

# The Chemistry of Food

## Lecture 3

Chemistry in Context  
06525/06529/06509

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## Browning Reactions

- *Caramelization*



- *The Maillard Reaction*



- Other enzyme-mediated browning reactions can take place, which do not involve sugars - *see lecture 2*

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## FLAVOURS

- We normally associate **taste** as the property of liquids, solids and gases in solution detected by the sensory cells on the **tongue and oral cavity** ....
- ... and associate **aroma** with the volatiles substances detected by the **olfactory system** of the nose.
- Very few **flavours** allow a clear distinction between these two.

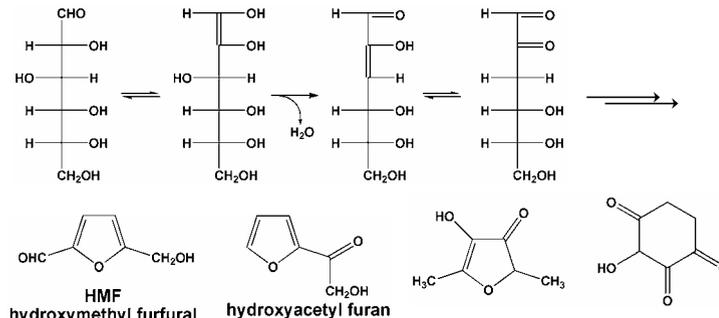
Sweetness  
Saltiness  
Sourness  
Bitterness  
(synthetic flavours)

**Astringency**  
**Pungency**  
**Meatiness**  
**Fruitiness**  
(off-flavours / taints)

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## Caramelization

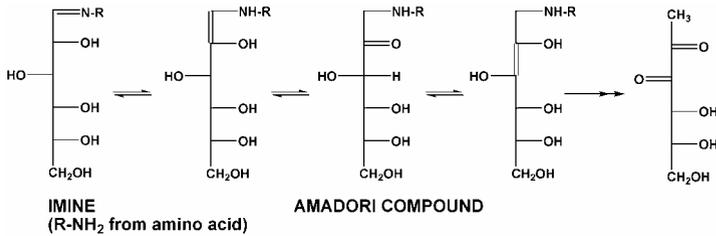
- acid / base catalysed (organic acids / water)
- any sugar – here glucose



**CARAMEL FLAVOURS** 4

# The Maillard Reaction

## AMADORI REARRANGEMENT



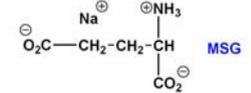
- deamination and further isomerization leads to several reactive **dicarbonyl** compounds (HMF and others)
- cyclic products polymerize to form **brown, insoluble poorly defined high MW materials**.

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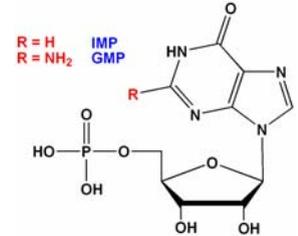
# Meatiness

- Water soluble, non-volatile taste components
  - Known as '*umami*' by the Japanese

- Monosodium glutamate, MSG, *umami*<sub>1</sub>
  - Levels of 10-35 mg/100 g meat

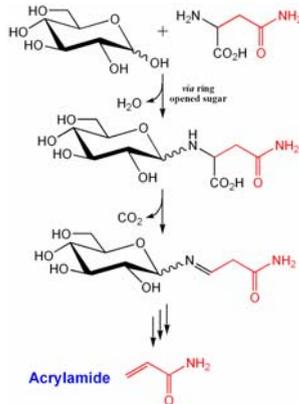


- Inosine monophosphate, IMP, *umami*<sub>2</sub>
  - Levels of 1-200 mg/100 g
  - Also, but less important, GMP (0-10 mg/100 g)



# The Maillard Reaction (continued)

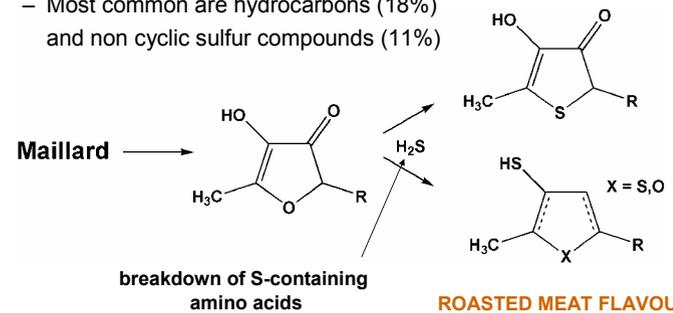
- Acrylamide, a **probable carcinogen** and agent **known to cause neurological damage**, has been detected in many roast and fried foods.
- Believed to arise from the Maillard reaction involving asparagine.
- Levels detected very variable, but best technique for extraction and analysis still a matter of debate.



