

Maillard chemie, hart van smaak: chocola tot vlees!

Woudschoten chemie conferentie 8 Nov 2024

"Chemie smaakt naar meer"

Jan Koek, Unilever, scientist flavour Chemistry

11/11/2024



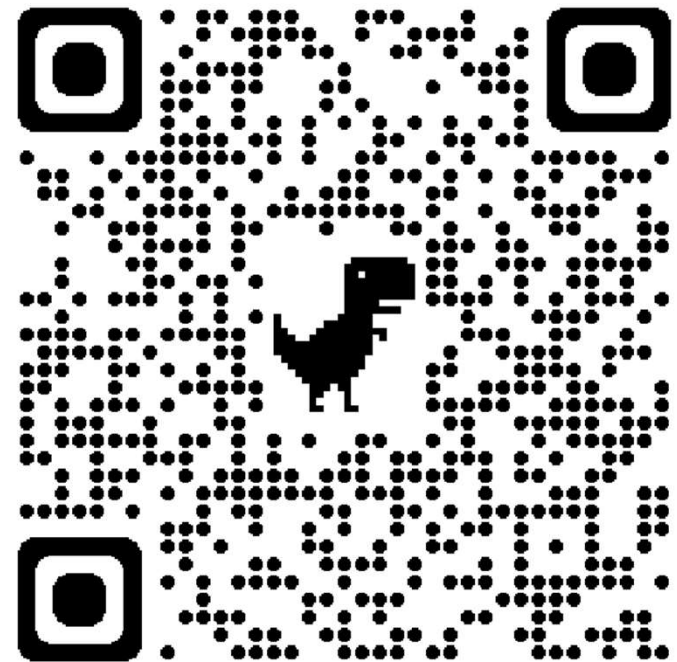
Interactive lecture Quiz

Participation

<https://b.socrative.com/login/student/>

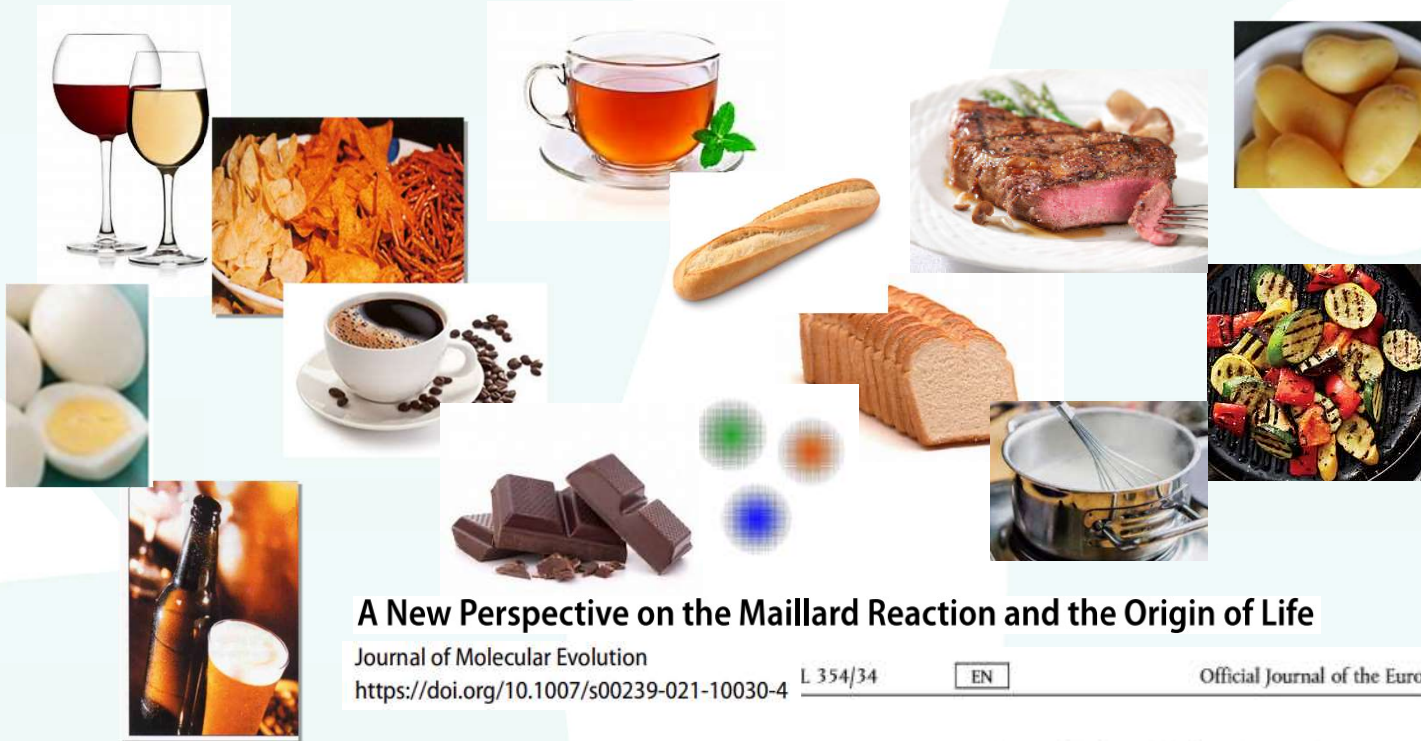
Room: KOEK6129

<https://b.socrative.com/login/student/>



De Maillard reactie

Bij voedselbereiding (koken, bakken, roosteren, fermentatie, veroudering)
Vorming van smaak en aroma via CHEMISCHE REACTIES = Aminozuur + Red.Suiker



