European FooD-STA

Sugars: …not only sweeteners
Technological functionality in food matrices

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7th June 2016

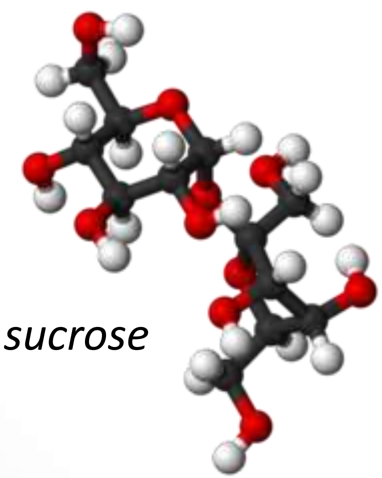
Sugars

Sugars: class of sweet-flavored substances used as food.

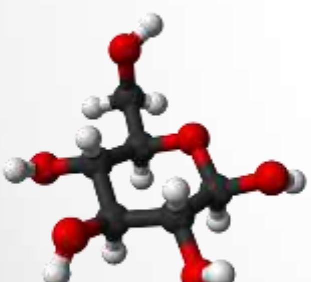
Hydrates of carbon (chemical composition $(C\,.\,H_2O)_n$ $n \geq 3$)
Derived from different sources….
Simple "sugars" includes

- **monosaccharides (glucose, fructose and galactose)**
- **disaccharides (sucrose, maltose, lactose, trehalose, …)**

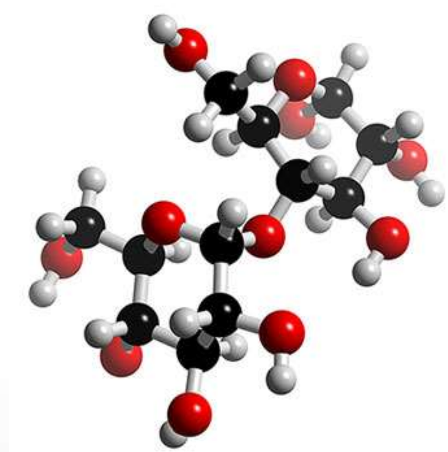
trehalose



sucrose



glucose



maltose

Sugars

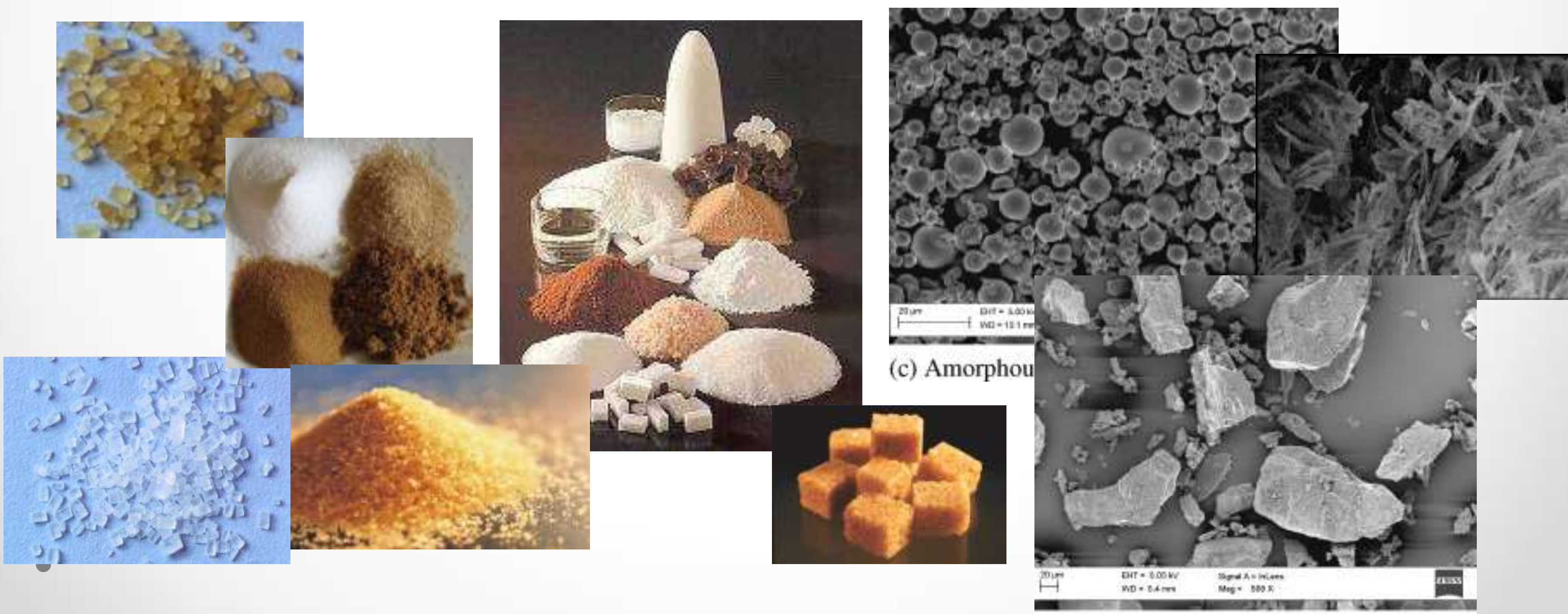
Hydrates of carbon (chemical composition $(C\,.\,H_2O)_n$ $n \geq 3$)

Derived from different sources….

Simple "sugars" includes

- **monosaccharides (glucose, fructose and galactose)**
- **disaccharides (sucrose, maltose, lactose, trehalose, …)**

…various polymorphs (α, β, ..), physical states, ….



Sugars

Hydrates of carbon (chemical composition $(C\ .\ H_2O)_n$ $n \geq 3$***)***

Derived from different sources….

Simple "sugars" includes

- **monosaccharides (glucose, fructose and galactose)**
- **disaccharides (sucrose, maltose, lactose, trehalose, …)**

…various chemical and physico-chemical properties

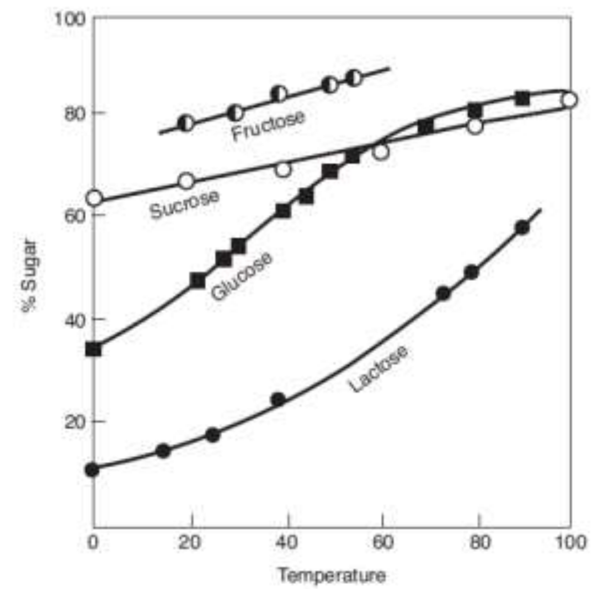
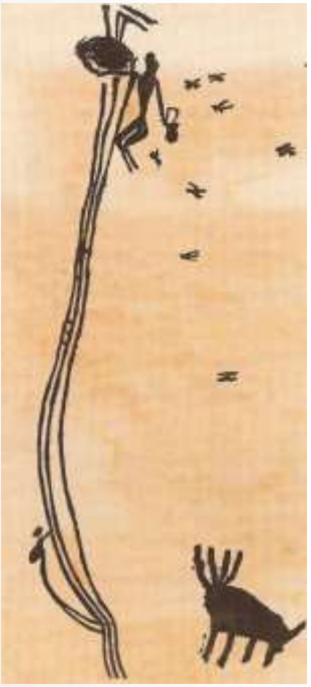


Figure 5.4 Approximate solubility of various sugars at different temperatures.
Source: Shallenberger and Birch 1975.

Hystory of sugars…

Humans apparently began hunting for honey at least 10,000 years ago



Mesolithic rock painting, showing two female honey-hunters collecting honey and honeycomb from a wild bee nest (Valencia, ES)

Egyptians used honey to prepare cakes (Egyptians hieroglyphs)

Hystory of sugars…

Sugar Cane – domesticated in New Guinea (?)

2992 B.C. – India: unrefined sugar from cane

642 A.D. – Arab-speaking peoples get sugar refining from Persia

11th Century – Europe by Crusaders (1099 in England)

1493 – America: Columbus takes sugar cane to West Indies

1700's – American "Sugar Triangle" (sugar, rum, slaves)

1700's – Sugar taxation → Revolution

1800's – Sugar beet provides competition in temperate areas

Saccharum officinarum – member of Poaceae (Grass family)

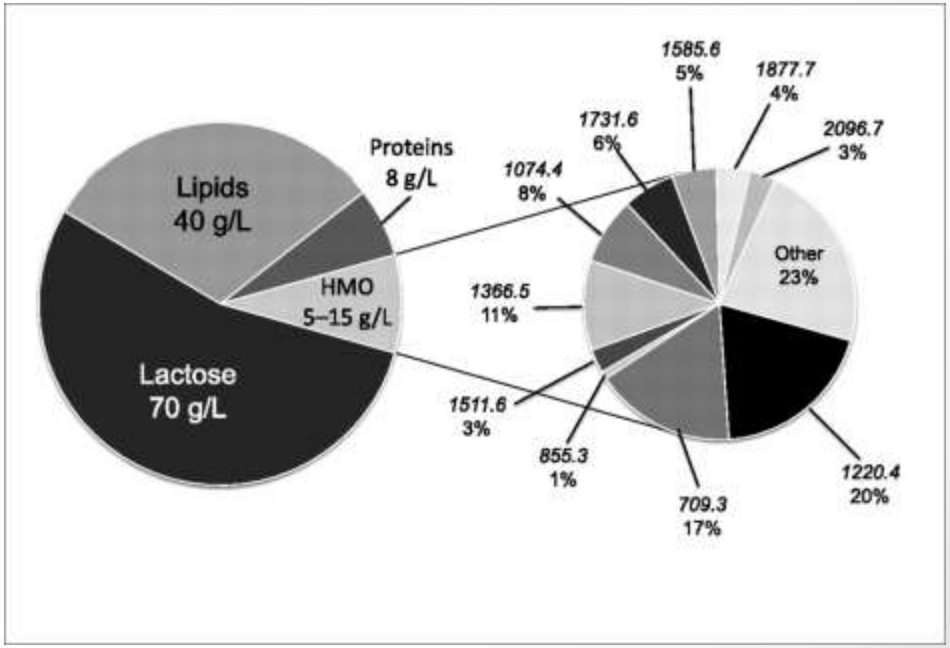
Native to: Polynesia

Beta vulgaris – Chenopodiaceae (Goosefoot Family)

Where sugar (sucrose) is produced…

Hystory of sugars…

Human milk composition



Lactose + Human Milk Oligosaccharides (HMO) = 75-85% solids

Zivkovic A M et al. PNAS 2011;108:4653-4658

Sugars «families»

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The sucrose-based family

Beet sugars

Cane sugars

Invert sugar

Fructose

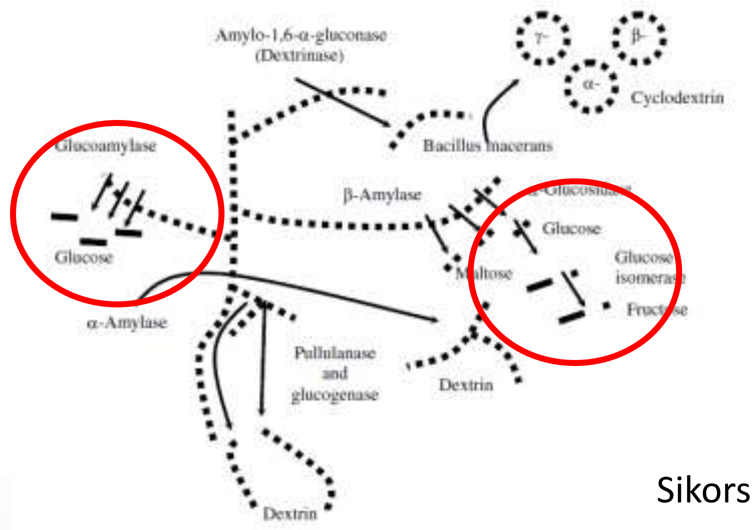
The starch-based family

Glucose syrups

Glucose/dextrose

High Fructose Corn Syrup

Isoglucose



Sikorski, 2007

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Other «sugar sources»…

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North America:

Acer saccharum – Sugar Maple

Sugars in foods

- Naturally present..

