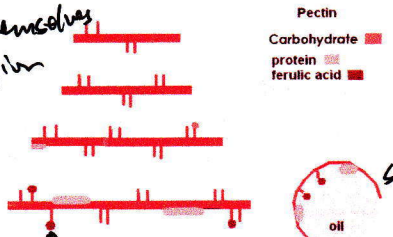
Hydrophobic components

classical emulsified agent

protein: hydrophobic ∴ amino acid

(protein) non-polar + polar (polysaccaride) ∴ in one molecule → emulsified

How do polysaccharides emulsify



PS can orient themselves (hydrophobic region face oil droplet; hydrophilic turn outside).

ferulic acid (higher molecular weight than other region)

polar outside

long molecule that has emulsify property

Overview

I. Monosaccharide and disaccharide chemistry
- Aldoses and ketoses
- Hemiacetal formation
- Tautomers
- Invert sugar
- Crystallization
- Candy-making
- Caramelization

II. Important sweet products
- Sucrose
- Honey
- Maple syrup

III. How is sweetness perceived? receptor on our tongue
- Low & high intensity sweeteners

artifical sweeteners bind to receptor like natural sweeteners.

Carbohydrates

- Polyhydroxy aldehydes (aldoses)
  - Reducing sugars e.g. glucose, dextrose
- Polyhydroxy ketones (ketoses)
  - Fructose most controversial
- Substances which may be hydrolyzed to polyhydroxy aldehydes and polyhydroxy ketones
  - e.g. starches, cellulose, plant gums, dietary fibre
- All natural sugars exist in the D conformation

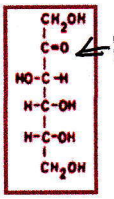
monosaccharides

Aldose or ketose?

Aldose

aldehyde group

Ketose

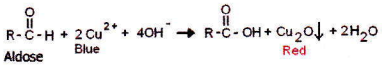


ketose

Aldoses are reducing sugars

- Sugar + alkaline cupric tartrate:

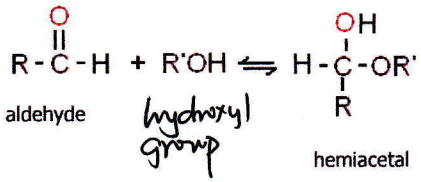
Following reaction occurs:



- Under the conditions of this test both glucose and fructose are reducing sugars
  - Alkaline conditions results in the conversion of fructose to glucose

free aldehyde group has reducing power

Aldehydes and alcohols react to form hemiacetal



When the aldehyde and alcohol groups are on the same molecules cyclic hemiacetals form

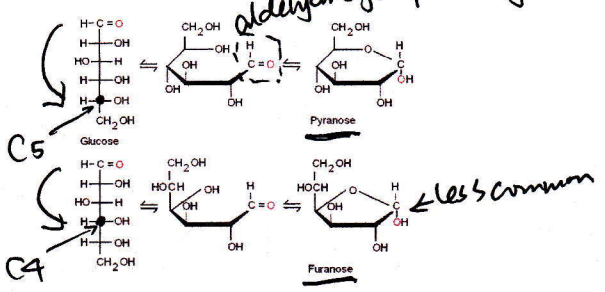
glucose: aldehyde & hydroxyl group → form ring structure

- Furanose:
  - 5- membered heterocyclic ring
  - 4 C, 1 O

- Pyranose: (more common)
  - 6- membered heterocyclic ring
  - 5C, 1O

Glucose can form cyclic hemiacetals in both pyranose and furanose form

aldehyde group always C1



less common

Hemiacetal formation is an example of tautomerism

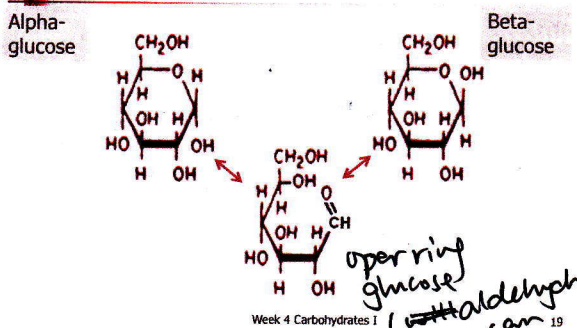
- Tautomerization:
  - Rapid interconversion of isomers
- Ring-chain tautomerism in sugars:
  - the aldehyde group (CHO) in a sugar chain molecule reacting with one of the hydroxy groups (OH) in the same molecule to give it a cyclic form
- Keto-enol tautomerism in sugars:
  - formal migration of a hydrogen atom or proton, accompanied by a switch of a single bond and adjacent double bond
  - Glucose ↔ C1-C2 enol ↔ fructose (Enolization: browning reactions- Protein lecture)
- Products = tautomers