[Louis Camille Maillard](#)

A New Perspective on the Maillard Reaction and the Origin of Life

Journal of Molecular Evolution
<https://doi.org/10.1007/s00239-021-10030-4>

L 354/34

EN

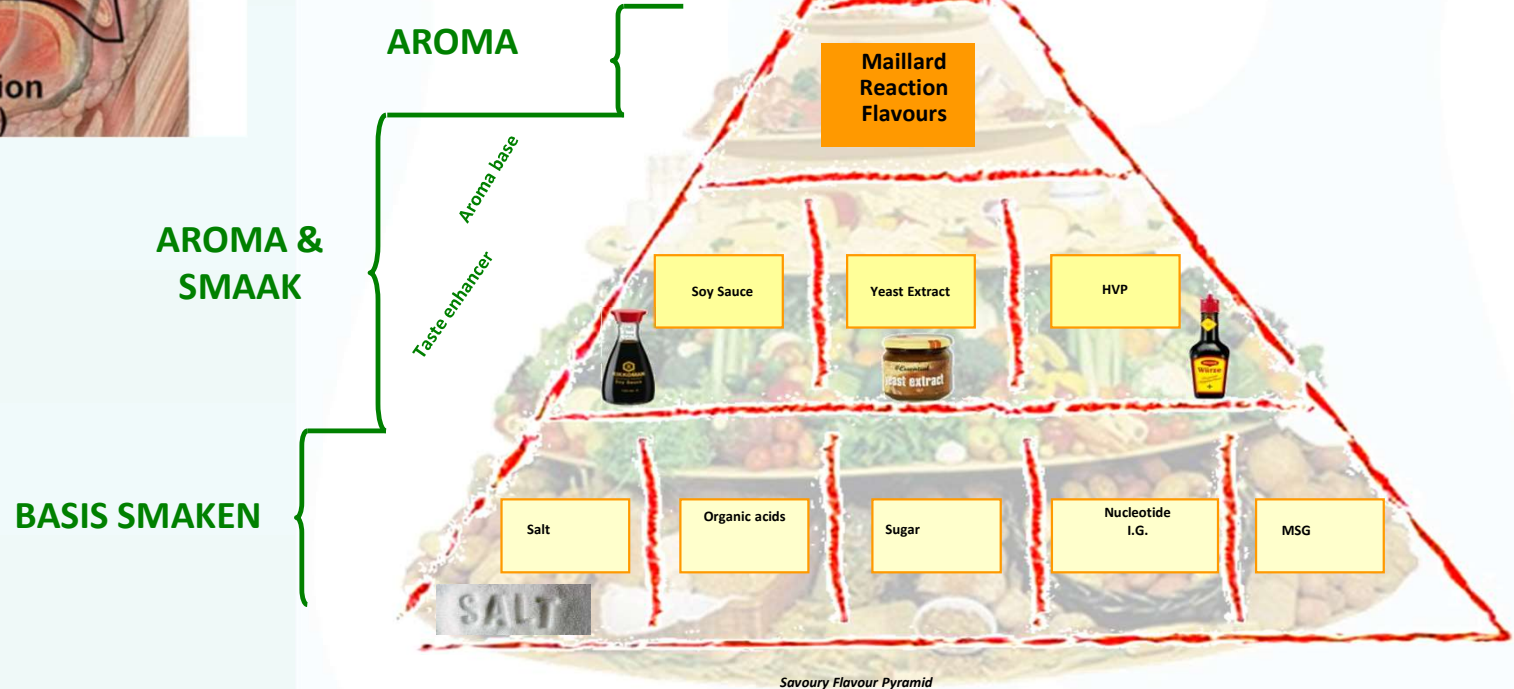
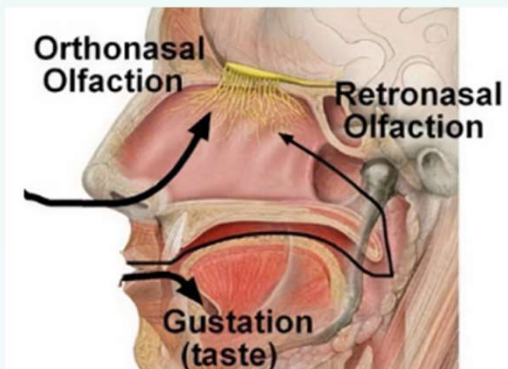
Official Journal of the European Union

31.12.2008

REGULATION (EC) No 1334/2008 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL
of 16 December 2008

on flavourings and certain food ingredients with flavouring properties for use in and on foods and
amending Council Regulation (EEC) No 1601/91, Regulations (EC) No 2232/96 and (EC) No 110/2008
and Directive 2000/13/EC