- …Enhanced natural content (drying, concentration)

- …Added (by mixing, by processing, e.g. osmotic processes) and by formulation (candies)

Sugars in formulated foods

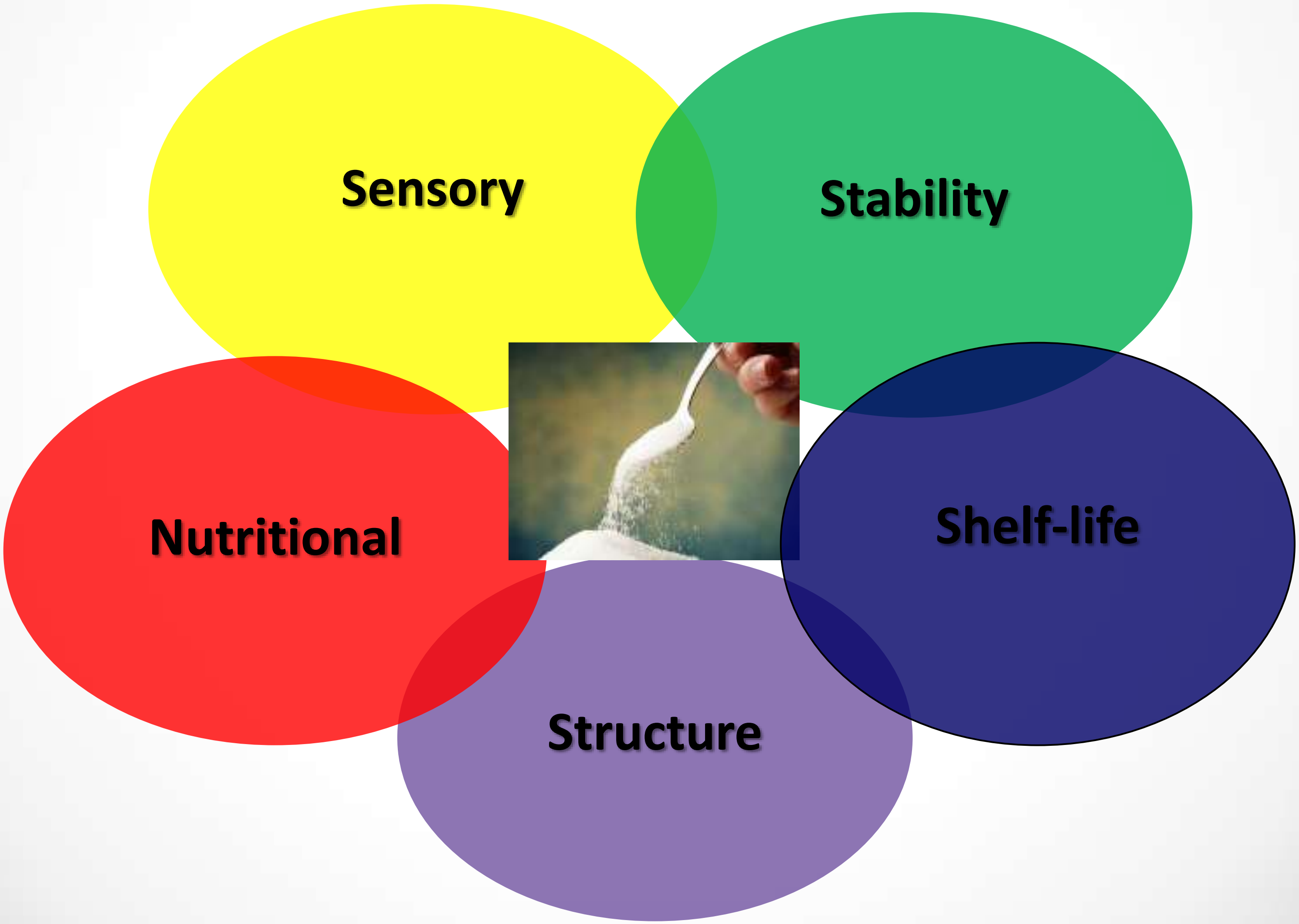
ADDED (IN FORMULATED AND PREPARED FOODS)

- From very low amounts to up 70 % (candies) ...

Various roles and «technological functions

Technological functionality of sugars

...not only sweetness!



Technological functionality of sugars

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Nutritional

Positive…

…easy energy sorce

Negative…

…!

•**Health Issues:** Contribution to and/or aggravation health including: ***asthma, mood disorders, mental illness, nervous disorders, diabetes, heart disease, hypertension, gallstones and athritis***.

•**Insulin Impacts:** Increase of insulin levels and

- release inhibition of the growth hormones and depression of the immune system.
- Promotion of the **storage of fat** → rapid weight **gain and elevate blood triglyceride levels.**

•**Degenerative disease:** Deteriorating effect on the endocrine system and one of the three main causes of degenerative disease

▪**Cariogenic dental effects**

Technological functionality of sugars

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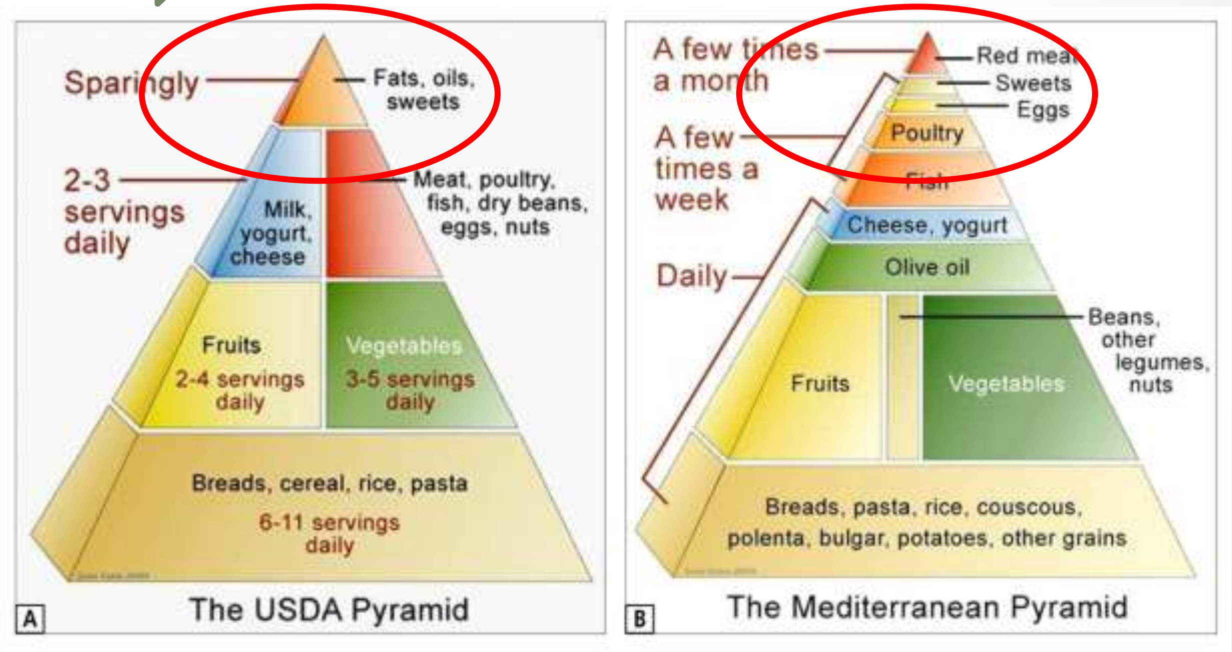
Nutritional

Negative, and….



https://jackwillmitchell.wordpress.com/2013/11/08/the-mediterranean-diet/

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Technological functionality of sugars

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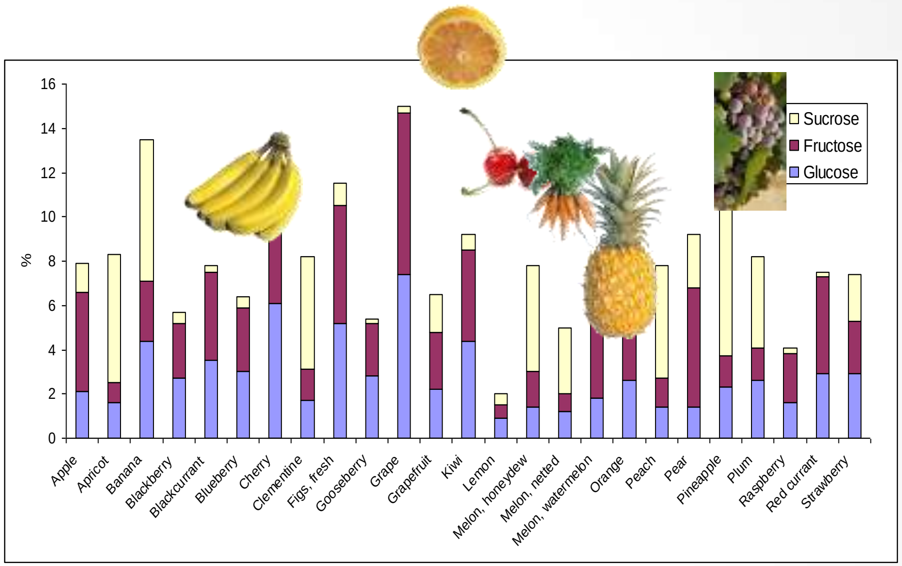
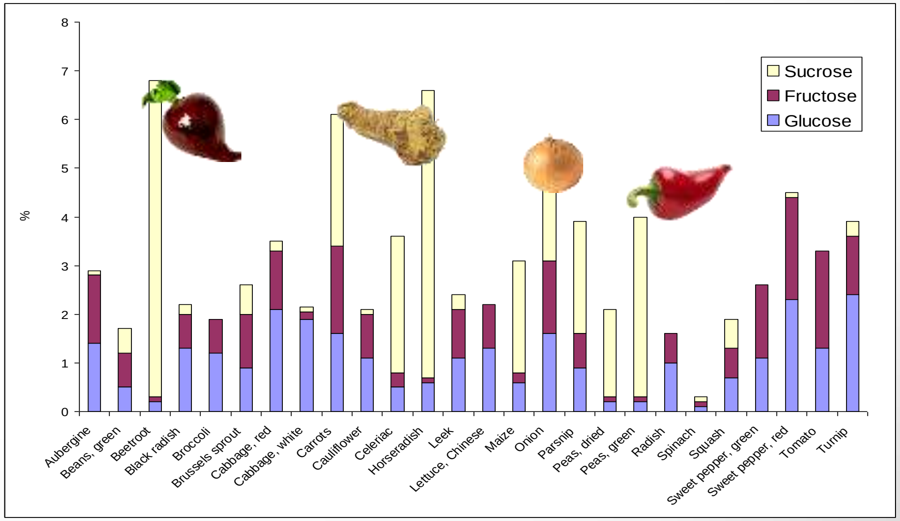
Nutritional

