The Role of pH in Maillard-Type Reactions

Chair J. de Clerck Symposium XI

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Outline of the presentation

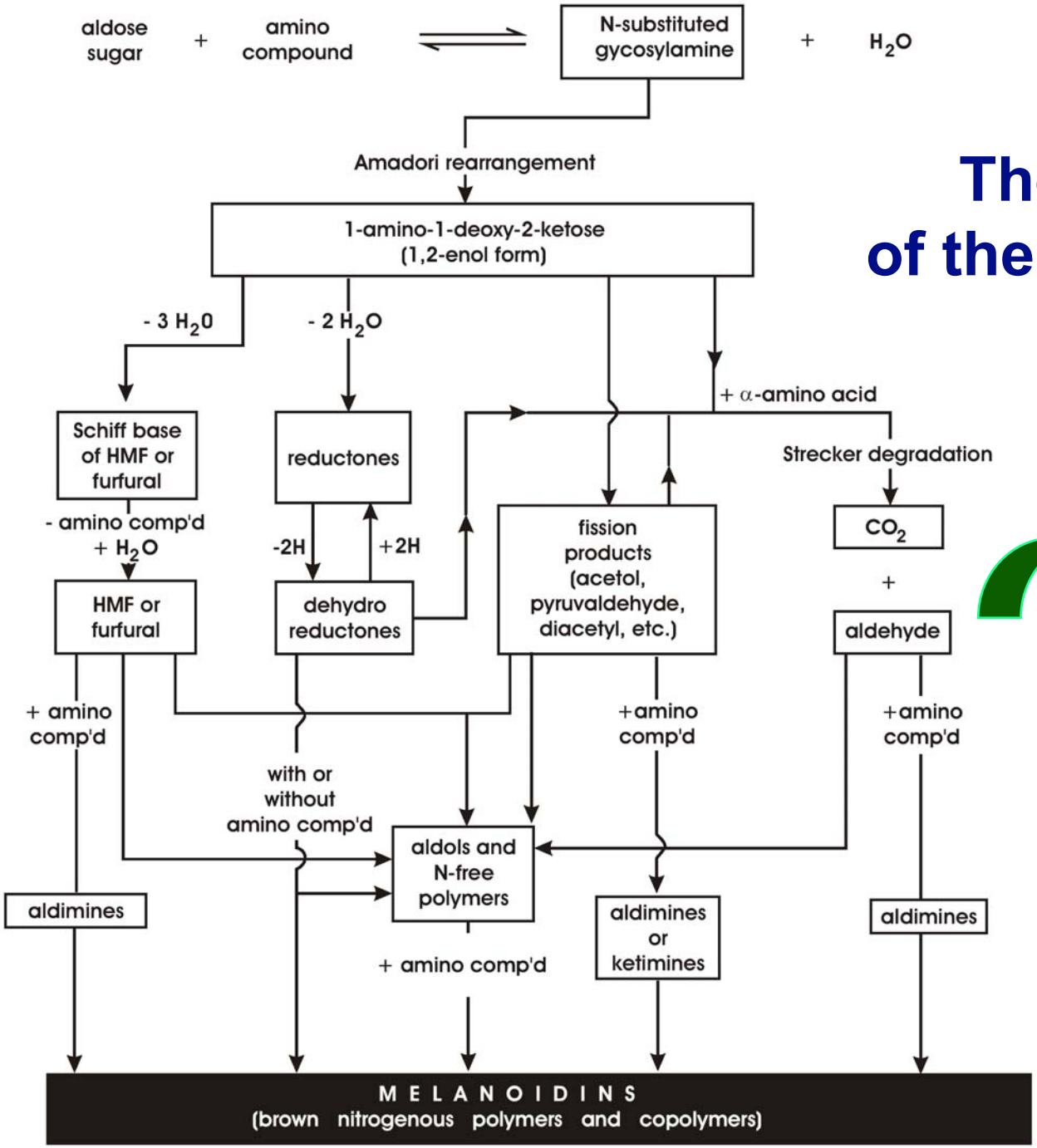
Basic principles of pH/Maillard

- pH versus reactivity (nucleophilicity)
- pH versus buffer
- pH to control the Maillard reaction

Examples from flavour research

- *O*-heterocycles – caramel-like/sweet
- *N*-heterocycles – raosty/sweet
- *S*-heterocycles – roasty/savoury

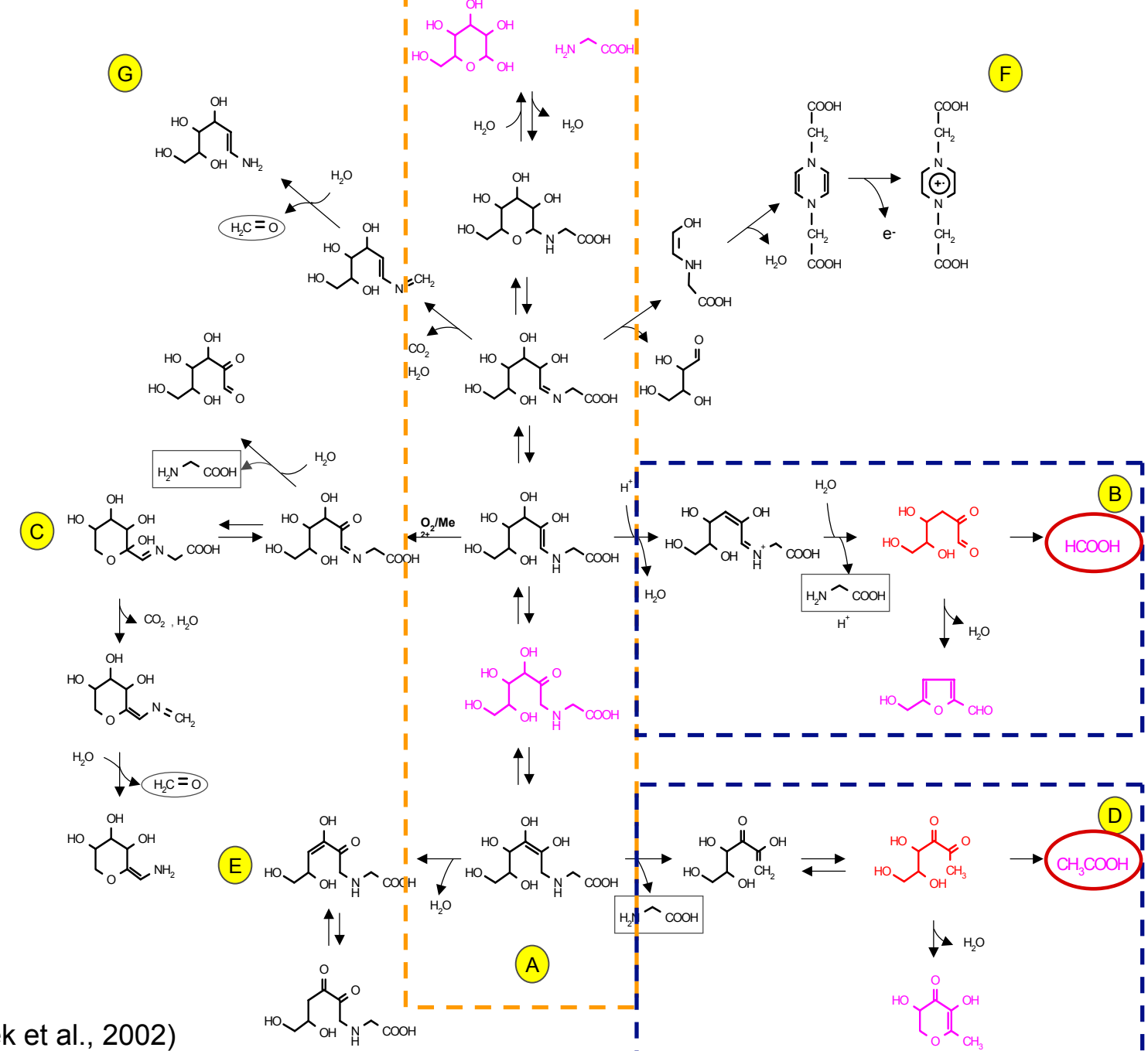
The first scheme of the Maillard reactio