De smaak pyramide



Ruiken en oordelen

Glycine	Leucine	PhenylAla	Methionine	Cysteine	Leu+Ala

Verhit ca 50 ml waterige oplossing bij ca 90 C in afgesloten glazen pot voor ca 1 uur
4 g Na_2HPO_4
4 g Xylose
3 g Amino zuur (Leucine lost niet goed op)
2g + 2g combinatie amino zuren

De pH hoeft niet ingesteld, temperatuur hoeft niet exact, i.p.v. wegen ook 'schempjes'
1e practicum uur maken oplossingen, 2e practicum uur ruiken, ook van elkaars oplossingen
Ook kleurverschillen zichtbaar. Eventueel pH voor en na laten meten (met stripje?)
Goed herkenbare voedsel aroma's (lekker en vies??)

Basis vlees flavour: Umami (Yamaguchi vergelijking)

Umami is een vd 5 basis smaken, **maar proef je pas goed met zout erbij**

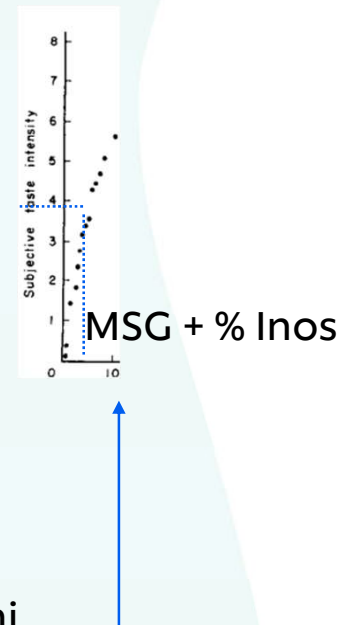
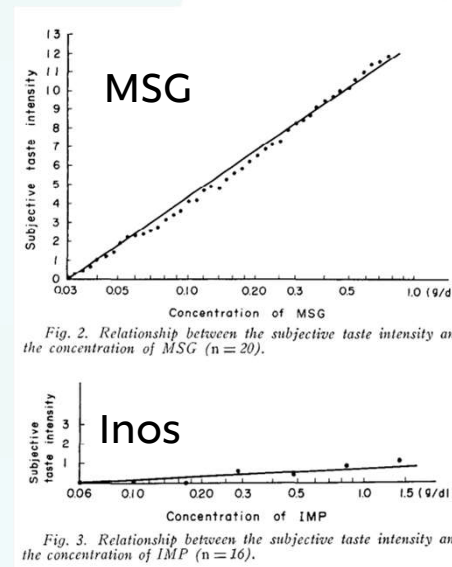
Bv 2 gram /L MSG met 5 gram NaCl sterk umami, zonder zout veel minder umami

Met **RiboNucleotide** Inosinaat / Guanylaat (zelf geen umami smaak) **verder versterken**

SHIZUKO YAMAGUCHI
Central Research Laboratory, Ajinomoto Co. Inc.
Suzuki cho, Kawasaki, Japan

The Synergistic Taste Effect of Monosodium Glutamate and Disodium 5'-Inosinate

JOURNAL OF FOOD SCIENCE-Volume 32 (1967) pg 473-477



Wij vinden in zout water: 1 g/L MSG + 50 mg/L Inos = ongeveer 4g/L MSG umami

Socratic question 1

What would be reasons for cooking / heating our food for preparation:

Answer:

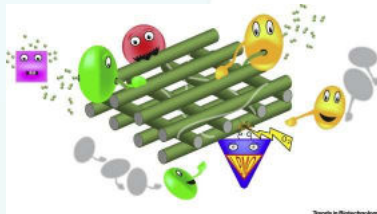
- Making food digestible (e.g. undercooked beans cannot be safely consumed)
- Making food hygienic (beer in Medieval Time safer to drink than water)
- Making food attractive (colour, aroma)



Welke stoffen zijn belangrijk om Maillard reacties te krijgen? Bv in Vlees geven ze aroma* en smaak**

Vers vlees, nog enzym activiteit bij 'besterven':

- Eiwitten => peptides => aminozuren*'*
- RNA => nucleotides** => ribose* & fosfaat*
- Gycogen => suikers (glucose*) => org. zuren**
- Membranen/vetten => (fosfo)lipiden => vetzuren* => aldehyden**