Negative…but





All agree that a banaced diet and proper physical exercise limit undesidered effects on human health by sugars

Nutritional

….sweetness, addiction and obesity

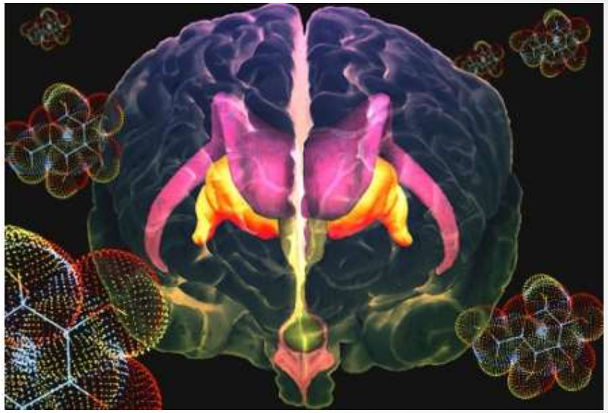
SUCROSE

↓

DOPAMINE receptors
(*striatum brain*)

↓

DOPAMINE release



Brain reward

Pleasure

Technological functionality of sugars

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Sensory

sweetness

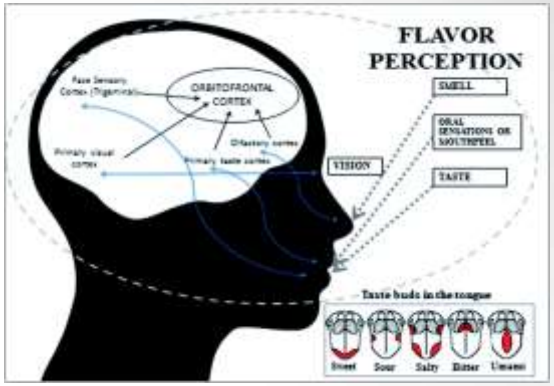

Table 5. Relative Sweetness (RS) of Sugars (w/w%)

Sugar	Solution RS	Crystalline RS
β-D-Fructose	100-175	180
Sucrose[a]	100	100
α-D-Glucose	40-79	74
β-D-Glucose	<α-Anomer	82
α-D-Galactose	27	32
β-D-Galactose	–	21
α-D-Mannose	59	32
β-D-Mannose	Bitter	Bitter
α-D-Lactose	16-38	16
β-D-Lactose	48	32
β-D-Maltose	46-52	–
Raffinose	23	1
Stachyose	–	10

Source: Wistler and Daniel in Food Chemistry O.R. Fennema (Marcel Dekker 1985)

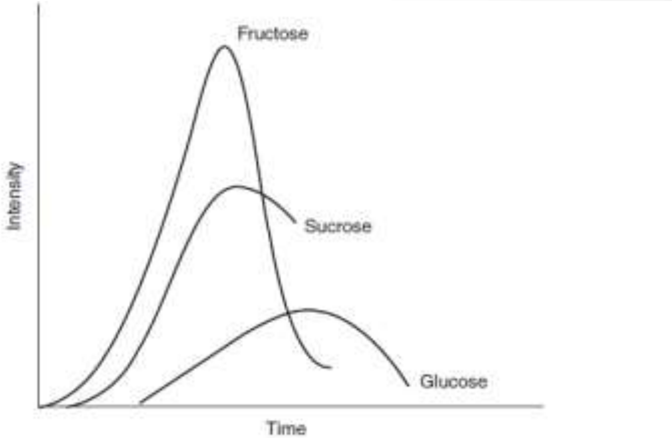

Figure 5.1 Partial sweetness taste profiles for common sugars. Modified from Shallenberger 1998, with permission.

Technological functionality of sugars

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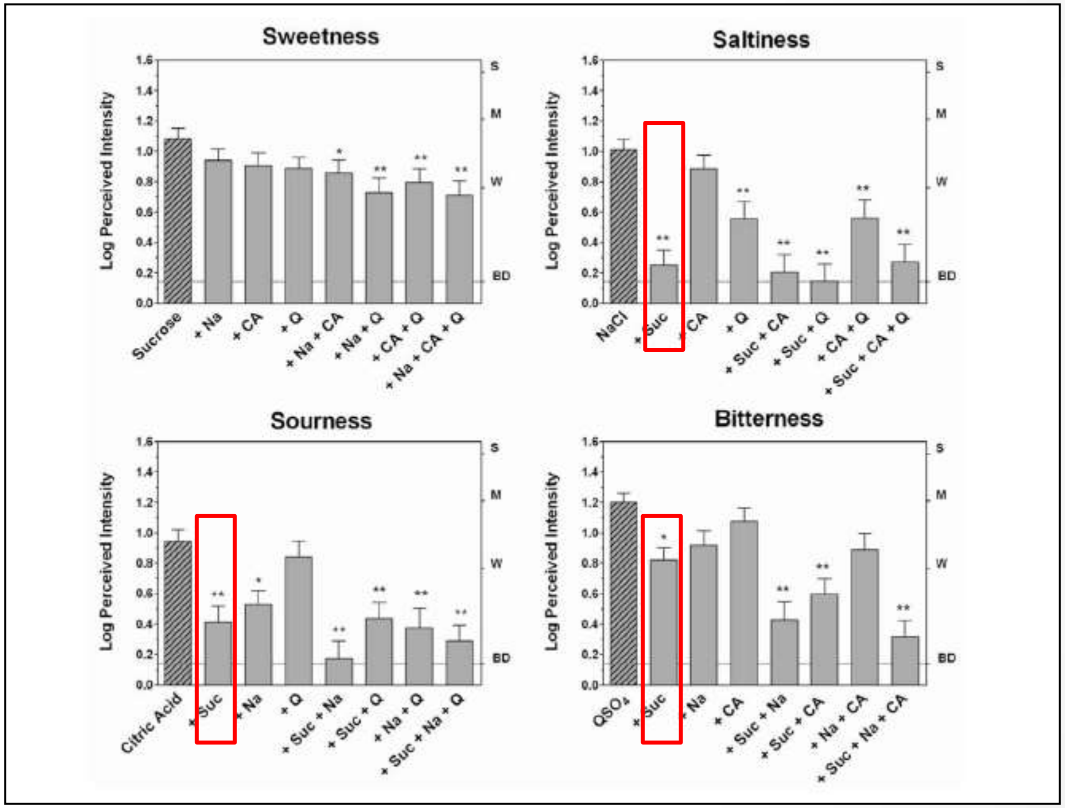
Sensory

….not only sweetness



Log-mean ratings of perceived intensity of sweetness, saltiness, sourness and bitterness made in response to each of the individual taste stimuli and all stimulus mixtures.. Suc=sucrose; CA=citric acid; Na=NaCl; Q=QSO4. Asterisks indicate statistically significant suppression of the primary taste quality (<0.05; **<0.01) and vertical bars represent the standard errors of the means (SEMs). Letters on the right y-axis represent semantic labels of the gLMS: BD=Barely Detectable; W=Weak, M=Moderate; S=Strong (Green et al., 2010)*

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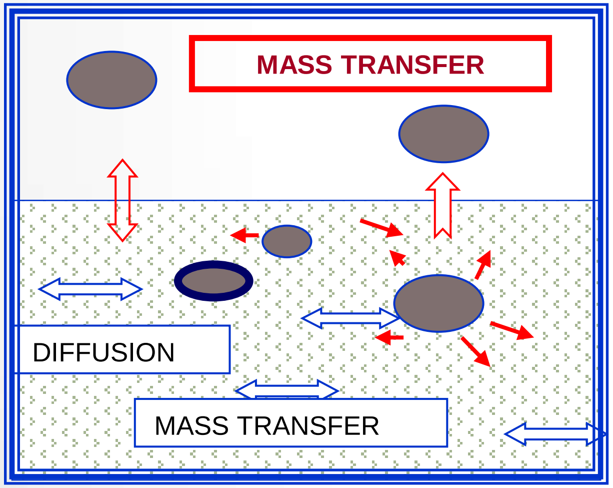
Sensory

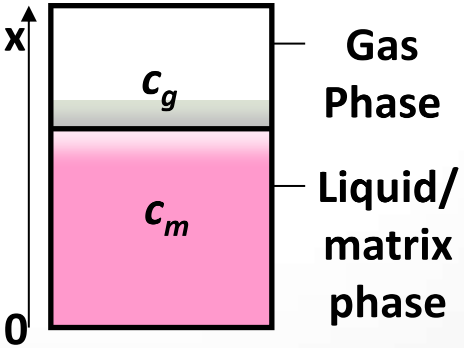
....not only sweetness...aroma perception



Release of aroma compounds

Thermodynamic equilibria

Kinetic aspects



Saccharides & aroma release

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Sensory

Thermodynamic aspects

``salting out'' effect

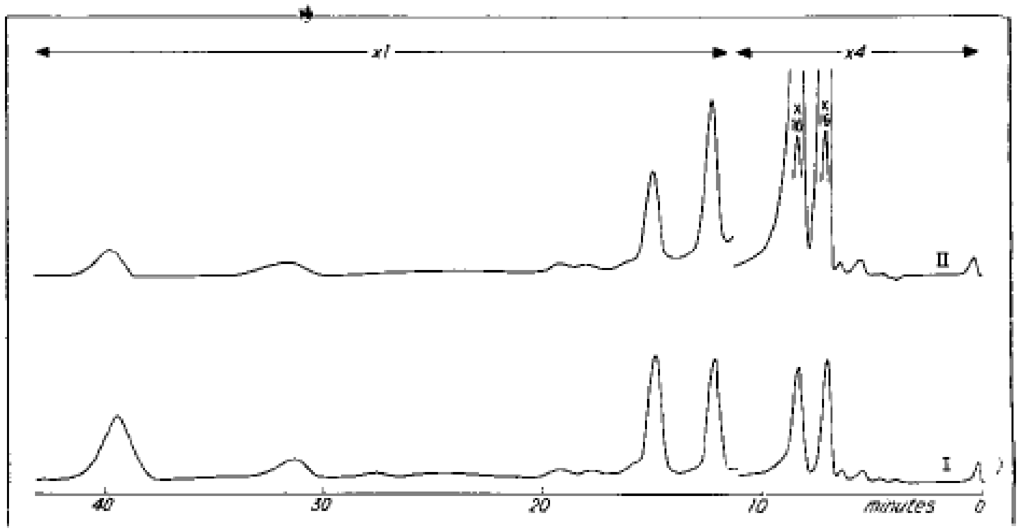

Fig. 1. Solution of strawberry aroma: I without invert sugar; II with 73.1% invert sugar.