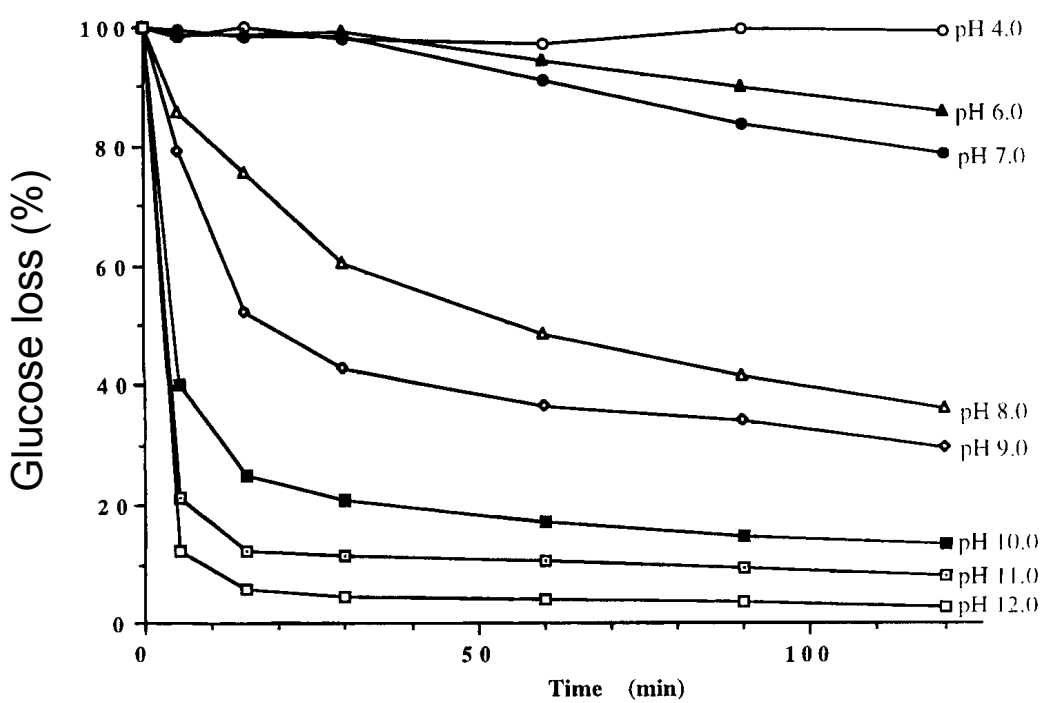
Aroma
Taste
Colour
Antioxidants
Texture

Nutritional value
Contaminants
Toxic compound

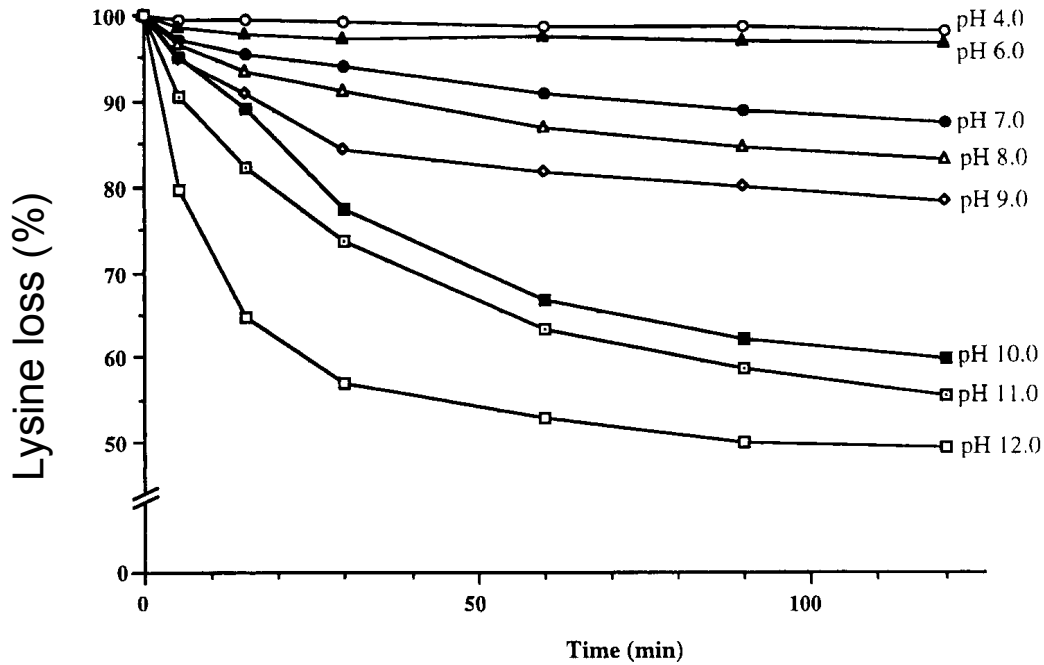
(Hodge, 195



(Davidek et al., 2002)