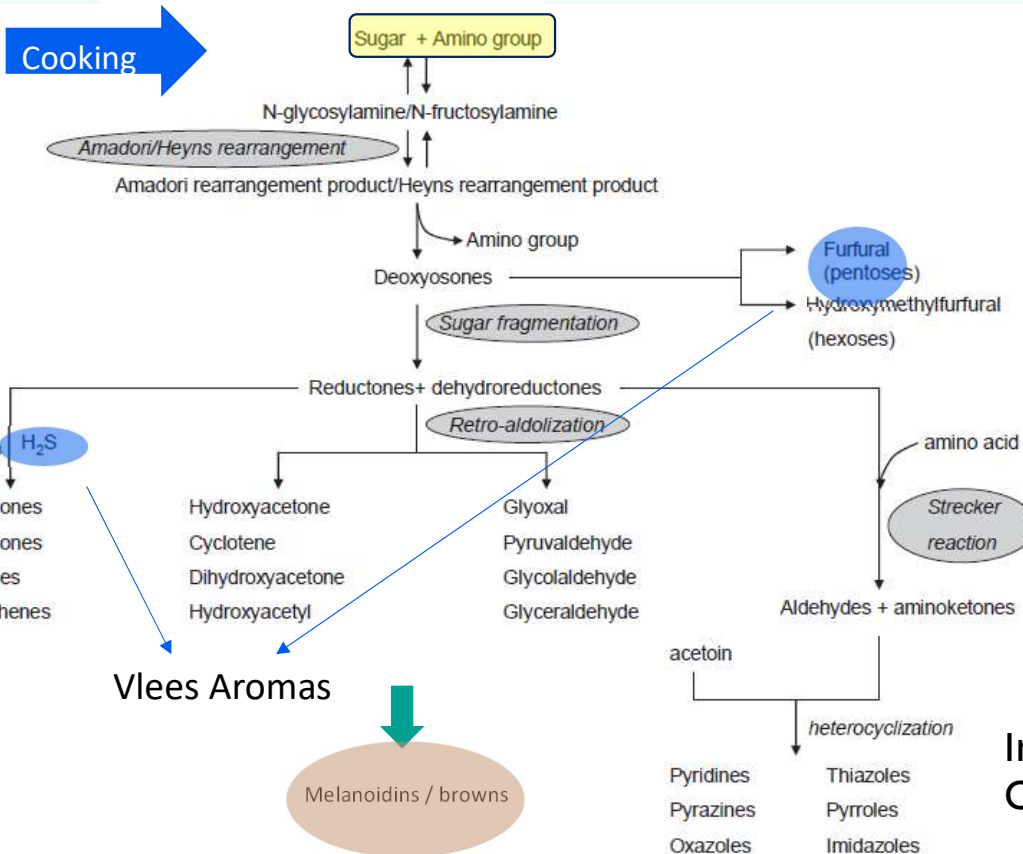


Smakeloos, moeilijk eet & verteerbaar,
microbiologisch risico

Lekker, voedzaam, veilig

Aroma: De Maillard reactie in detail (vlees)

Sugars, Amino-acids,
Phosphate, Org.Acids
Fatty Acids, Aldehydes



Zeer complex!
Gevormde producten
Reageren verder!!

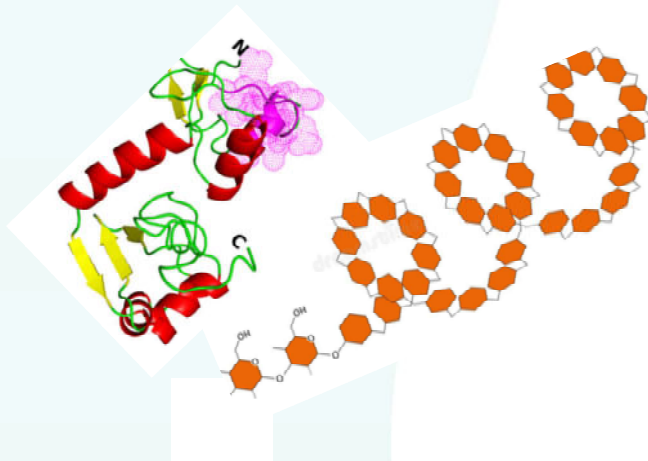
Indien geen **Cys**
Geen **S** geen Vlees

Socratic question 2

Heating of a protein with starch will give a Maillard reaction: False – True?

Answer:

- False: Only the free (non-bound) amino acids and non bound sugars are reactive. Not when bound in polymer.



However lysine in protein has a free amino group which might react e.g.

Diabetes Patients =>

Advanced Glycemic Endproducts (AGE)

BBA - Molecular Basis of Disease 1868 (2022) 166283

Comparison of bovine serum albumin glycation by ribose and fructose *in vitro* and *in vivo*

Lixian Mou^{a,b,d,e,f,1}, Pingdong Hu^{b,1}, Xiao Cao^{a,b}, Yue Chen^{d,e,f}, Yong Xu^a, Tao He^a, Yan Wei^b, Rongqiao He^{a,b,c}

Advanced glycation end products (AGEs) play a critical pathogenic role in the development of **diabetic** complications. Recent studies have shown that **diabetes** is associated with not only abnormal glucose metabolism but also abnormal ribose and fructose metabolism, although glucose is present at the highest concentration in humans. The glycation ability and contribution of ribose and fructose to **diabetic** complications remain unclear. Here, the glycation ability of ribose, fructose and glucose under a mimic physiological condition, in which the

Socratic question 3

The browning of apples after having a bite is a Maillard reaction: False – True?