Volume 33 (1968)—JOURNAL OF FOOD SCIENCE—1

A. G. WIENTJES*
Department of Food Science, Agricultural University Wageningen, The Netherlands

The Influence of Sugar Concentrations on the Vapor Pressure of Food Odor Volatiles in Aqueous Solutions

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Saccharides & aroma release

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Sensory

Thermodynamic aspects

$$K_{gl}^{i} = \left(\frac{\gamma_{\cdot i} P_i^0(T)}{P_T}\right) \cdot \frac{\overline{V}_l}{\overline{V}_g}$$

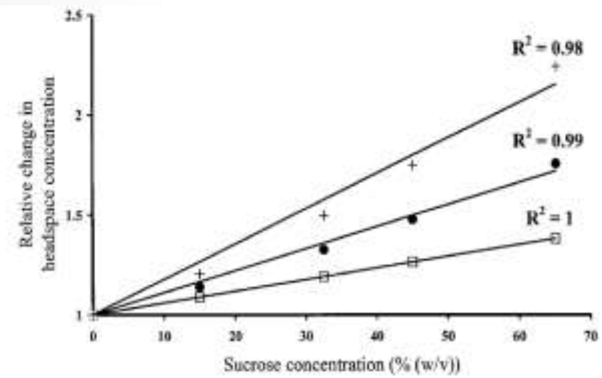

Fig. 1. Relative changes in the headspace concentrations of three volatiles (isoamyl acetate +, ethyl hexanoate ●, eugenol □) with increasing sucrose concentration in an aqueous matrix.

``salting out'' :

Increase of the head space concentration of a volatile when a solute (sugar) is added to the solution due to change of :

- mole fraction of the liquid phase

- activity coefficient

Friel et al., 2000

Please note: it does not occur for all the aroma compounds (no effect, "salting in" effect) and it could be concentration dependent

Saccharides & aroma release

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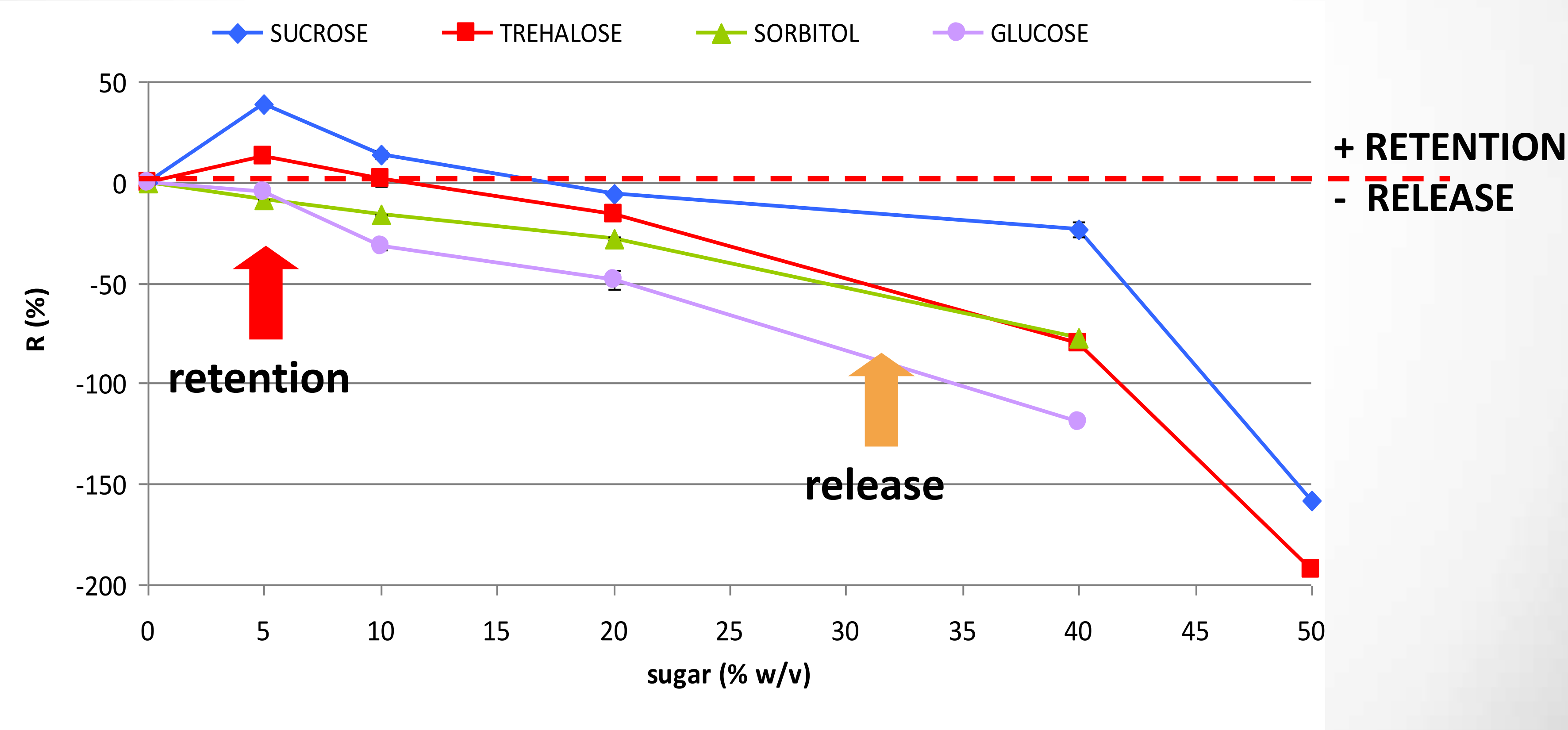
Effect of Sugars on the Release of Aroma Compounds in Model Systems

P. Pittia, P. Piccone, and M. Martuscelli

Water Stress, in Biological, Chemical, Pharmaceutical and Food Systems, Springer, 2016

Release/retention of Ethyl Acetate (logP: 0.73) in sugar solutions
Effect of sugar type, [sugar]: 0-50%w/v)



"Retention Index" R (%) = $[(A_{H2O} - A_{sugar\ sol})/A_{H2O}] \times 100$

Saccharides & aroma release

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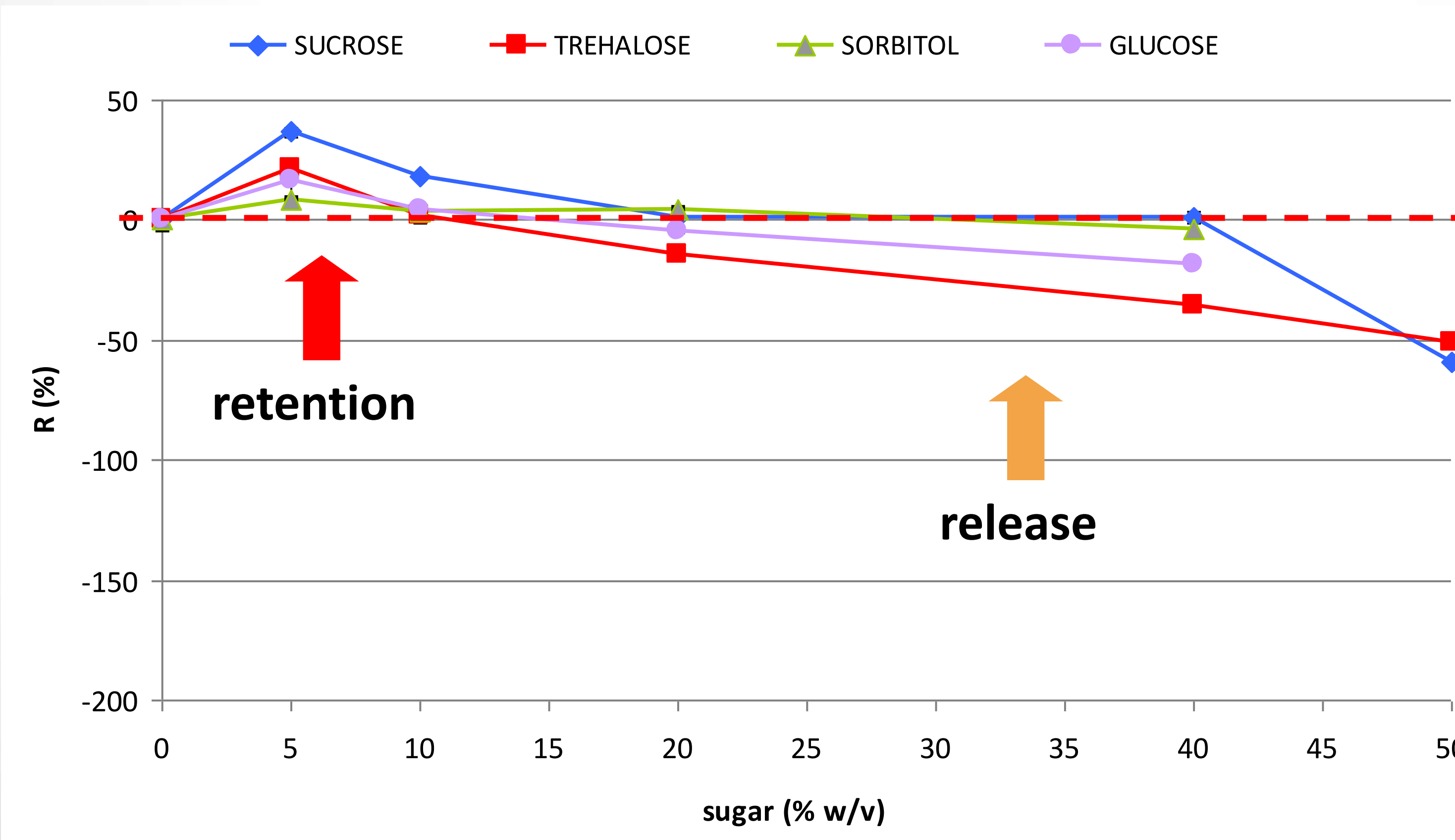
Effect of Sugars on the Release of Aroma Compounds in Model Systems

P. Pittia, P. Piccone, and M. Martuscelli

Water Stress, in Biological, Chemical, Pharmaceutical and Food Systems, Springer, 2016

Release/retention of <u>Ethyl Hexanoate</u> (logP: 2.13) in sugar solutions
Effect of sugar type, [sugar]: 0-50%w/v)



+ RETENTION
- RELEASE

"Retention Index" R (%) = $[(A_{H2O} - A_{sugar\ sol})/A_{H2O}] \times 100$

Saccharides & aroma release

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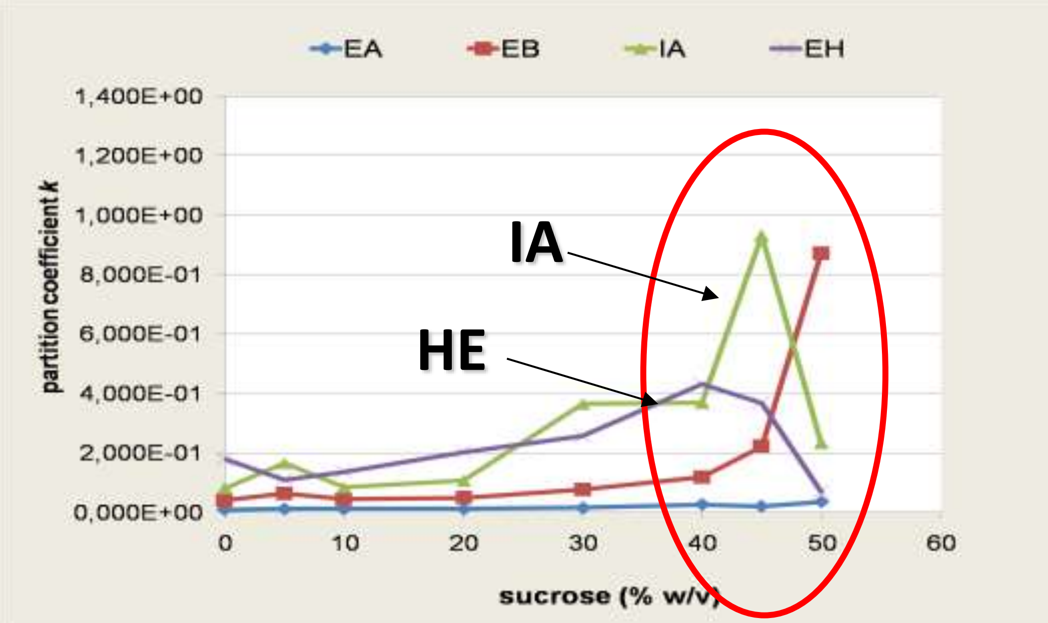