talk in protein session

Formation of anomeric isomers is an example of tautomerism

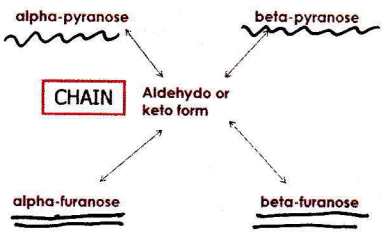
- When a sugar forms a ring structure an asymmetric carbon is formed (carbon has 4 different groups on it)
  - This is the anomeric carbon
- The terms α and β refer to the orientation of the hydroxyl group about the anomeric carbon

Tautomerization of glucose



open ring glucose (aldehyde group can form α or β glucose) (5 or 6 member ring)

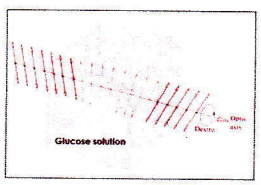
When monosaccharides are dissolved in water five structures are possible



Mutarotation is observed when glucose is dissolved in water

don't understand in five.

- Different tautomers form and eventually reach equilibrium
- During the process of equilibrium if polarized light is passed through the mixture the angle of the plane of the light will change until equilibrium is established

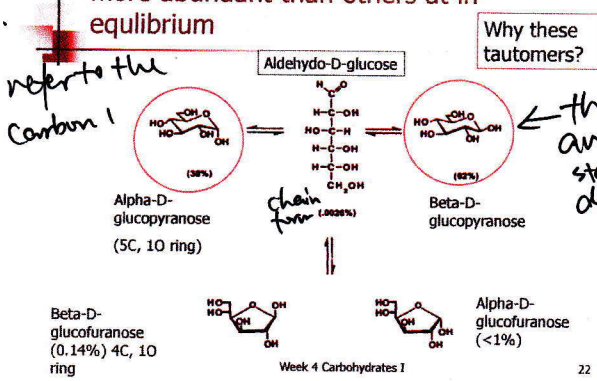


angle of light changes!

Some tautomeric forms of glucose are more abundant than others at in equlibrium

put glucose in solution → Σ compounds.

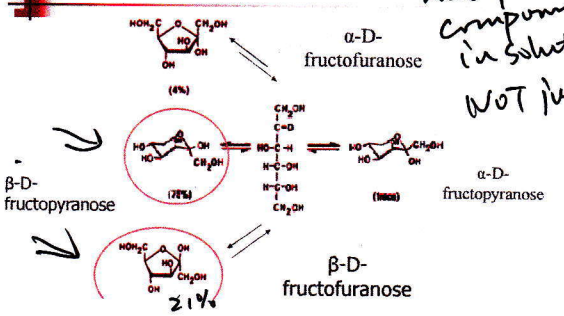
refer to the carbon!



these two are more stable dominant.

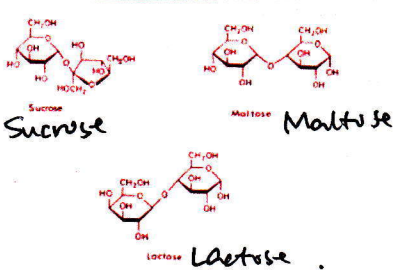
Tautomeric forms of fructose in equilbrated aqueous solution at room temperature

multiple compounds in solution! NOT just 1.



most stable.

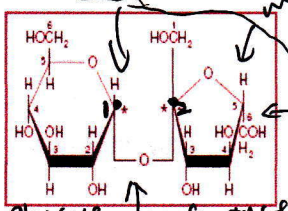
Below are some important Disaccharides



Sucrose Maltose Lactose.