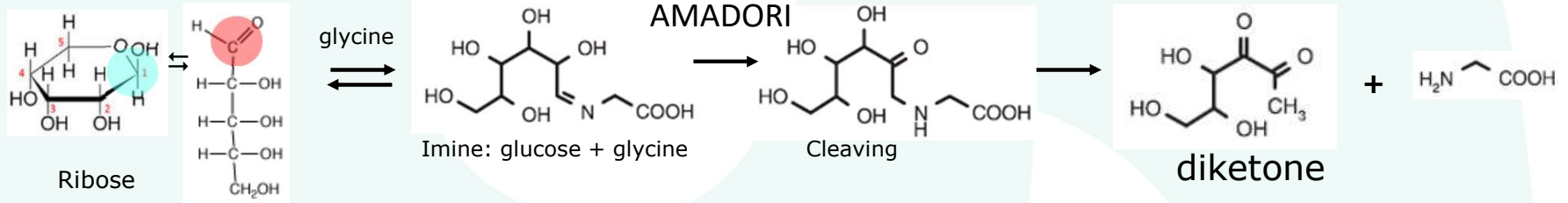
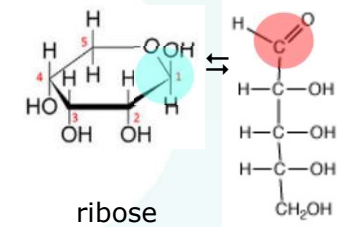
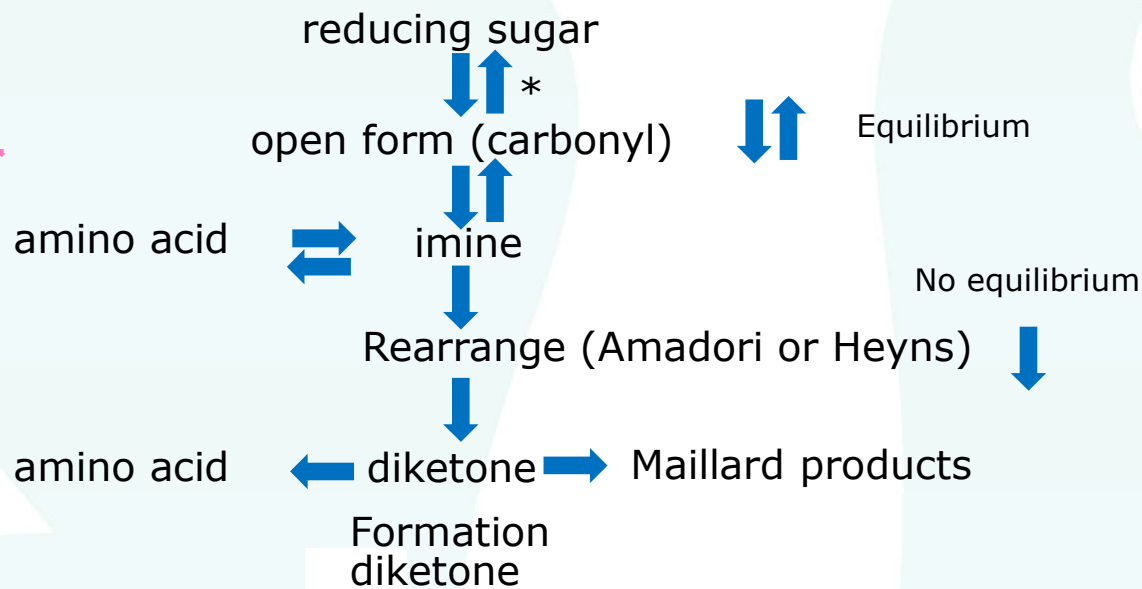
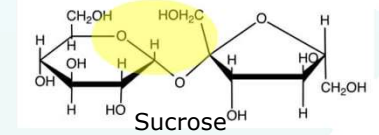
Answer:

- False: Browning already fast at room temperature and is caused by enzymatic polyphenol oxidation. No amino acids required.



Van suiker (aldehyde) naar reactieve diketon

Alleen reducerende suikers (open vorm). Sucrose niet (geen open vorm)



Socratic question 4

Starch is a reducing sugar : False – True ?

Answer:

- False: only the glucose monomer at the end have a reducing group, but almost all glucoses are connected via their reducing group and hence not have a free reducing group (1 in 1000)



Socratic question 5

Browning is a Maillard reaction. A cake baked with reducing sugar fructose will have:

Answer:

- Dark brown / blackened, burned aroma



no colour, no aroma



colour, no aroma



Blackened, burned aroma

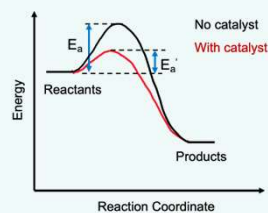
Socrative question 6

What is the role of the amino acid in the formation of diketones from reducing sugars:

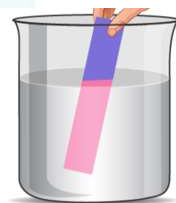
Answer: Catalyst - The amino acid is involved in the reaction but returns unchanged