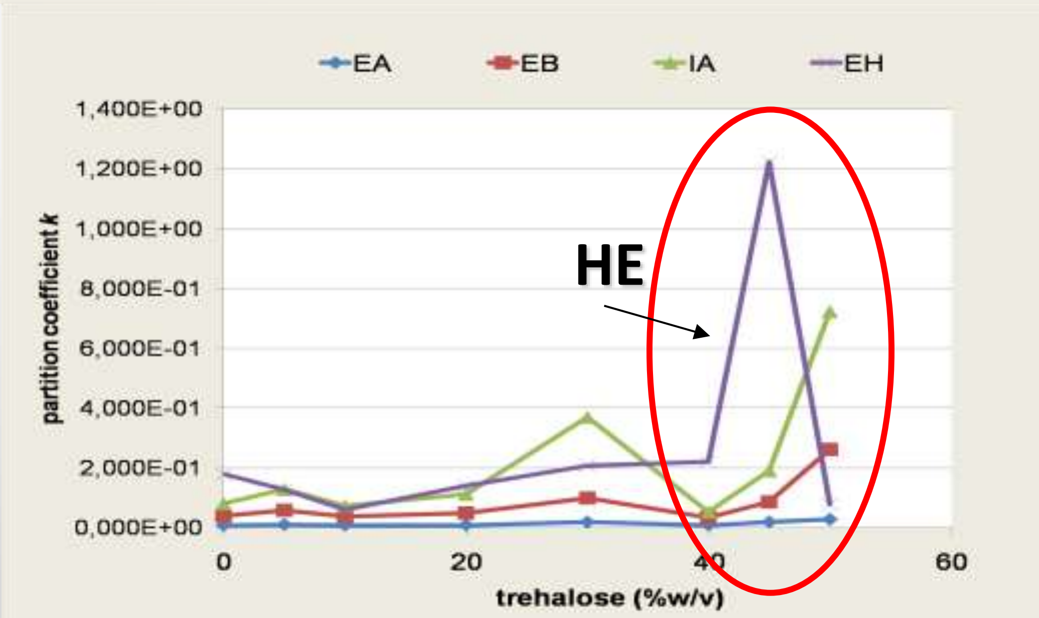

Differences due to

-sugar type

- **Sugar concentration**

-aroma compound (polarity)

Sugars could modify:

- **physico-chemical properties of water**
- **solubility of volatile compounds**

Effect of Sugars on the Release of Aroma Compounds in Model Systems

P. Pittia, P. Piccone, and M. Martuscelli

Water Stress, in Biological, Chemical, Pharmaceutical and Food Systems, Springer, 2016

Saccharides & aroma release in real foods

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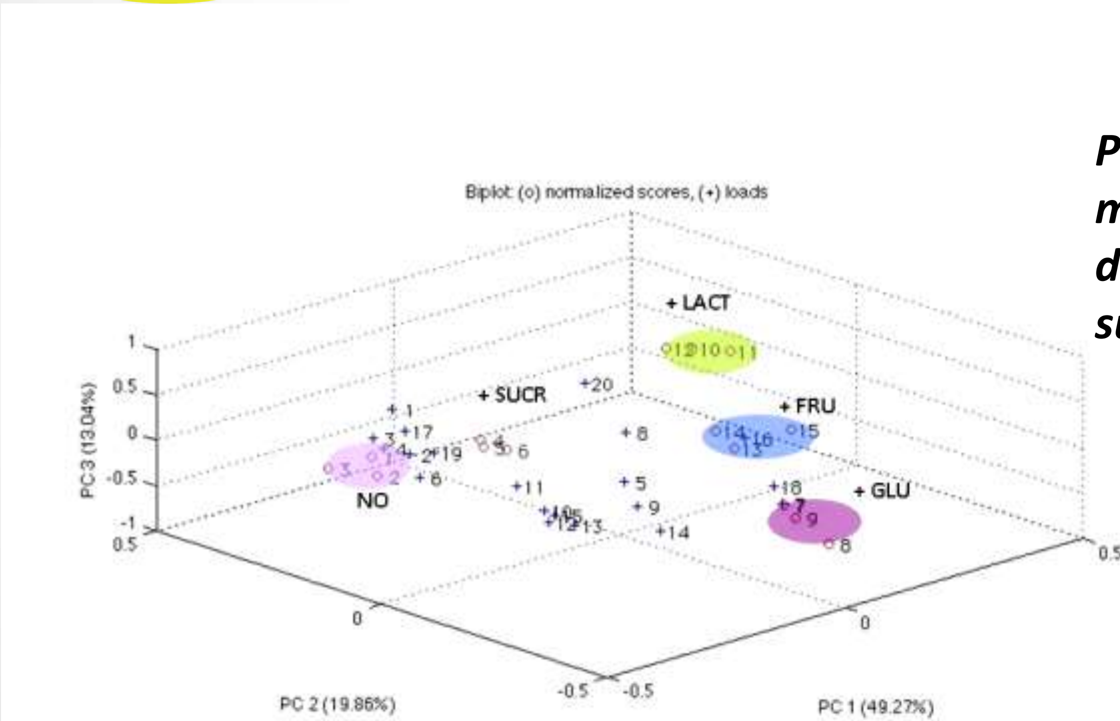
Sensory

Thermodynamic aspects & effects on sensory perception



Plot of the first three PC of the PCA model made with the GC peak area data of RTD on the five differently sugar added coffee RTD


Research article

MASS SPECTROMETRY

Effect of sugars on liquid–vapour partition of volatile compounds in ready-to-drink coffee beverages†

P. Piccone,[a] V. Lonzarich,[b] L. Navarini,[b] G. Fusella[a] and P. Pittia[a]*

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Saccharides & aroma release

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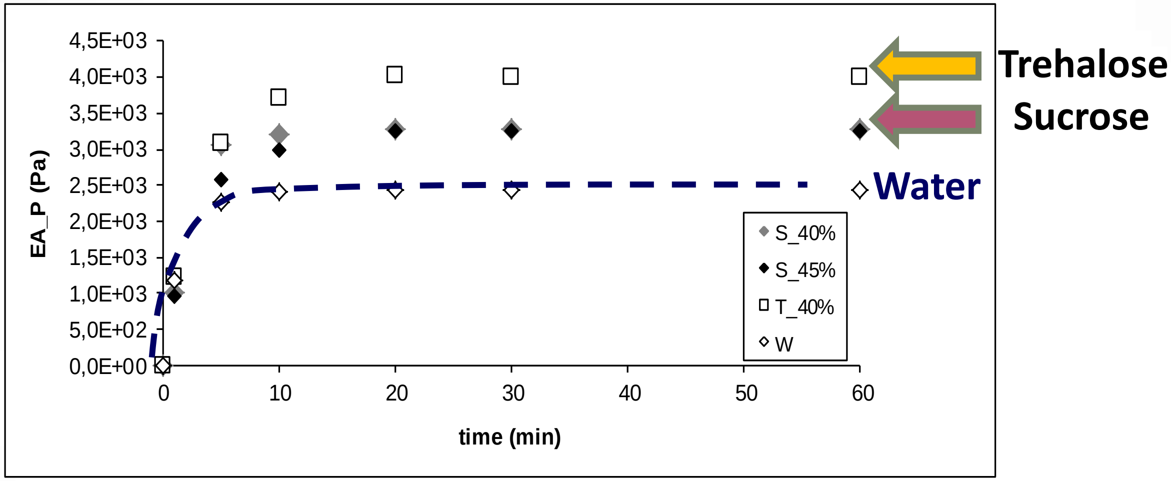
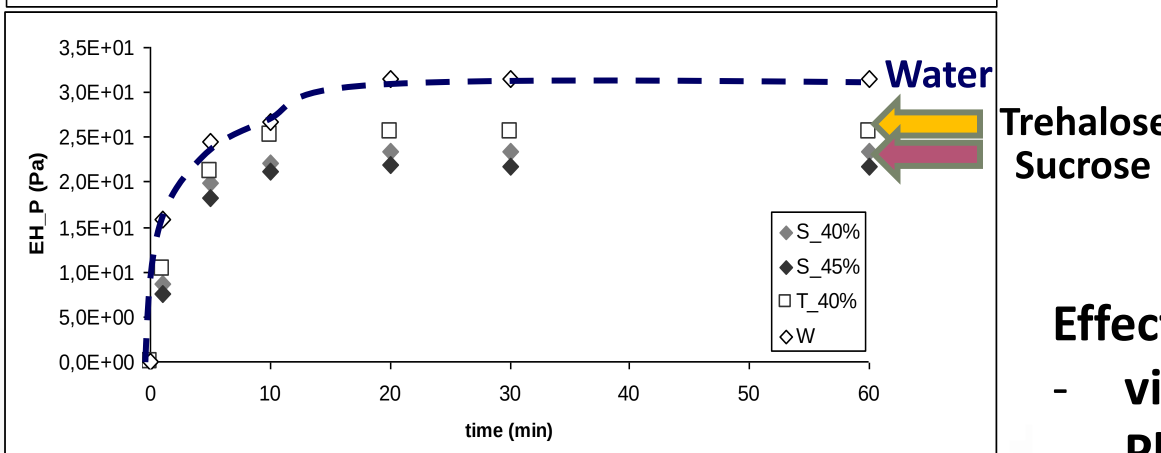
Kinetic aspects

Ethyl acetate



Ethyl hexanoate



Release of ethyl acetate and ethyl hexanoate as a function of time in water and in sucrose (40 and 45%) and trehalose (40%) solution.
W: water; S_40%: sucrose 40%; S_45%: sucrose 45%; T_40%: trehalose 40%; T_45%: trehalose 45%. Pittia et al. (unpublished data)

Effects of:

- **viscosity**
- **Physico-chemical properties of sugar solutions**

Technological functionality of sugars

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Stability

Many effects…

- ❑ Water sorption/binding Capacity (a_w)
- ❑ Osmolarity (inhibiton microbial growth)
- ❑ Physical properties
- ❑ Inhibition enzymatic activity
- ❑ Cryo-, thermo- protectant
- ❑…