Sucrose

- α-D-glucose
- β-D-fructose
- 1,2' linkage
  - Glucose → Fructose
  - Fructose is turned 180 degrees, inverting it

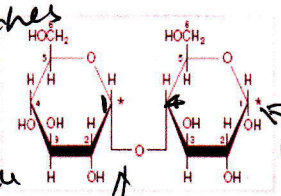


not free C1; it's bound
not a glucose
∴ No free carbon
Not a reducing sugar
fructose is drawn upside down
glucose
fructose
covalent link.
(w/ free C1 from glucose)

Maltose

- α-D-glucose
- 1,4' linkage starches
- Isomaltose
  - 1,6' linkage

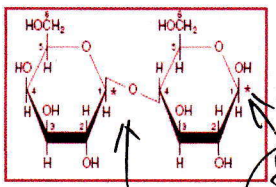
between 2 Glucose molecule (precursor of most food additives).



free Carbon atom
uncovalent link ∴ reducing sugar

Lactose

- β-galactose
- β -glucose
- 1,4' linkage



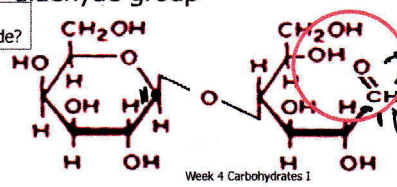
uncovalent link.
free Carbon atom
∴ reducing sugar

In this course, whether this is a free carbon atom, only concerns with C1 on glucose

Reducing disaccharides

- A disaccharide will have reducing properties if at least one sugar can convert to chain form, exposing a free aldehyde group

What dissacharide?



reducing carbon
aldehyde
this is free to form

Carbohydrate jeopardy

Answer	Question
Maltose and lactose are examples of this. Sucrose is not.	What is... reducing sugar.

only 1 glucose, C1 is covalently link to C2 of fructose. Can't reform.
has free C1, can reform the chain formation

Sucrose can be hydrolyzed to a mixture of 1:1 glucose and fructose

- Sucrose → glucose + fructose
  - Invertase, H+ ← acidic
- Optical rotation:
  - +66.5° -28.2°
  - Invert sugar → invert the 'sign' of the angle.

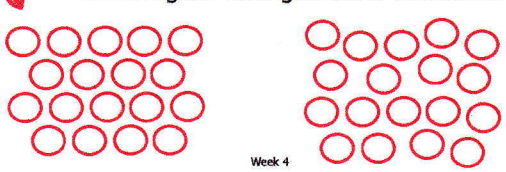
Non-reducing sugar

Reducing sugar.

Physical Properties

The crystallinity of sugar effects the properties of food

- Crystalline very ordered
  - Regular arrangement of molecules
- Amorphous not as neat & tight
  - No regular arrangement of molecules



True or false:

- The purer a solution of a sugar the easier it will be to recover the sugar in crystalline form

has to be fairly pure.

True

Which will crystallize more readily from solution given the same molar concentration?

- A) sucrose
- B) fructose
- C) glucose
- D) there is no difference between them
- Hint: Think tautomers

no tautomers in sucrose solution. can't open up. Just pure solution w single molecule

dissolve them form 3 different Compounds and 2 tautomers (mixture).

True or false

- Sucrose, in solution, will crystallize out more slowly in the presence of glucose, compared to pure sucrose.

Impurity.

True

Crystallization of sucrose effects the type of candy produced.

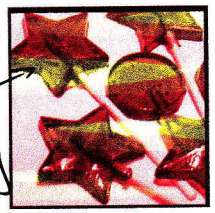
- Which is crystalline?
- Which is amorphous?

super saturated solution.

crystalline

lollipop

hard boiled candy



granulated sugar corn syrup

Hard Candy Chemistry

- http://www.youtube.com/watch?v=VY8q0hN6KwA

Hard boiled candy

Ingredients

- Sucrose sugar
- Water
- Glucose syrup / corn syrup

starch broken down to glucose and put in water

releasing agent: soy oil (on the mould that can prevent sticking.

~~Interfering~~ agents.

Other examples: Corn syrup; Maltose.

Acid can prevent crystallization, can also add flavour

Methodology

- Heat the sucrose solution (149-166°C)
  - sucrose melts and water evaporates
- Cool down
- Result:
  - Amorphous glass amorphous glass
  - What is the purpose of glucose syrup?

Any non-sucrose molecule will work

not as sweet as glucose

Coloured compounds form by heating sucrose: a process called caramelization

breakdown starch → sugar & flavour compound

colour flavour

- A step-wise reaction produced by the heating of a sugar (e.g. sucrose)

1) Reactions: removal of water and polymerization
   - Results in the production of brown-coloured compounds of heterogeneous structure
2) Reactions: degradation:
   - Flavor compounds small molecular weight compound

Caramelization

- Heat sucrose in the absence of water

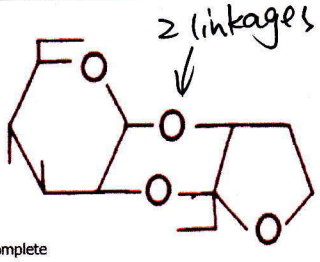
elimination of water in sucrose

  - At 200°C reaction consists of three distinct stages:
  - STAGE 1:
    - 35 min heating 4.5% loss (by weight)
    - $C_{12}H_{22}O_{11} - H_2O \rightarrow C_{12}H_{20}O_{10}$ (isosachrosan)

↑ Right formula.