Buffer



Catalyst



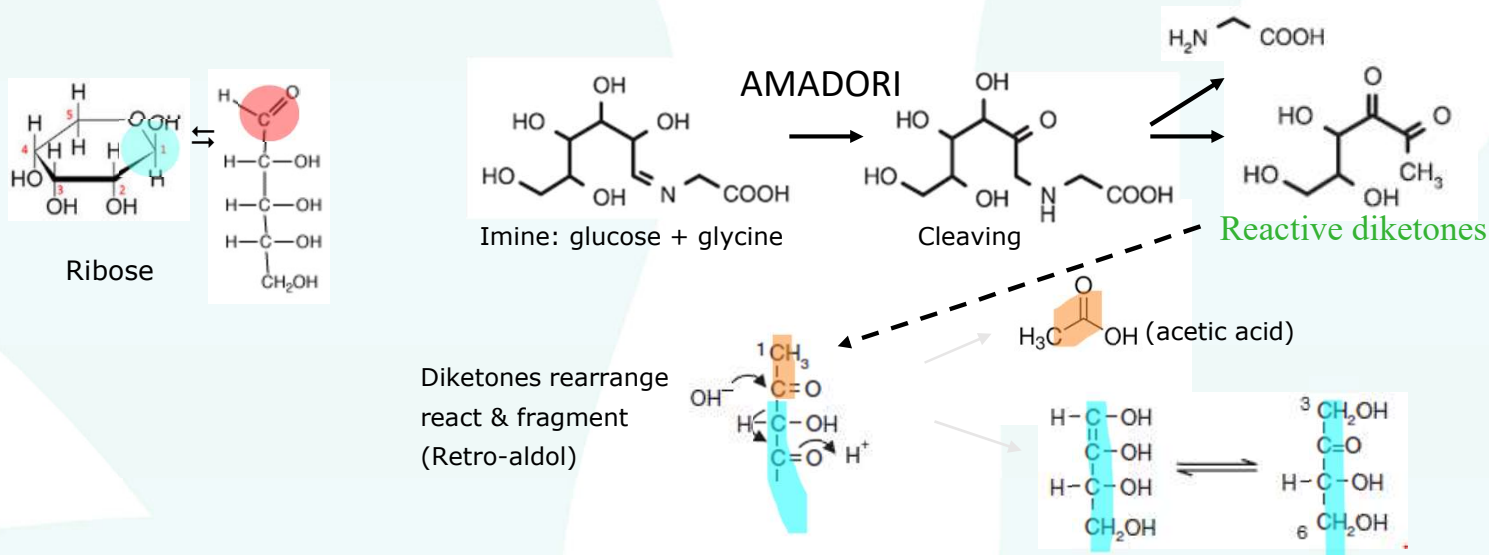
Acid



Oxidant

Diketonen => Fragmentatie (retro-aldol)

Reducing sugars can have a keto or aldehyde group (e.g. ribose) => Imine => Amadori

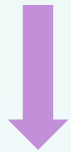


Socratic question 7

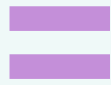
What pH change would you expect with fragmentation:

Answer:

- pH drop: Formation of acid so pH drop



Drop



Same



Rise

Socratic question 8

Type of amino acid important for caramel formation: False – True?

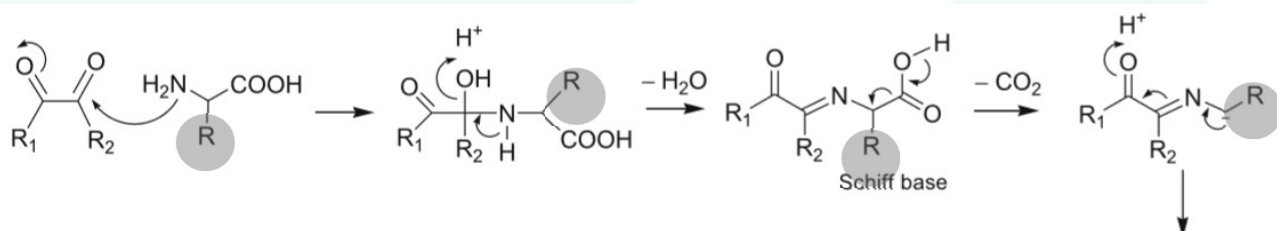


Answer:

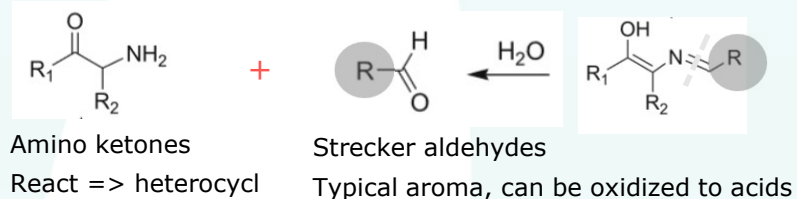
- All amino acids lead to these type of products, even ammonia can be used

Diketones: Amino acids – Strecker

Amadori/Heyns $\Rightarrow$ Release of amino acid $\Rightarrow$ Diketones
 Catechol type oxidation (e.g. in Tea polyphenols) $\Rightarrow$ Diketones