Stability: inhibition of enzymatic activity

European FooD-STA

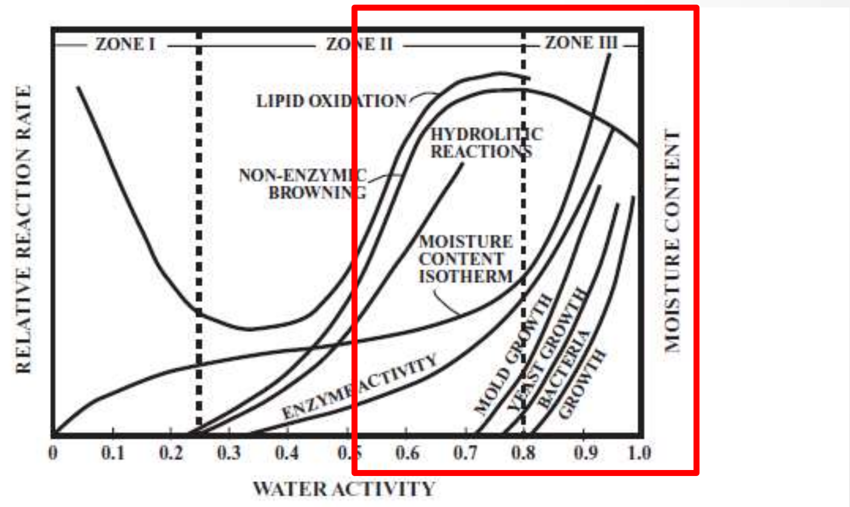
Stability

1 - Osmolarity and water activity

TABLE 5.5 Minimum Water Activities of Some Solutions at Room Temperature

Solute	Solubility (% w/w)	Minimum activity
Sucrose	67	0.86
Glucose	47	0.91
Invert sugar	63	0.82
Sucrose + Invert sugar (37.6:62.4)	75	0.71
NaCl	27	0.74

Karel & Lund, 2003



Labuza, 1970

Stability

2- Glass transition, molecular and system mobility

Effect of molecular size

TABLE 1

Glass Transition Temperatures (T_g), Change of Specific Heat at T_g (Δc_p), Melting Temperature (T_f), and the Ratio of T_f/T_g for Anhydrous Pentoses, Hexoses, Disaccharides and Alditols (Roos, 1993*a*)

Compound	T_g (°C)[a]	Δc_p (J/g °C)	T_f (°C)[a]	T_f/T_g[a]
Pentoses				
Arabinose	−2	0·66	150 (160)	1·56 (1·60)
Ribose	−20	0·67	70 (86)	1·36 (1·42)
Xylose	6	0·66	143 (157)	1·49 (1·54)
Hexoses				
Fructose	5	0·75	108 (127)	1·37 (1·44)
Fucose	26	—	133 (145)	1·36 (1·40)
Galactose	30	0·50	163 (170)	1·44 (1·46)
Glucose	31	0·63	143 (158)	1·37 (1·42)
Mannose	25	0·72	120 (134)	1·32 (1·37)
Rhamnose	−7	0·69	— —	— —
Sorbose	19	0·69	153 (163)	1·46 (1·49)
Disaccharides				
Lactose	101	—	— (214)	— (1·30)
Maltose	87	0·61	— —	— —
Melibiose	85	0·58	— —	— —
Sucrose	62	0·60	173 (190)	1·33 (1·38)
Trehalose	100	0·55	— —	— —
Alditols				
Maltitol	39	0·56	139 (149)	1·32 (1·35)
Sorbitol	−9	0·96	85 (99)	1·36 (1·41)
Xylitol	−29	1·02	89 (95)	1·48 (1·51)

[a]Onset temperatures for the transitions; the values in parenthesis refer to the peak temperature values of the melting endotherms.

Roos, 1995

Stability: inhibition of enzymatic activity

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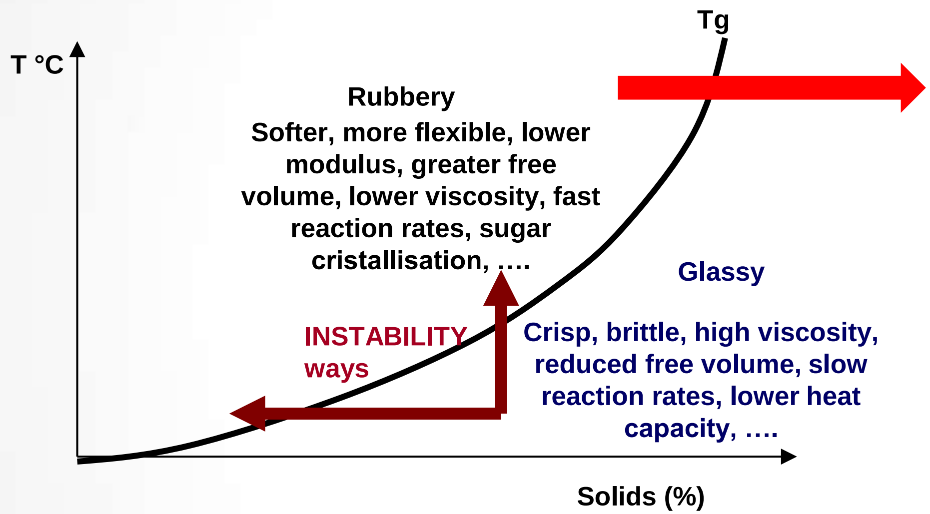
Stability

2- Glass transition, molecular and system mobility



Crystallisation, collapse, caking, softening ….

Labuza, 2002

Effect of moisture

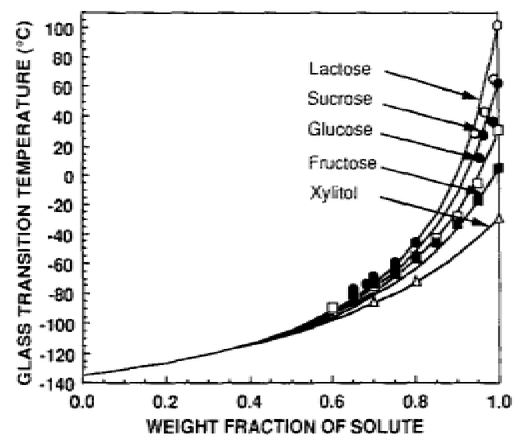


Fig. 2. Glass transition temperatures (T_g) of common mono- and disaccharides as a function of water content according to Roos (1993*a*). Experimental T_g values are indicated with symbols. The T_g curves are calculated with eqn (2) using T_g = 135°C for water (Johari *et al.*, 1987).

Roos, 1995

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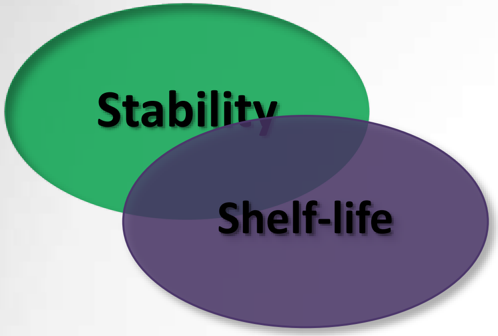
Technological functionality of sugars



Crystallisation state (in sugar-based systems):

- sucrose/glucose (inhibitor) ratio
- moisture

Moisture penetration

Glassy-amorphous structure

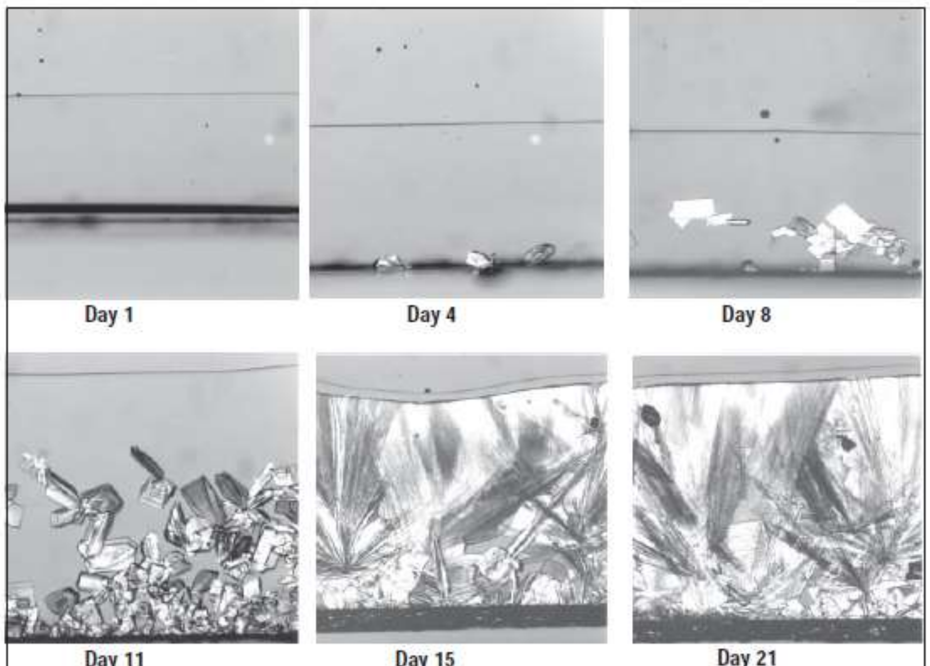


Fig. 1—Penetration of moisture into an amorphous sugar system followed by nucleation and crystal growth. Photos in Figs. 1-3 courtesy of Richard Hartel, University of Wisconsin.

Technological functionality of sugars

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Stability

Shelf-life

Crystallisation state (in sugar-based systems):

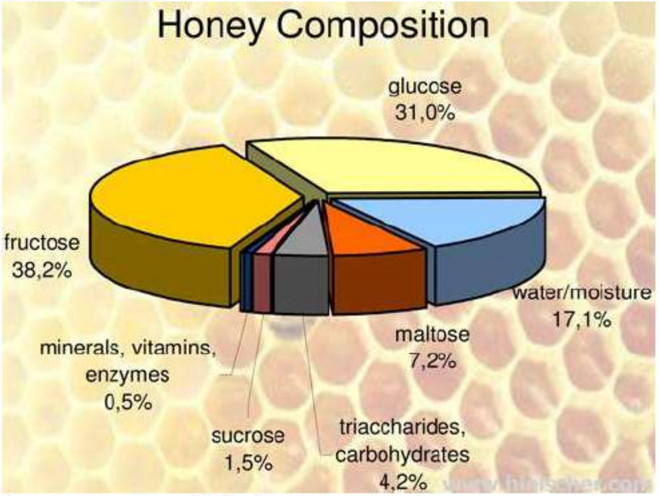

Image source: hielschr.com

Onset of crystallisation and crystal sedimentation

The fructose/glucose balance (depending on origin) affects the tendency of honey to crystallize: higher [glucose] (lower solubility) > crystallisation

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Stability

3 - Effect on enzymatic activity:
Case study: Horseraddish Peroxidase (HRP)

Food Chemistry

Multidisciplinary approach to study the effect of water status and mobility on the activity of peroxidase in solutions

Giampiero Sacchetti, Lilia Neri, Luca Laghi, Francesco Capozzi, Dino Mastrocola, Paola Pittia

SPECIAL ISSUE ARTICLE

Multiple Effects of Viscosity, Water Activity and Glass Transition Temperature on Peroxidase Activity in Binary and Ternary Carbohydrate Solutions

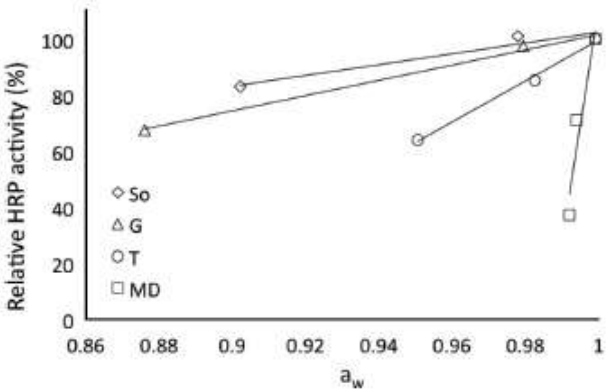

Fig. 1. Relative HRP activity as a function of a_w in 18.56% and 50% w/w sorbitol (So), 16.33% and 50% w/w glucose (G), 27.18% and 50% w/w trehalose (T) and 15% and 30% w/w maltodextrin (MD) solutions. HRP activity and a_w data of sorbitol and maltodextrin solutions were taken from Neri et al. (2010).