Isosacchrosan: 2 ether linkages

2 linkages.



NB structure incomplete

Caramelization

- Stage 2
  - After an additional 55 min (total 35 + 55) of heating:
  - Dimerization of sucrose and elimination of water:
  - Weight loss of ~9%
  - $2C_{12}H_{22}O_{11} - 4H_2O \rightarrow C_{24}H_{36}O_{18}$ doesn't mean the sucrose is there
  - Brown pigment = caramelan used in beverage
    - Water-soluble
    - Heterogeneous chemical structure

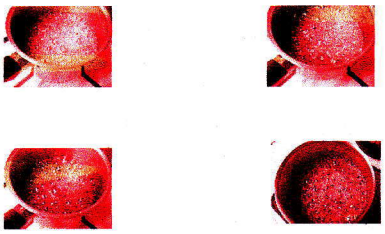
Caramelization

- Stage 3:
- After an additional 55 minutes (35 + 55+55):
- Sucrose trimerization and elimination of water:
- Weight loss ~14%
- $3C_{12}H_{22}O_{11} - 8H_2O \rightarrow C_{36}H_{50}O_{25}$
- Brown pigment = caramelen ≠ caramelan
  - Water-soluble, heterogeneous

Caramelization

- Stage 4 (not commercially important):
- Additional heating results in the formation of dark brown pigment high molecular weight pigment
- =humin or caramelin

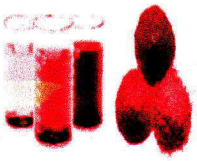
Caramelization



http://www.food-info.net/uk/colour/caramel.htm

Caramel Colours

- Widely used in the food industry
- Dark brown to black liquids or solids
- Water-soluble
- First used to color beer



heating sucrose : yellow-to brown

Caramelization

- Degradation products of sucrose flavour compounds
  - Diacetyl : butter scotch
  - Hydroxyacetylfuran: sweet aroma
  - Maltol: taste of freshly baked bread

Caramel Colour and Safety

- Caramel Colour
- Industrial process heats sucrose in the presence of ammonia → contaminants:
  - 2-methylimidazole
  - 4-methylimidazole
- Animal carcinogen at very high doses
  - 1000 cans of pop/day
- CSPI-raised concerns about safety of caramel colours
- http://www.cspinet.org/reports/chemcuisine.htm#caramel

center for science and particular interest →

II. Important Sweet Products

- Sucrose
- Honey
- Maple Syrup

What are these?

sugar cane

1

sugar beets

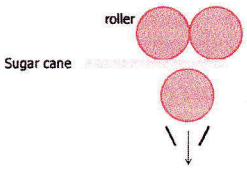
2

How is sucrose processed?

Sugar cane
- crushed between rollers
  - juice formation
- crushed cane sprayed with water
  - removes the juice (16% sucrose)
- juice is made slightly basic by adding calcium hydroxide (Why?)
- mixture is heated to denature and coagulate proteins
  - Scum forms, removed by filtration

How is sugar cane processing into sucrose?

- Sugar cane is crushed between rollers, releasing the juice

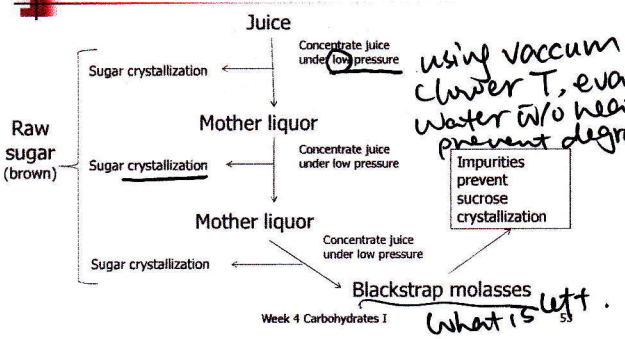


Cane Juice (sucrose)

How is sugar cane processed into sucrose?

- Cane Juice
  - + $Ca(OH)_2$ (Why?)
  - + heat → scum (coagulated protein)
  - + filter
- Debris-free, protein-free cane juice

How is sugar cane processed into sucrose?