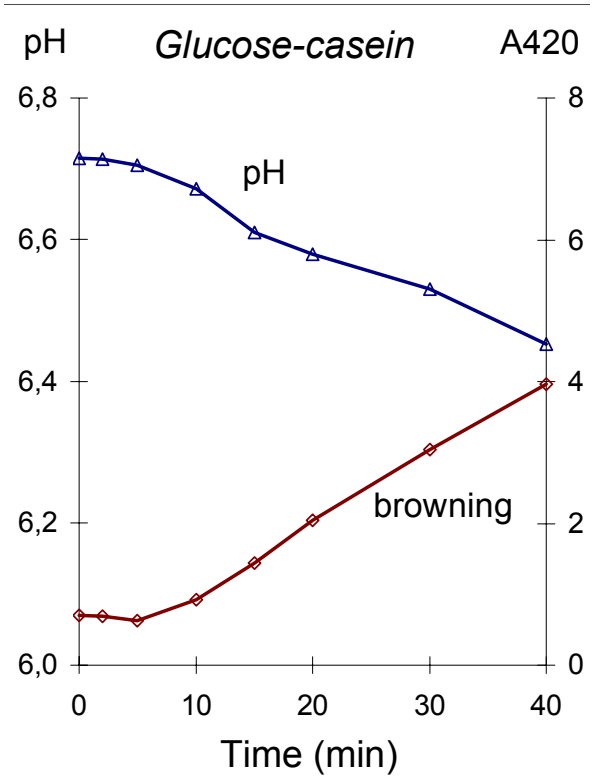
Loss of Glc under boiling conditions:
- rapid loss at pH 10-12
- high loss at pH 8-12

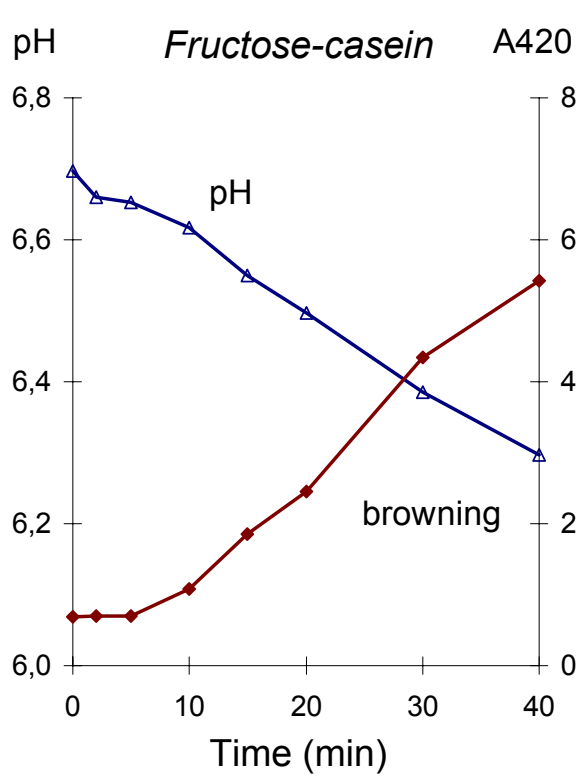


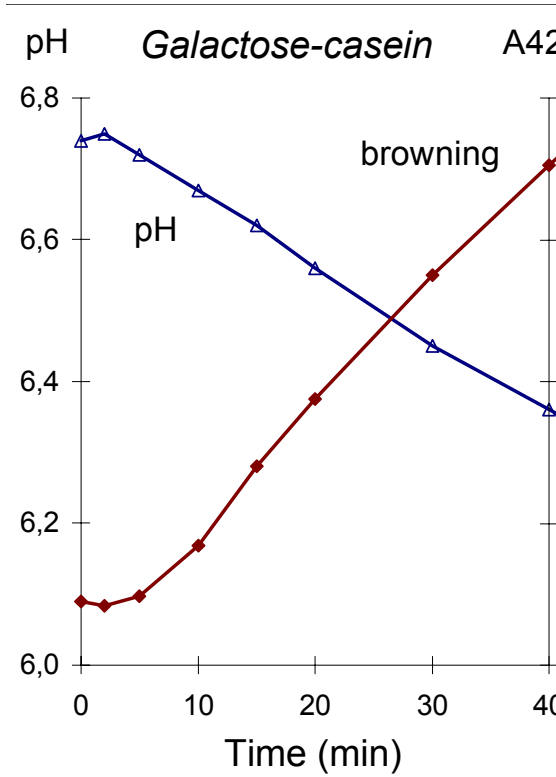
Loss of Lys under boiling conditions:
- slower decrease at pH 10-12
- small loss at pH 4-9

(Ames, 1998

pH decrease and browning as affected by the type of sugar



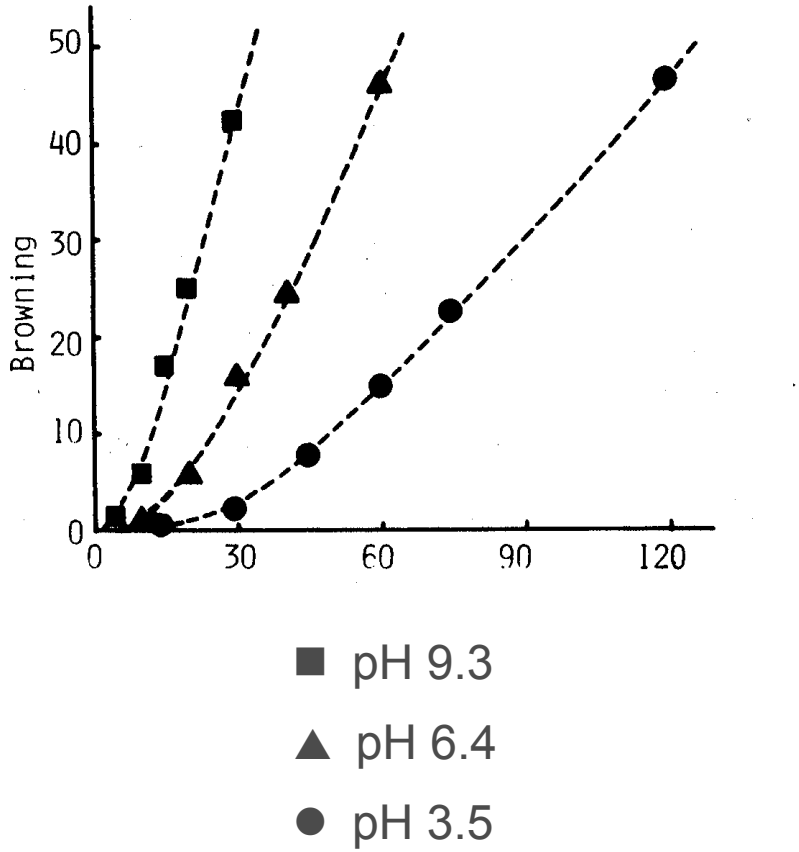




(van Boekel et al., 2000)