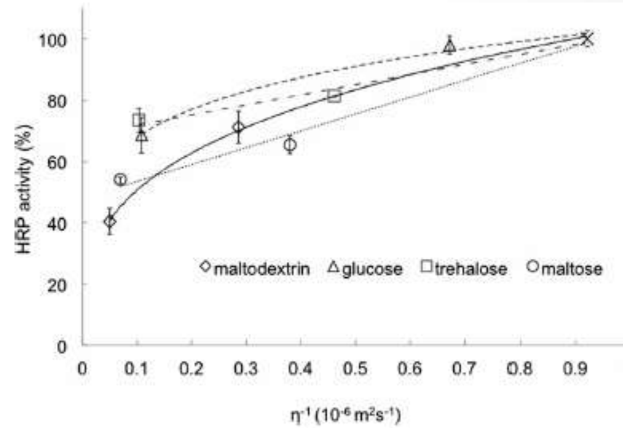

Fig. 1 Horseradish peroxidase activity of maltodextrin, glucose, trehalose and maltose solutions as a function of the inverse of viscosity (η^{-1}) of the system. Phosphate buffer (×), maltodextrin (◊), glucose (▵), trehalose (■), and maltose (○), solutions

Sugars inhibit the HRP activity by both hindering the mobility of the system (increasing viscosity and Tg') and by lowering its a_w.

Stability & preservation

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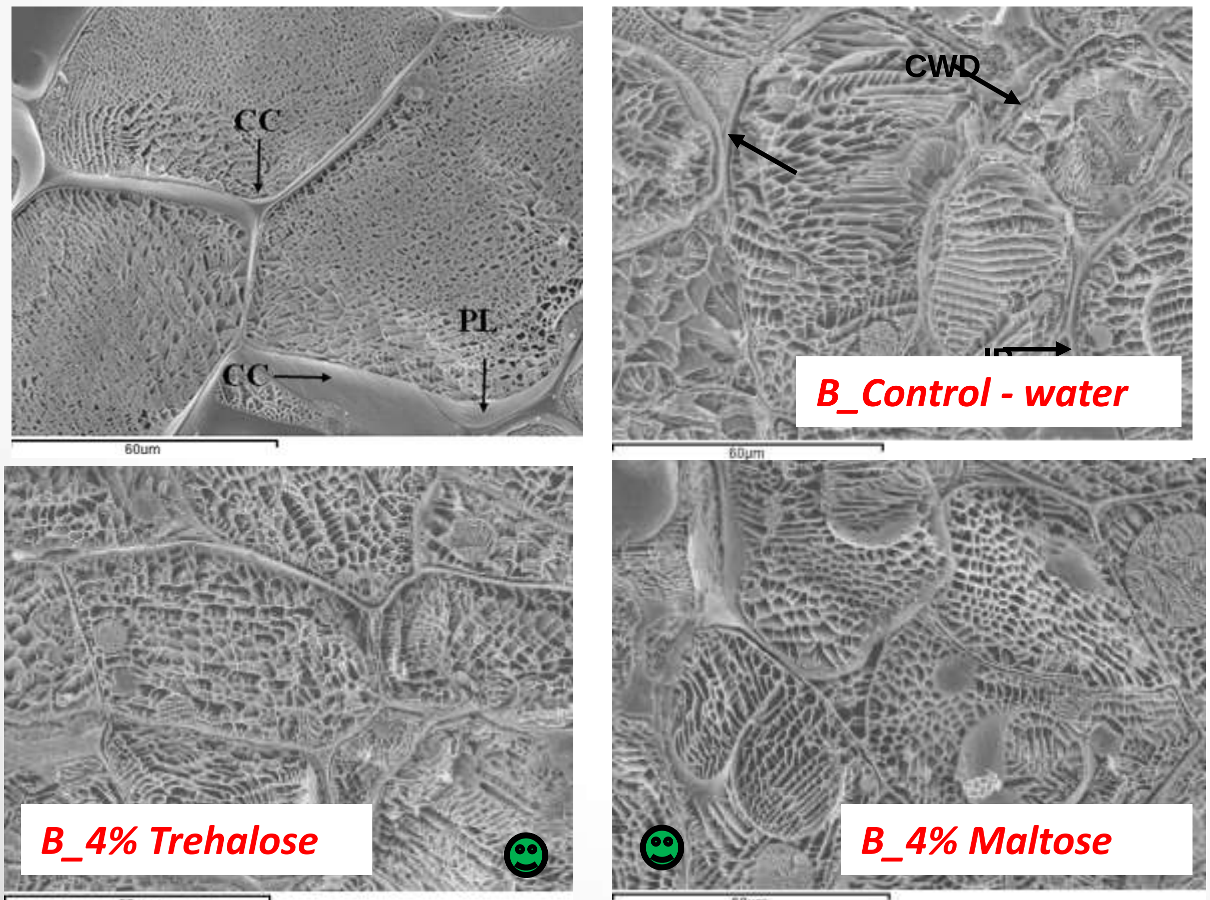
Stability

4- Cryo- & thermo-protectants

Effect of Blanching in Water and Sugar Solutions on Texture and Microstructure of Sliced Carrots



<u>**Blanching**</u> : 90°C, 3min

Cryo-SEM analysis


Food Chemistry

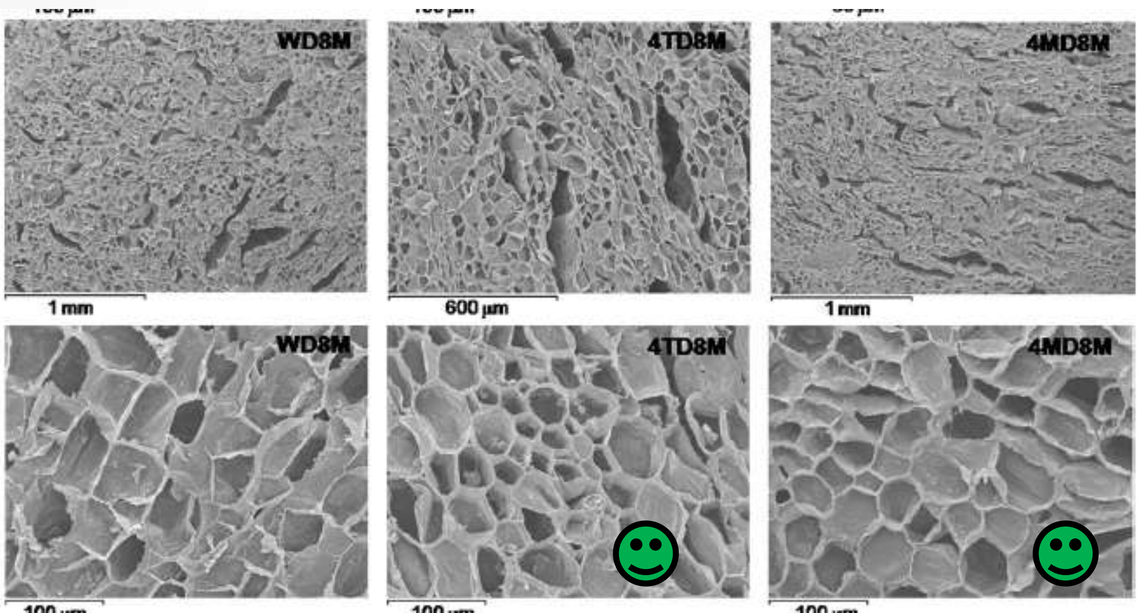
Mechanical properties and microstructure of frozen carrots during storage as affected by blanching in water and sugar solutions

Stability

Shelf-life

4- Cryo- & thermo-protectants

Effect of Blanching in Water and Sugar Solutions on Texture and Microstructure of Sliced Carrots



B_Control -water *B_4% Trehalose* *B_4% Maltose*

Blanching: 90°C x 10 min

Storage: 8 months, -18°C

SEM analysis

Food Chemistry

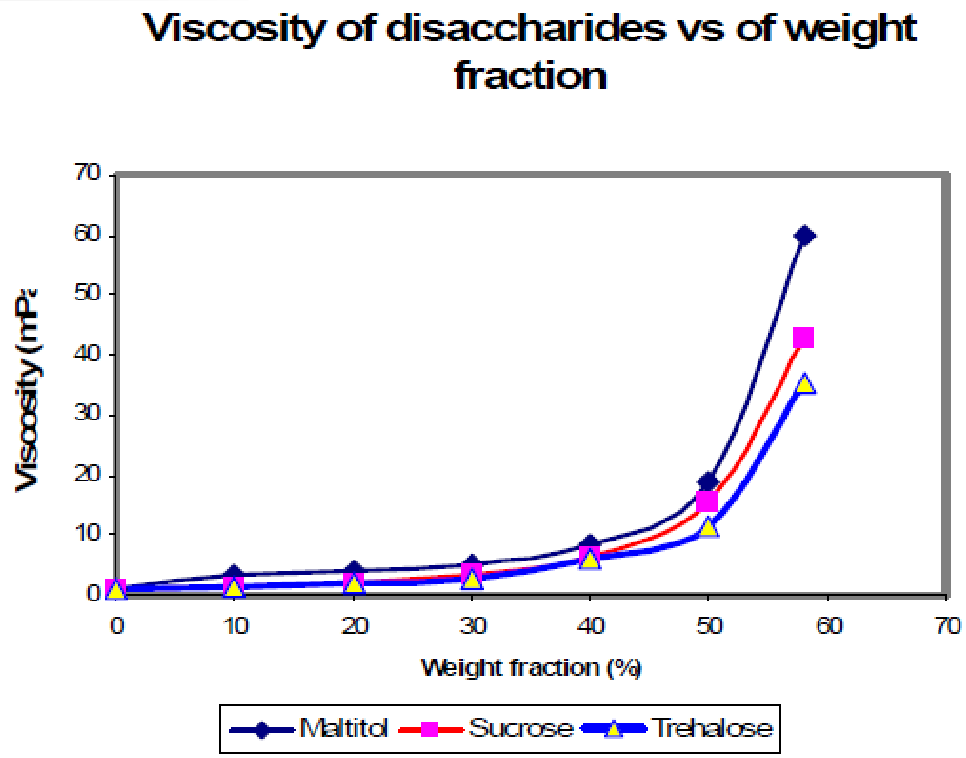
Mechanical properties and microstructure of frozen carrots during storage as affected by blanching in water and sugar solutions

Technological functionality of sugars

European FooD-STA

Structure

- **Physical properties**
  Viscosity



Mathlouthi et al., 2006

Viscosity effect:

- Molecular weight,
- Concentration
- Molecular interactions
- (at higher concentratoions)