How is sugar processed into sucrose?

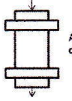
Raw sugar (brown) → Sugar solution

+ H_2O
+ $Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$
+ filter

Sugar solution

T or F:
Granulated sugar is bleached to make it white.

False.



SUCROSE ← Decoloured sugar solution

How is sugar beet processed into sucrose?

- Sugar beet processing:
  - Similar to sugar cane
  - Instead of rollers the beet is sliced and extracted with warm water → juice

How is honey made?

Or why don't vegans eat honey?

Nectar Honey

- Nectar = sweet substance secreted by flowers to attract pollinators (contains sucrose)
- Nectar collected by bees
- Enzymes in bees digestive tract invert sucrose
- Bees regurgitate the "processsed" nectar and deposit it in honey comb (beeswax)
- Bees dry the honey by flapping of wings to prevent mold growth (18% water content)

convert to glucose and fructose.

↑ relative low water content.

vegan don't eat honey -: animal products.

Honey-Composition

- 30% glucose
- 39% fructose
- 18% water
- Other minor components:
  - Sucrose, protein, fatty acids (wax), pollen, minerals
- Honey can be classified by the plant source of the nectar
  - E.g. buckwheat, clover

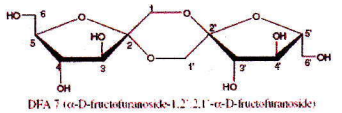
Honeydew Honey

another kind of honey

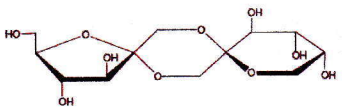
An aphid produces honeydew for an ant in a relation of mutualistic symbiosis

- Processed by honeybees
- Not nectar but secretions from insects (e.g. aphids) sucking on plants
- Honeydew honey is darker than nectar honey and more expensive bizarr process.
- Add caramel colour to nectar honey → fraudulent honeydew honey regular
  - How do you check for authenticity?

Difructose anhydrides (DFA) can be used as quality markers



DFA 7 (α-D-fructofuranoside-1,2' 2,1'-α-D-fructofuranoside)



DFA 9 (α-D-fructofuranoside-1,2' 2,1'-β-D-fructopyranoside)

Caramel colour contains DFA

Difructose anhydride.

Source: Montilla and others. 2006. Food Research International 39(7):801-806.

How would you test for authenticity?

- Gas chromatography
  - No detectable DFA in honeydew honey
  - No detectable DFA in nectar honey

Use DFA as a marker of caramel colour.

Maple Syrup

- Sap of maple tree is evaporated to a concentrated solution 97% water 3% ~~solid~~ sucrose
- Sap of maple tree is 3% wt % solids
  - Predominant component of sap = sucrose
  - Sap also contains other carbohydrates, organic acids, ash, protein , lignin-like material
- Characteristic flavour and colour are formed during evaporation

Maple Syrup

- Collection of sap is best when the temperature is 7°C during the day and below freezing at night winter ends spring starts.
- Taphole is drilled into the tree and a spout attached

Collecting the sap

Evaporating the sap to make syrup

- Water is evaporated from sap
- Final sap is 66% solids

Maple Syrup Colour and Flavor

- What reactions occur to create the characteristic maple syrup flavour and color?

Caramelization.

brown. ← Natural occurring sugar heating process breakdown product

III. How is sweetness perceived?

- Taste receptors on tongue
- Structural features all small molecule sweeteners similar → theory on structure of active sites i.e. glucophore
- E.g. sugars, artificial sweeteners

sugar & artificial sweetner both have these structure.

milk sugar very sweet

dipeptide (protein)

Sweeteners

Sugar	Relative Sweetness	
fructose	175	← standard
sucrose	100	
glucose	60	Low-intensity sweetener
mannose	59	
lactose	16-38	
maltose	46-52	
raffinose	23	
Artificial Sweeteners		
Sucralose	60,000	High-intensity sweetener
Aspartame	19,000	
Acesulfame	20,000	

don't need to use a lot. Just a little. Calorie content is very little.

fructose + glucose
1 : 1
175 + 60 = 115

Cheaper than sucrose

sucrose 100.

Sucrose & fructose not difference with perspectives of nutrition.

Consider the following: sucrose and invert sugar. Which is sweeter?

- A) Invert sugar is considerably sweeter.
- B) Both invert sugar and sucrose are similar in sweetness.
- C) Sucrose is considerably sweeter.