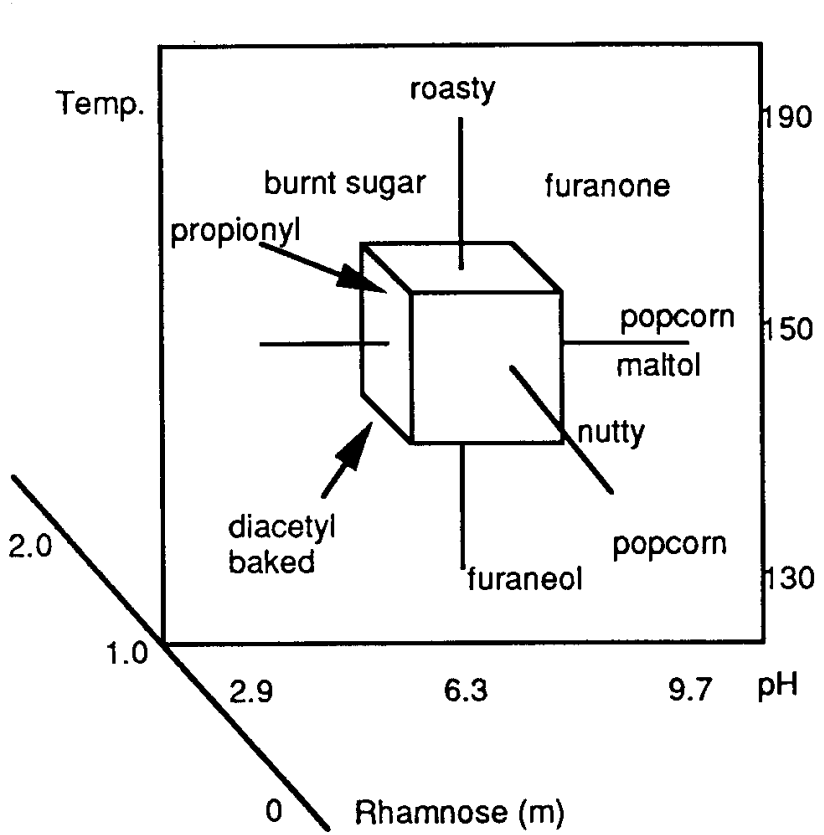
Colour and flavour formation *via* Maillard reactions depend very much on the pH

Glucose + β-alanine



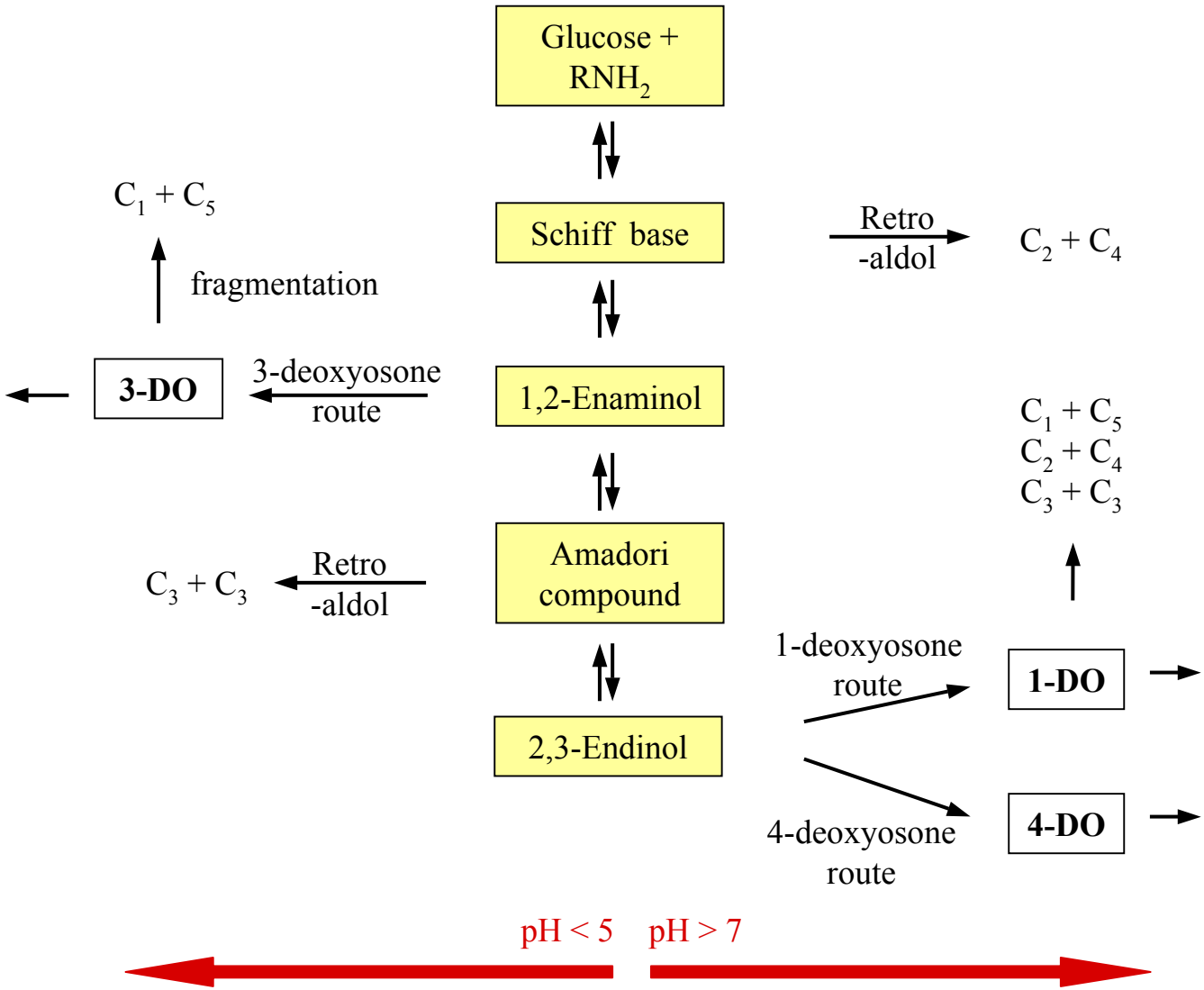
(Hayashi & Namiki, 1986)