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# Meatiness

- Many volatile aromas present in meats
  - Over 650 identified in beef
  - Most common are hydrocarbons (18%) and non cyclic sulfur compounds (11%)



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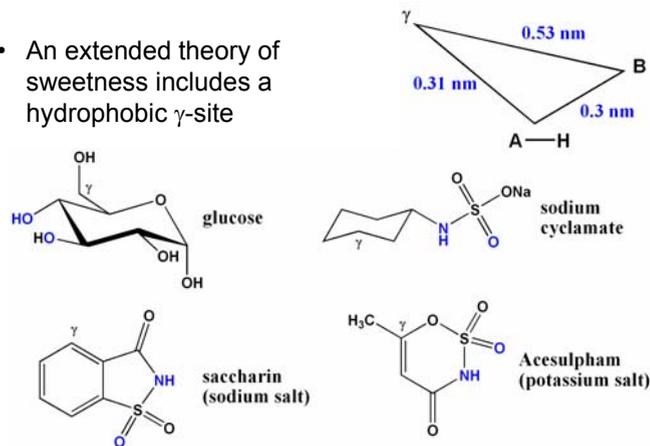
## Sweetness

- Sweetness is found in many types of molecules (not just sugars), and relative sweetness is normally compared to sucrose
- Natural sugars
  - sucrose (1.0); glucose (0.76); fructose (1.52)
- Also artificial sweeteners
  - sodium cyclamate (30); acesulpham K (140); aspartame (200); saccharin (350); 1-*n*-propoxy-2-amino-4-nitrobenzene (4000)

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## Extended theory

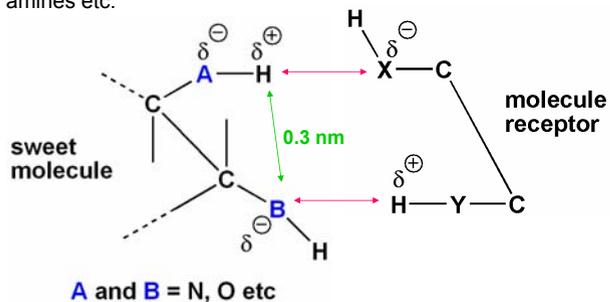
- An extended theory of sweetness includes a hydrophobic  $\gamma$ -site



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## Schallenberg's "saporous unit" theory

- Sweet molecules contain H-bonding groups such as hydroxyls, amines etc.



- Geometry of so-called "saporous" units crucial for interaction with a "sweetness" receptor

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## Sourness

- Sourness *assumed* to be linked with acidic solutions
- However the presence of unionized organic acids (i.e.  $R-CO_2H$ ) is more important for the taste of sourness
  - citric, malic, tartaric (grape), isocitric, oxalic, acetic, lactic
- In foods:
  - Sourness of vinegar due to **acetic acid**, but also adds importantly to aroma, such as with fish and chips
  - Lactic acid** in pickled foods such as sauerkraut comes from bacterial fermentation of the sugars in the vegetables
  - Sodium lactate** is used in salt and vinegar flavoured crisps

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## Bitterness

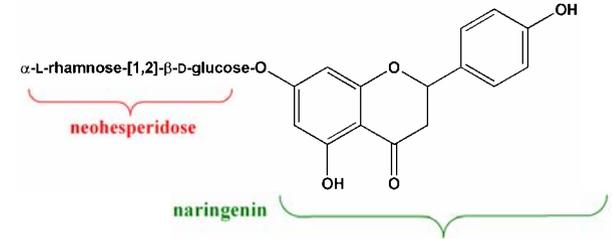
- Several classes of compounds exhibit bitterness
- Taste buds at back of tongue responsive to
  - group 1 and 2 halide salts
  - certain phenolics
- KBr is both salty and bitter
  - Halide salts with the sum of their ionic diameters greater than KBr are **bitter**, if the sum is less then they are **salty**

NaCl (0.556) < KBr (0.658 nm) < KI (0.706) < MgCl<sub>2</sub> (0.850)

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## Phenolics: *Seville oranges*

- **Phenolics** in the form of flavanoids are source of bitterness in citrus fruits.
  - **Naringin** is a bitter sugar-flavanone conjugate found in Seville oranges. Its bitterness is detected at 1:50,000 dilution.