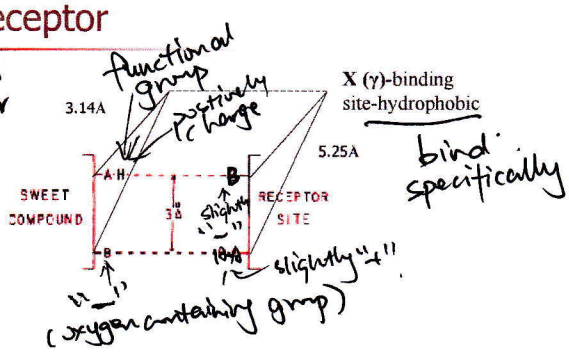
Hint: Slide 67: Assume relative sweetness is additive

- What are the economic implications of the answer to this question?

Sweet taste receptors

- Located on the tongue
- 1960-2001
  - Determination of glucophore
    = structural similarities between sweet compounds
    AH, B, X theory for the active site of the receptor
- 2001
  - Protein structure of the sweet taste receptor was identified

Active site-sweet taste receptor



1 hydrogen bond to each other

functional group

positively charge

bind specifically

slightly "+"

slightly "-"

(oxygen containing group)

Binding sites on receptor

- AH: hydrogen bond donor
  - OH, COOH, NH_3^+, -NH-, C-H
  - Present on sugars
- B: hydrogen bond acceptor
  - -OH, -C=O, NO_2, $-SO_2$
  - Present on sugars

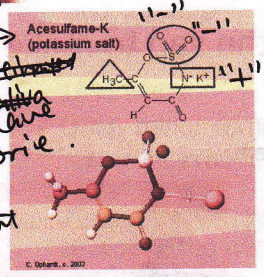
Sweet Taste Receptors

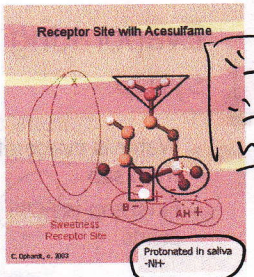
- T1R2_T1R3 heterodimer
  - G protein coupled receptor (GPCR)
    - Seven transmembranes domain
    - Large extracellular domain =Venus flytrap domain which contains active site for the ligand
  - One active site that corresponds to AH, B, X theory
  - Additional active sites which explains the sweetness of compounds that structurally do not fit the AH, B, X theory
  - E.g. sweet proteins that do not have a glucophore

Don't worry about details.

- Ref (FYI):
  - Tamusei, P. The history of sweet taste: not exactly a piece of cake. Journal of Molecular Recognition 2006:19:188-199. Available online through UTL

Artificial Sweeteners: AH, B, γ/χ





"+" in ~ "-" on match.

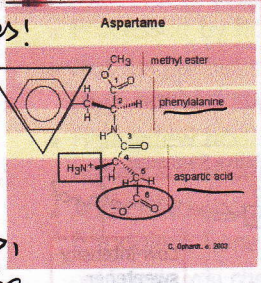
doesn't have any calorie. (go into blood, but not into tissue. be excreted directly)

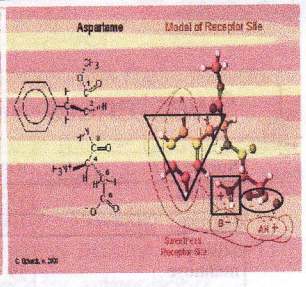
三维立体 (3-dimentional)

fit on receptors very tightly!

Artificial Sweeteners

use in mg quantities!

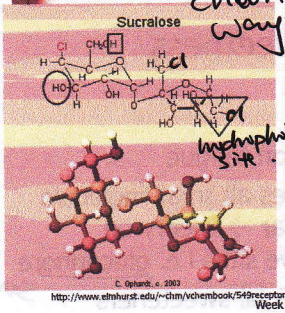




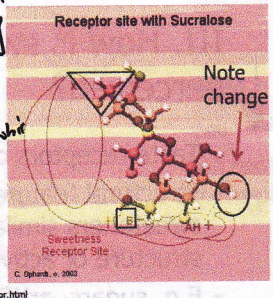
has calorie from aspartame, body does break it up, products can be detected. But quantities is so small that it's eligible.

Artificial Sweeteners: Sucralose

chlorine atoms get in the way



of hydrophobic site.



Totally unabsorbed. ∴ chlorine (too big, enzyme can't digest it) Ends up in large intestine.

And fit on receptors better than sucrose.