Technological functionality of sugars

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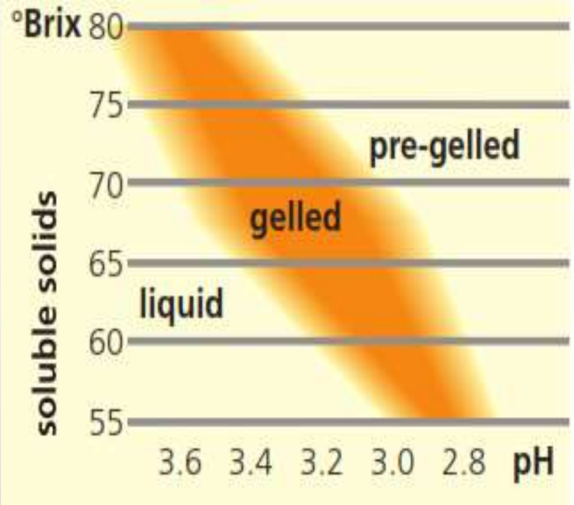
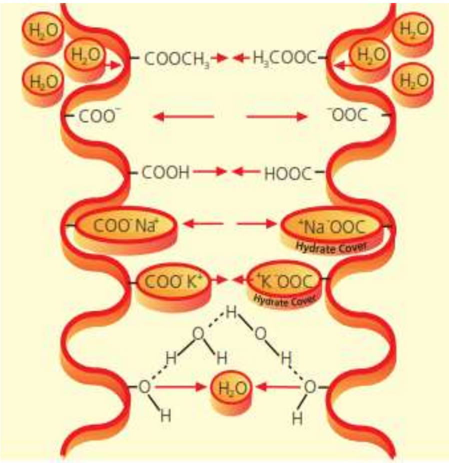
Structure

- **Structures**
  - <u>in combination </u>with:
    - biopolimers **(e.g. pectines = gels)**
    - complex saccharides (MD)

Gelation mechanisms of high-methylester pectins (HM)





Sugars dehydrates pectines and favour the interaction between the pectin chains

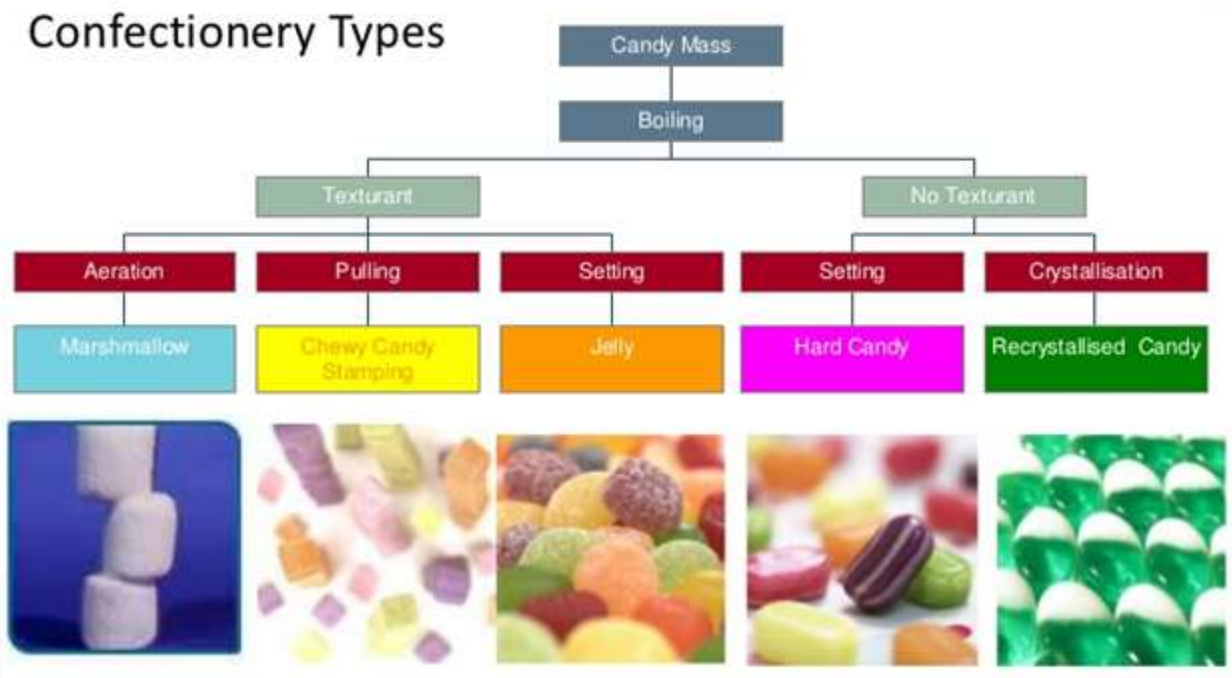
The **<u>pH decrease </u>**decreases the repulsion between the chains with negative charge

Structure

- **Structures**

  - alone: crystals, amorphous systems…

confectionery



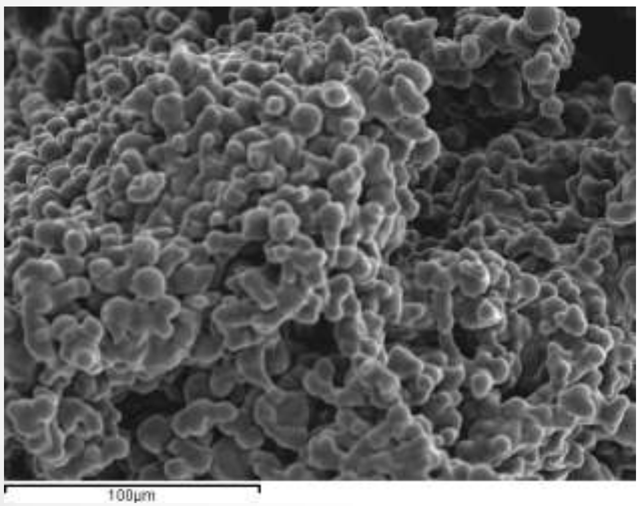
Technological functionality of sugars

Structure

- **Structures**

  - <u>alone</u>: crystals, amorphous systems…

  aroma encapsulation



Spray-dried TREHA 20% + 10 % limonene (aroma retention ca. 15-20 %)
Pittia et al. (unpublished data)

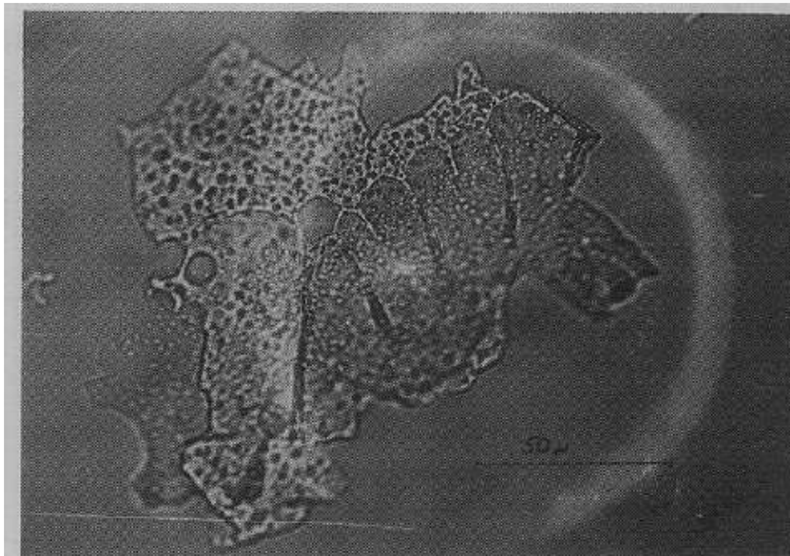


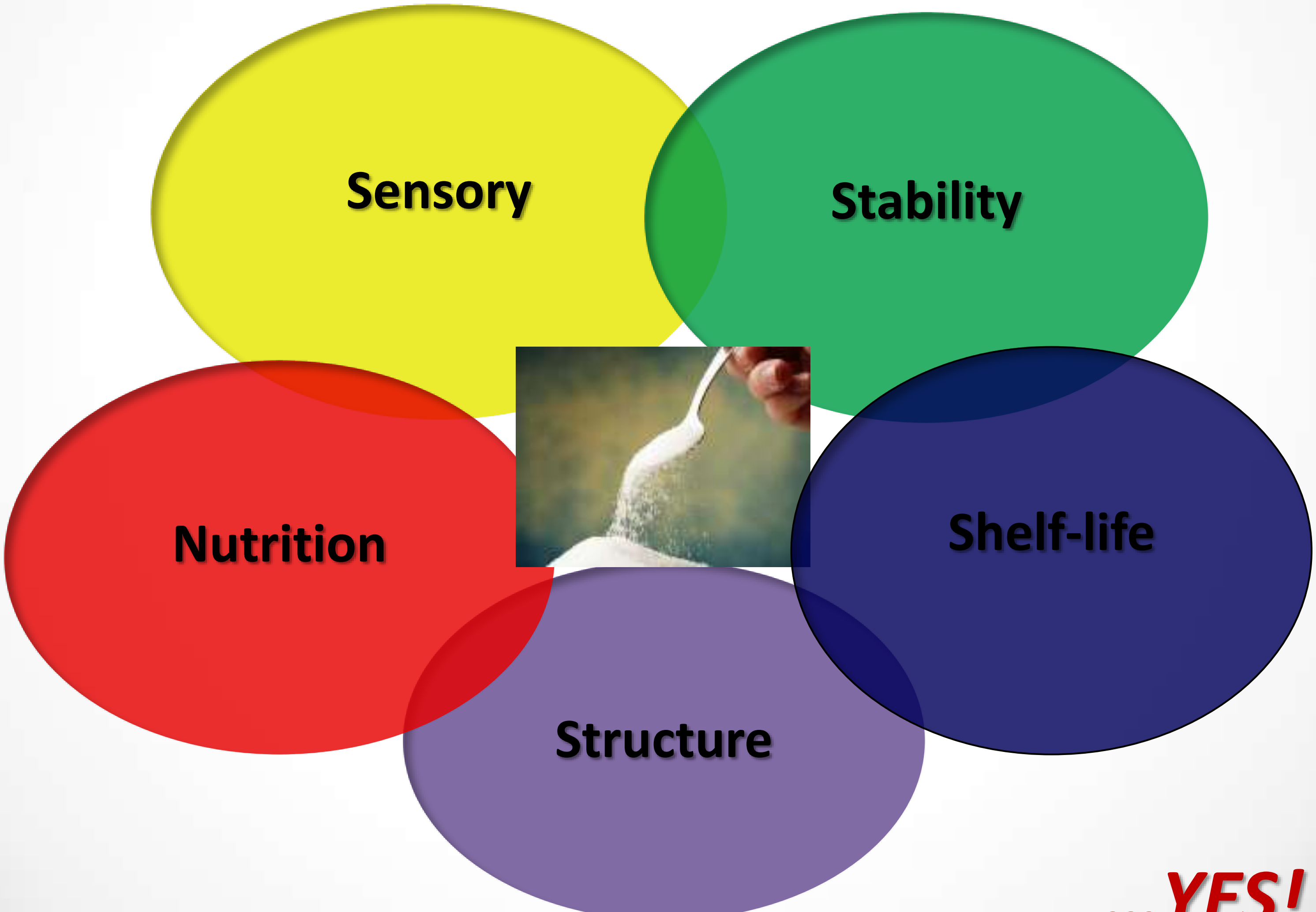
Figure 3. Hexanal droplets in a freeze-dried maltodextrin and hexanal system (400×)

Flink & Karel, 1970

Retention mechanism for volatile during freezing and drying of "microregions" impermeable to the release of the aroma compounds " (entrapping mechanism)

Technological functionality of sugars

…not only sweetness!



…YES!

Technological functionality of sugars

Thanks to….

-the co-workers and co-authors

- colleagues and friends with whom I had/have the pleasure and honour to collaborate with in these studies

- all students and PhD students (past/current)

…you all for your attention!

European FooD-STA

Co-funded by the Erasmus+ Programme of the European Union

UNIVERSITÀ DEGLI STUDI DI TERAMO

ISEKI-Food Association

https://www.iseki-food.net/

We look forward to seeing you soon in Vienna….!

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