Rhamnose + L-proline

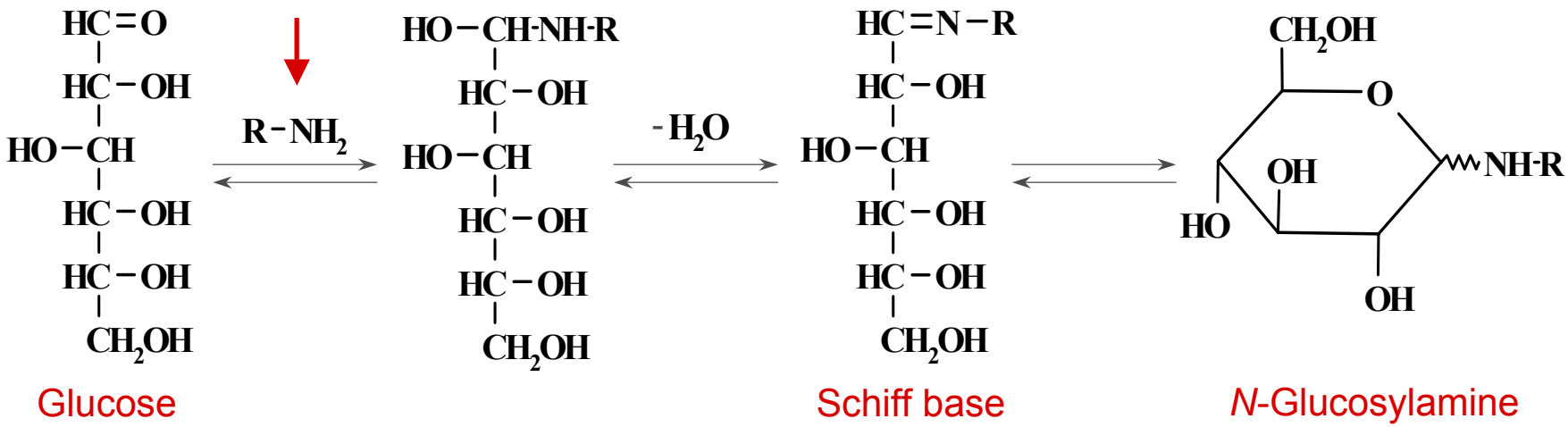


(Shaw et al, 1990)

Major reaction pathways as affected by the pH



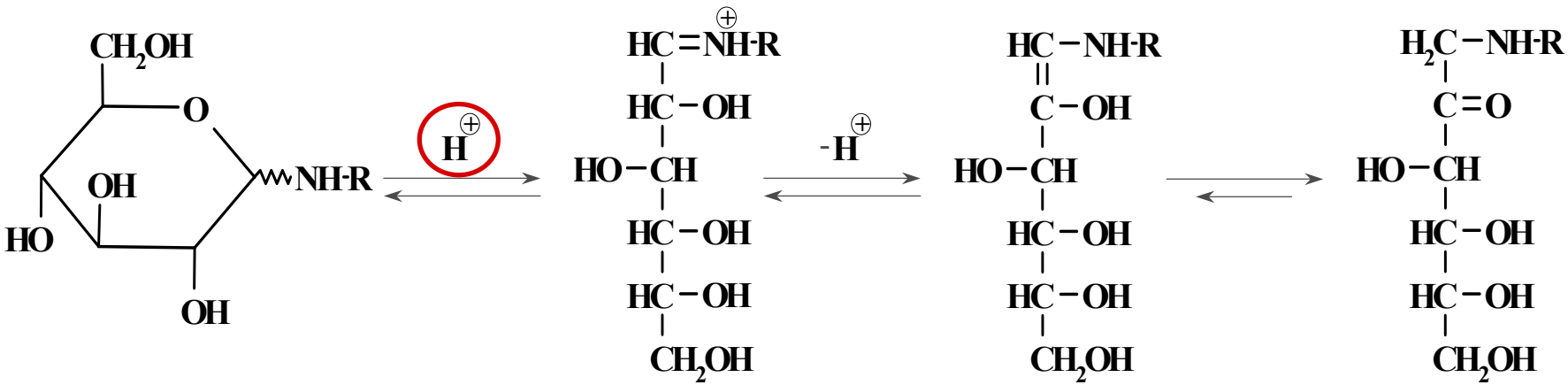
Major steps of the early stage of the Maillard reaction