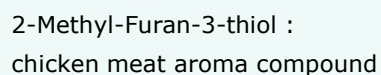
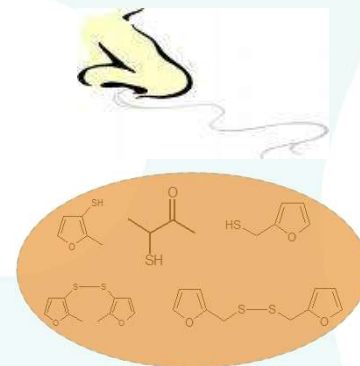
Cysteine $\Rightarrow$ H_2S
 Important for meat aroma's



<chem>CC(C)C(N)C(=O)O</chem> Valine	$\rightarrow$ <chem>CC(C)C=O</chem> Isobutyraldehyde	fresh aldehydic herbal green malty
<chem>CC(C)C(C)C(N)C(=O)O</chem> Leucine	$\rightarrow$ <chem>CC(C)C(C)C=O</chem> Isovaleraldehyde	fruity dry green chocolate nutty leafy cocoa
<chem>c1ccc(cc1)C(N)C(=O)O</chem> Phenylalanine	$\rightarrow$ <chem>c1ccc(cc1)C=O</chem> Phenylacetaldehyde	green sweet floral hyacinth clover honey cocoa
<chem>CC(C)C(N)C(=O)O</chem> Isoleucine	$\rightarrow$ <chem>CC(C)C(C)C=O</chem> 2-Methylbutanal	musty cocoa coffee nutty
<chem>CSCC(N)C(=O)O</chem> Methionine	$\rightarrow$ <chem>CSCC=O</chem> Methional	musty tomato, potato, vegetative, mold ripened cheeses, onion, beefy brothy and egg and seafood nuances

Na verhitten combinaties van geuren: Voedsel veel verschillende aminozuren

Unilever



Socratic question 9

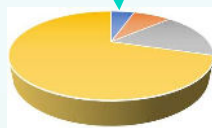
Why are sulfur compounds important for meat aroma:

Answer:

- Some sulfur compounds important for meat have a very low threshold)



Sulfur Compds
More abundant



Some Sulfur Compds
Low Threshold



All Sulfur Compds
Low Threshold



No Sulfur Compds
in Vegetables

Unilever first with
'vegan' meat aroma

2,934,437
FLAVORING SUBSTANCES AND THEIR PREPARATION
Ian Douglas Morton, Bedford, Philip Akroyd, Rushden, and Charles Gerard May, St. Neots, England, assignors to Lever Brothers Company, New York, N.Y., a corporation of Maine
No Drawing. Application November 12, 1958
Serial No. 773,197
Claims priority, application Great Britain April 7, 1955
20 Claims. (Cl. 99—140)
The present invention provides, therefore, a process for making a flavoring substance which comprises reacting a pentose or hexose monosaccharide with cysteine or cystine in the presence of water at an elevated temperature until a flavoring substance having the aroma and flavor of cooked meat is formed.

A circular diagram mapping 18 food descriptors to their corresponding chemical structures. The descriptors are arranged in a circle around a central white circle. Starting from the top and moving clockwise, the descriptors and their chemical structures are:

- ONION: CCSCCSCC
- GREEN, GRASSY: CC(=O)CC
- HERBACEOUS: CC(=O)CC
- SPICY: C1CCN(C1)C2=CC=CC=C2C3C(C)C(C)C3
- FRUITY, ESTER-LIKE: CC(=O)OC
- TROPICAL: CC(C)C1=CC=CC=C1C1
- BLACKCURRANT, CASSIS: CCOC1=CC=CC=C1C1
- VEGETABLE: CC(=O)CC
- NUTTY: CC(=O)CC
- CARAMEL: O=C1C=CC(=O)O1
- SMOKY: O=C1C=CC(=O)O1
- BURNT, ROASTED: O=C1C=CC(=O)O1
- BEEFY: CC(=O)CC
- PORK, LAMB, CHICKEN: CC(=O)CC
- SAVOURY, BOUILLON: CC(=O)CC
- FATTY: CC(=O)CC
- RANCID, CHEESY: CC(=O)CC
- MUSHROOM, EARTHY: CC(=O)CC
- TRUFFLE: CC(=O)CC
- GARLIC: CCSCCSCC
- ONION: CCSCCSCC