- The non-sugar unit attached to sugar known generally as the **aglycone**
- Here the sugar is **neohesperidose**, and the **aglycone** is **naringenin**

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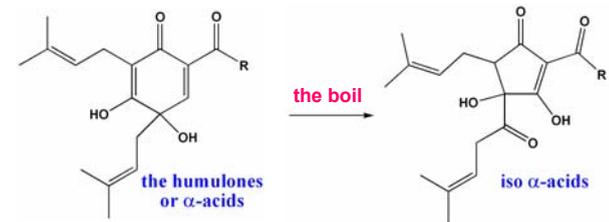
## Bitterness

- Many plants contain molecules which we perceive as very bitter
  - Nicotine, atropine, emetine, quinine
- Role in plants unknown.....
  - but many have undesired pharmacological properties
  - **physostygmine (eserine)**
- Animals' ability to perceive these have undoubtedly evolved to avoid eating these plants
  - Quinine antiplasmodial agent used to **prevent and cure malaria** by consumption of **tonic waters**

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## Phenolics: *beer*

- Before the fermentation stage of the brewing process, the flowers of the hop plant, *Humulus lupulus*, are added to the wort
- Hops are added to add both flavour and bitterness

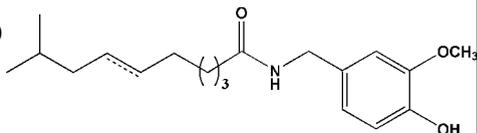


- The **humulones** are converted to the more soluble and more bitter **iso α-acids** in the boil

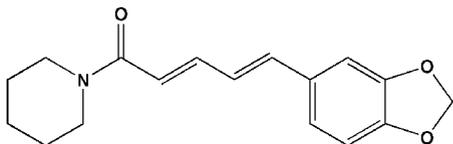
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## Pungency: chillies, peppers, ginger

- Chillies  
(*Capicum frutescens*)  
– Capsaicin and dihydrocapsaicin



- Black pepper  
(*Piper nigrum*)  
– Piperine

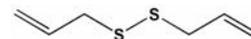


- Ginger  
(*Zingiber officinale*)  
– Gingerols and shogaols – ketones similar to capsaicin with hydroxy or alkene groups in a variable length aliphatic side chain

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## Pungency: onion and garlic

- Garlic and onions – belong to *Allium* species
- Early (19<sup>th</sup> century) studies using steam distillation isolated **non-odorous** species
  - Gave rise to trivial name of 'allyl' for the prop-1-enyl unit



garlic oil

allyl disulfide



onion oil

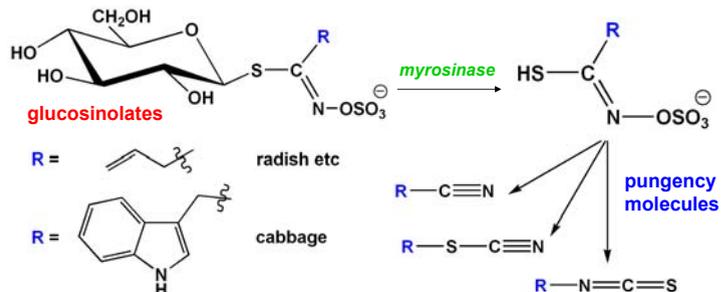
propionaldehyde

- Gentler extraction processes (lower temp, ethanol as solvent) isolated more interesting molecules!

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## Pungency: mustards and brassica

- Pungency in certain raw vegetables [mustards, (horse)radish, cabbages etc.] are due to thiosugar derivatives – **glucosinolates**

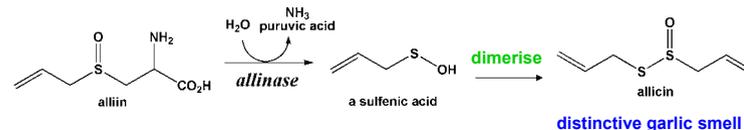


- When cells are damaged, such as in cutting or chewing, the action of **myrosinase** triggers the breakdown of **glucosinolates**

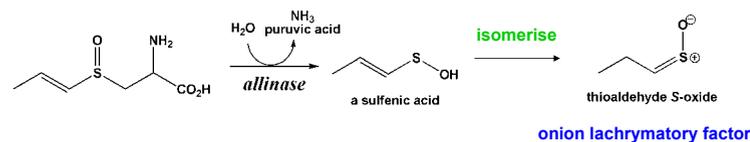
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## Pungency: onion and garlic

- Garlic:** on cell rupture **allinase** reacts with alliin, a derivative of the amino acid cysteine



- Onion:** **allinase** reacts with an isomer of alliin



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## Conclusions

- Carbohydrates: saccharides
- Proteins: amino acids and peptides
- Lipids: oils and fats
- Colourings
- Flavour chemicals

.....affect the physical and chemical properties, and of course our enjoyment, of foodstuffs