Glucose

Schiff base

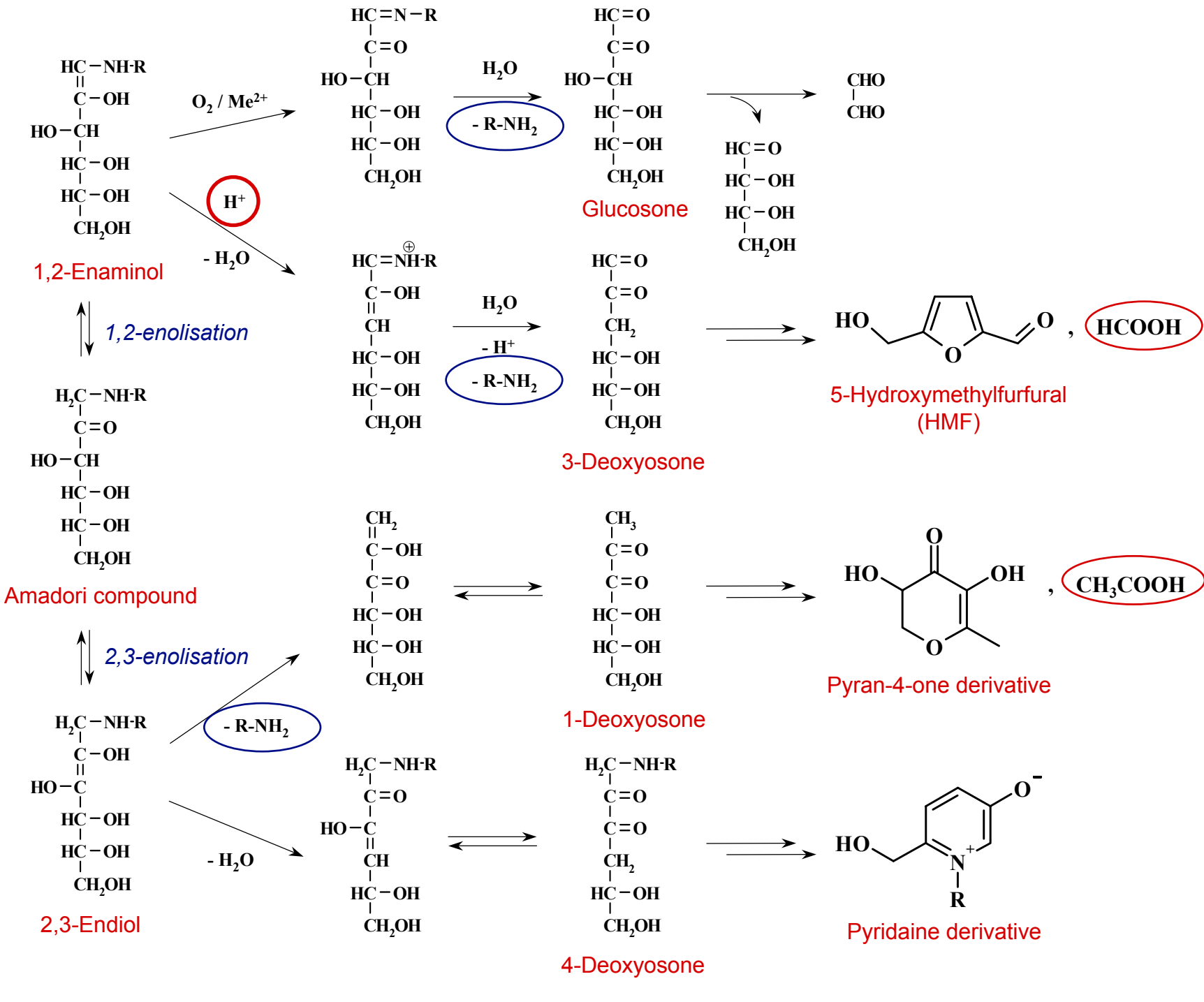
N-Glucosylamine



N-Glucosylamine

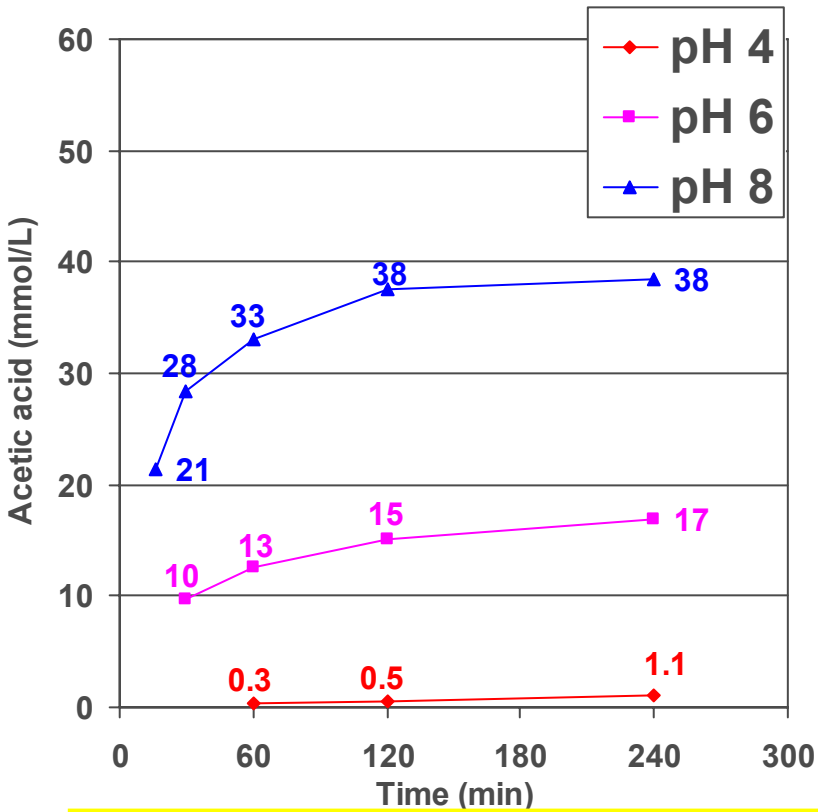
1,2-Enaminol

Amadori compour

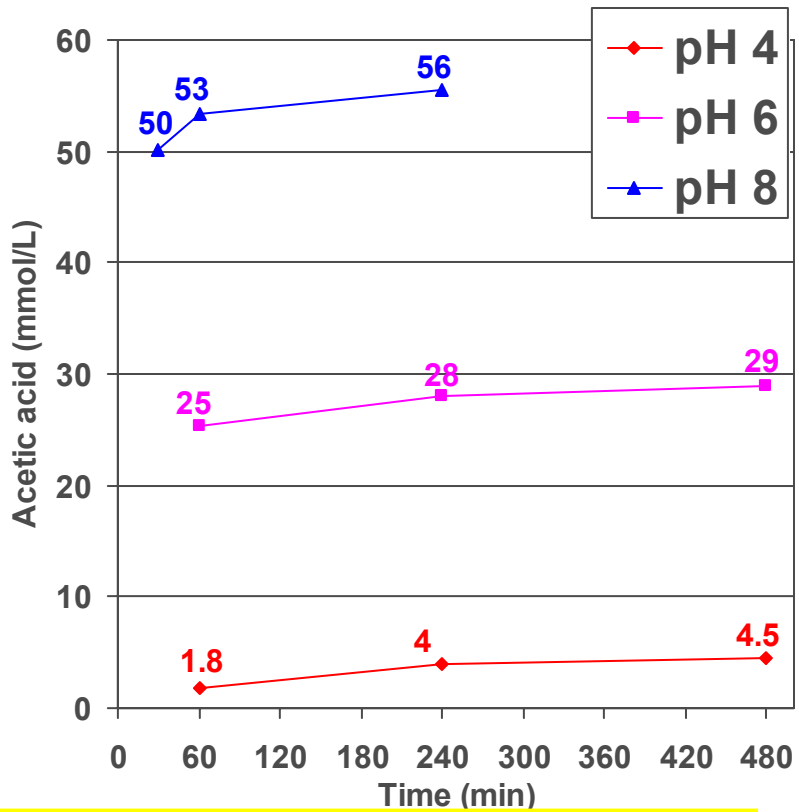

1,2-Enaminol
O_2 / Me^{2+}
H^+
- H_2O
H_2O
- R-NH_2
Glucosone
1,2-enolisation
Amadori compound
2,3-enolisation
- R-NH_2
- H_2O
2,3-Endiol
H_2O
- H^+
- R-NH_2
3-Deoxyosone
5-Hydroxymethylfurfural
(HMF)
HCOOH
1-Deoxyosone
Pyran-4-one derivative
CH_3COOH
4-Deoxyosone
Pyridaine derivative

Formation of acetic acid (Phosphate buffer, 0.2 mol/L, 120°C)