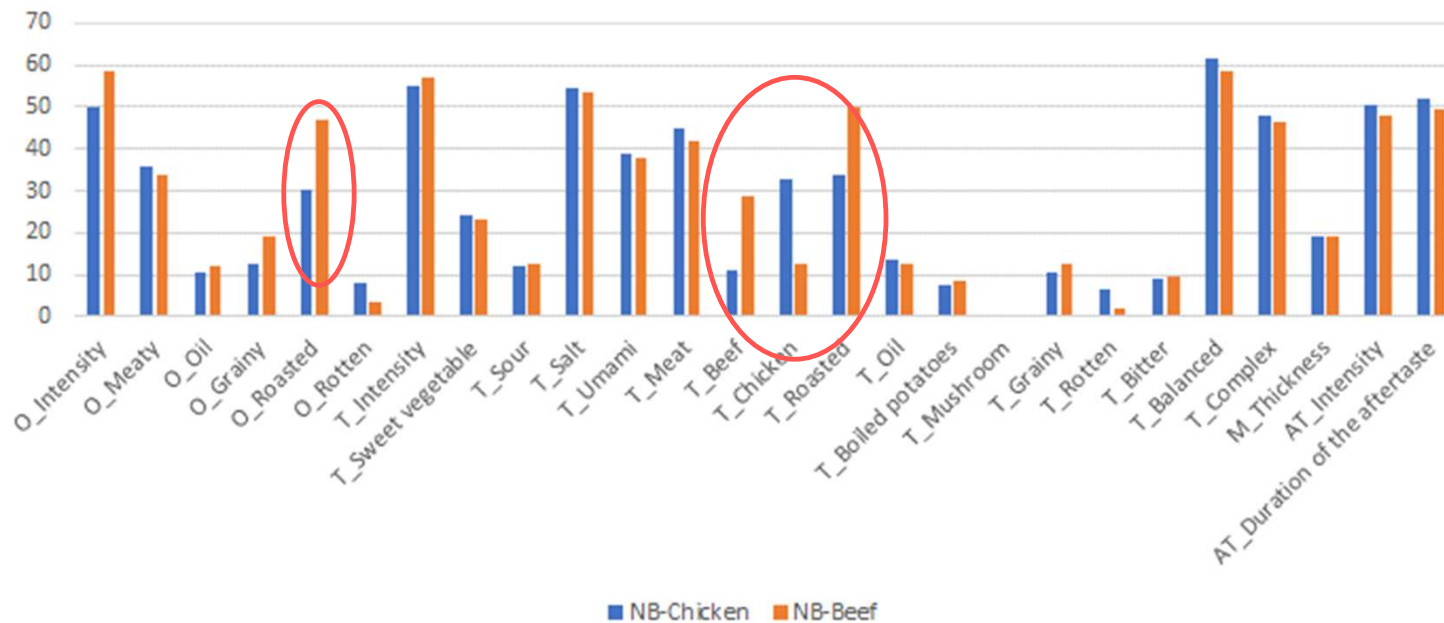


Rowe, David. (2002). High Impact Aroma Chemicals II - The Good, the Bad and the Ugly. *Perfumer & Flavorist*. 27. 24 - 33.

Quantitative Descriptive Analysis Chicken & Beef flavours

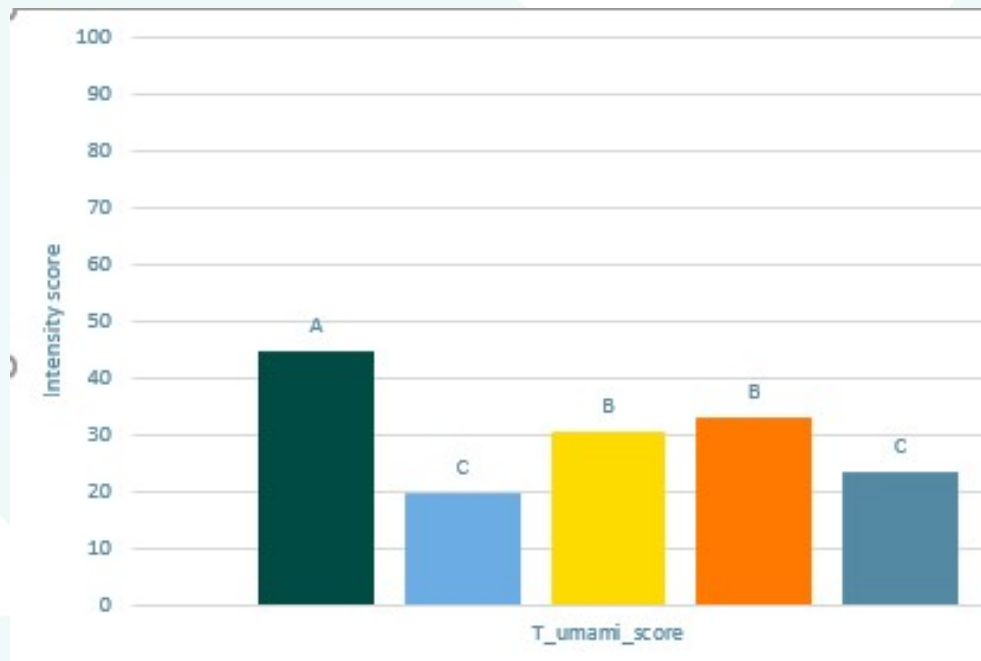


Essensor Panel sensory results



Many attributes scored by 10 -12 panelists

➤ **Rank & Score test - What is the umami efficacy of:**



■ MSG, ■ Yeast extract, ■ Flavour 1, ■ Flavour 2, ■ Model Mix

Conclusies

1. Tijdens voedsel bereiding met verhitten / lang staan
Maillard reacties => Geur / Kleur / Smaak
2. Zeer complexe chemie: tafelsuiker weinig reactief,
druivesuiker, fructose (en xylose) wel – Open Vorm!
3. Zeer eenvoudig met zuivere stoffen te doen - Practicum
WUR nu 4e jaar met 180 studenten in groepjes van 5 tot 6
studenten.

Vragen??