From glucose/glycine



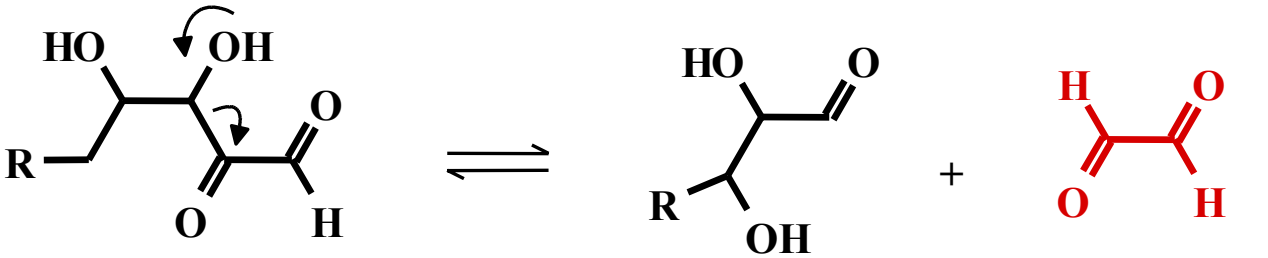
From Amadori compound



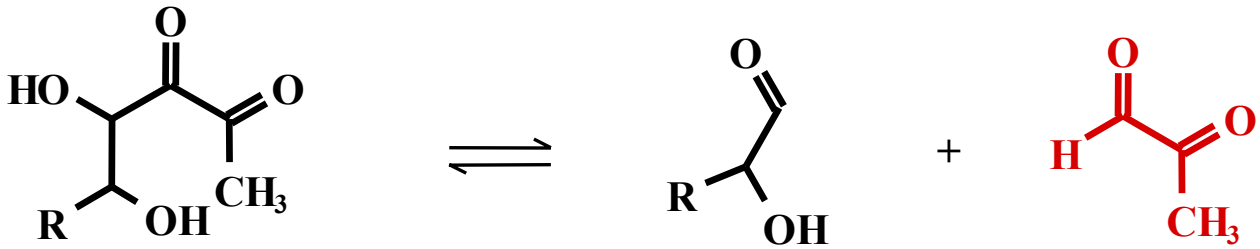
(Davidek et al., 2003)

Formation of some C_2 and C_3 degradation products by the Maillard reaction

Glycosone



1-Deoxyosone

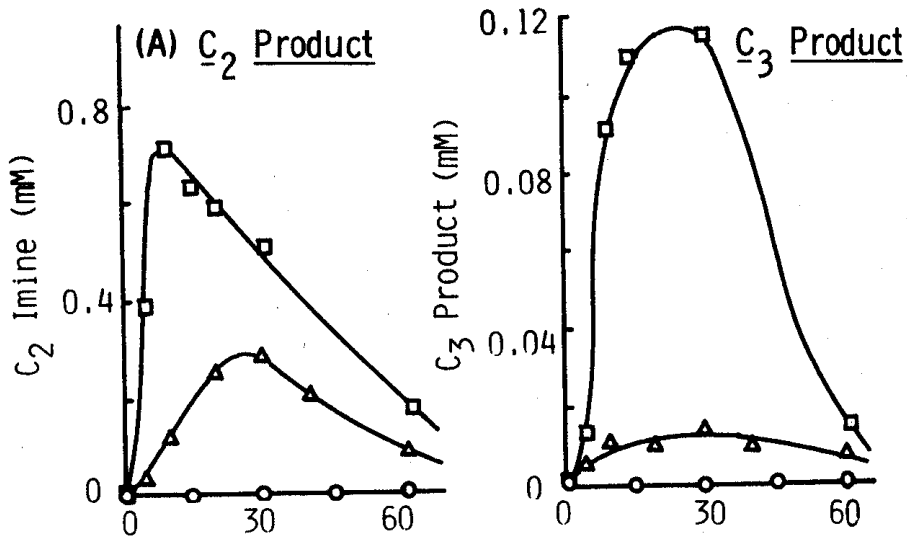


□ pH 9.3

Δ pH 6.4

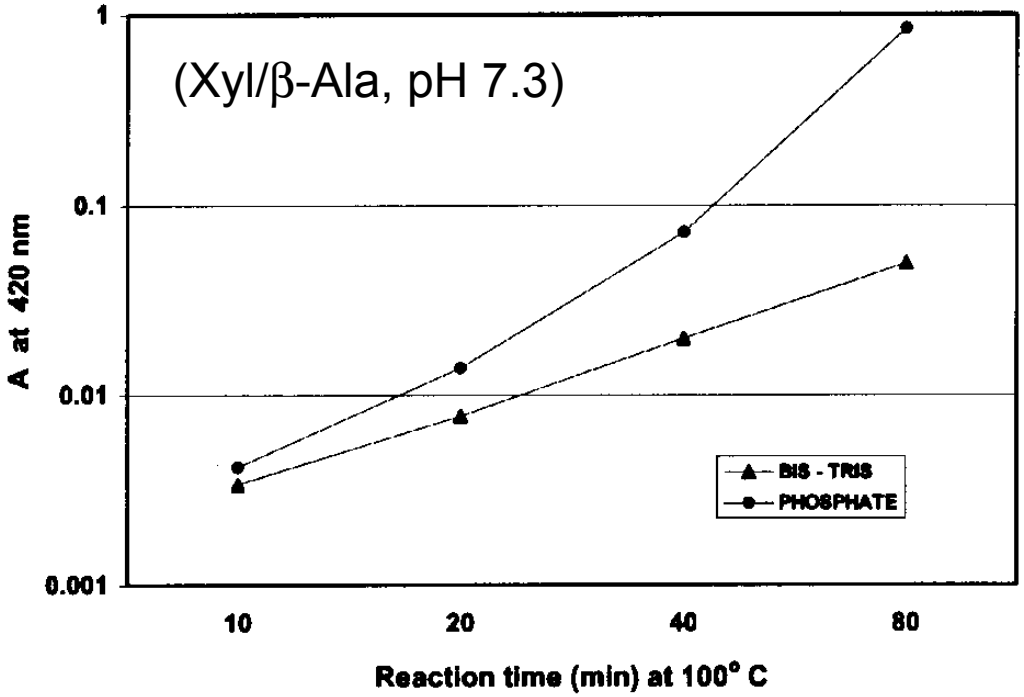
○ pH 3.5

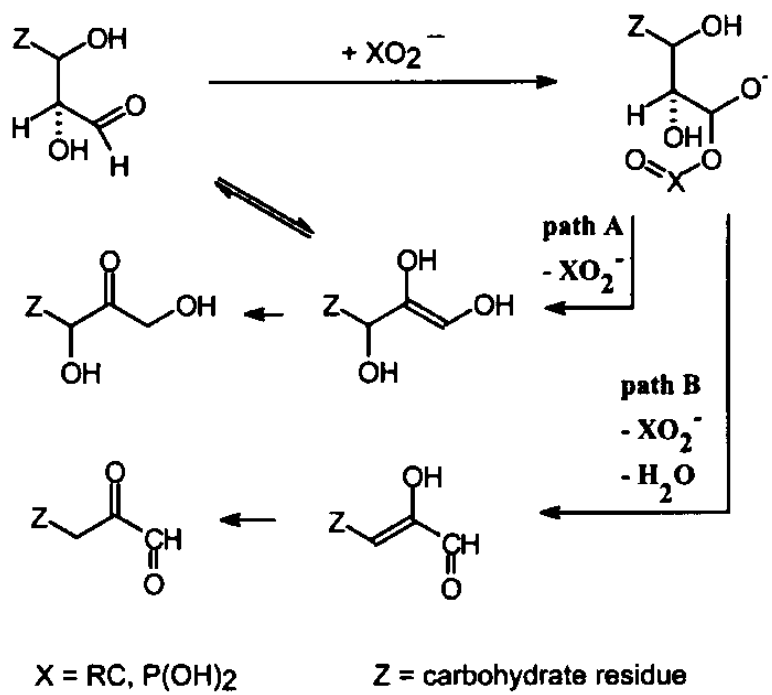
(Glucose/β-alanine)



(Hayashi & Namiki, 1986)

Role of buffer on pH control and reactivity in the Maillard reaction





Conclusion:

Intramolecular proton abstraction with XO_2^-
→ more efficient, catalytic effect

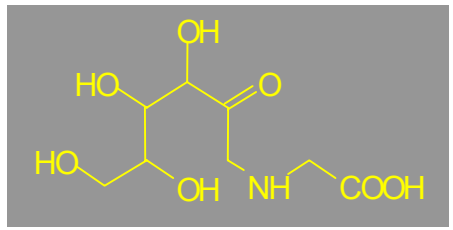
Intermolecular proton abstraction with OH^-

Mechanism:

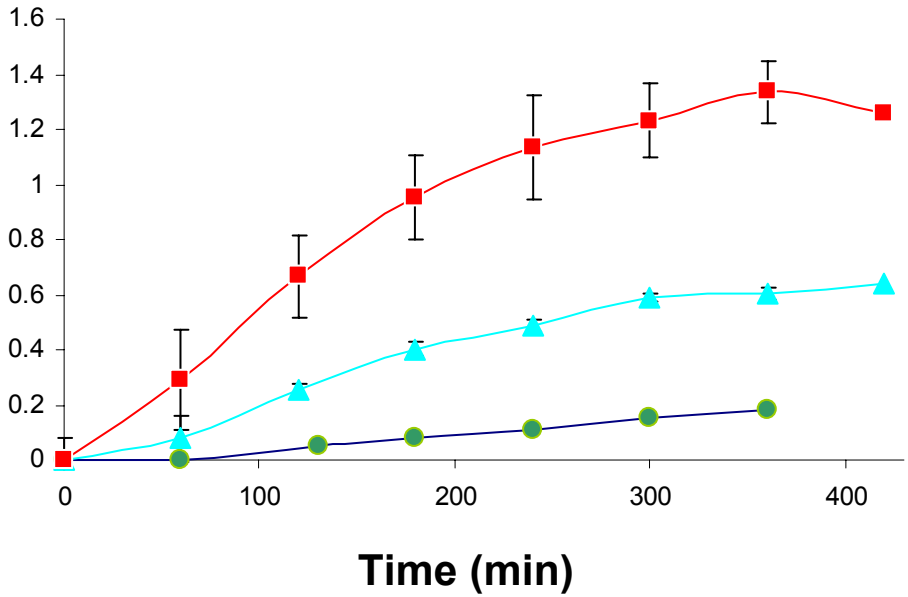
- Nucleophilic addition
- Proton abstraction from α-position
- Enolisation: A, sugar isomerisation
- Dehydration: B, 3-deoxyosone formatio

(Rizzi, 2004)

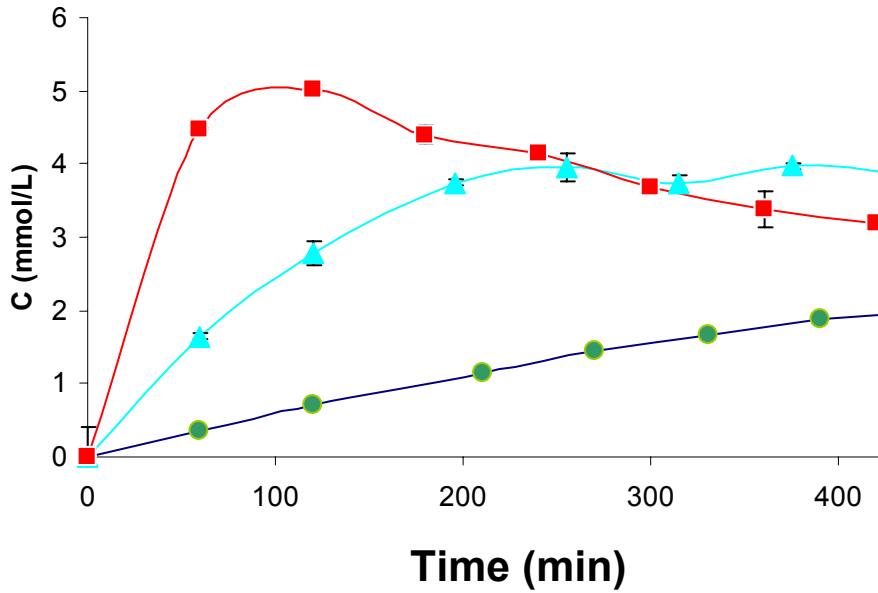
Formation of the Amadori compound in the Glc/Gly system



No buffer



Phosphate buffer



(D-glucose 0.1 M and glycine 0.1 M, H_2O or phosphate buffer 0.1 M, T = 90°C)

● pH 5, ▲ pH 6; ■ pH 7

(Kervella et al., 2002)

Summary: pH effects on reactions occurring in the Maillard cascade

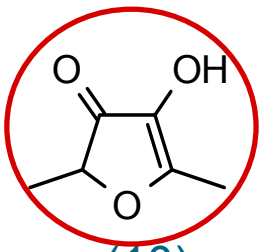
pH changes depend on:

- Formation of acid/base : HCOOH, HOAc, glycolic acid
- Consumption of acid/base : aminoketones $\rightarrow$ pyrazines
- Buffering capacity of Maillard/food system

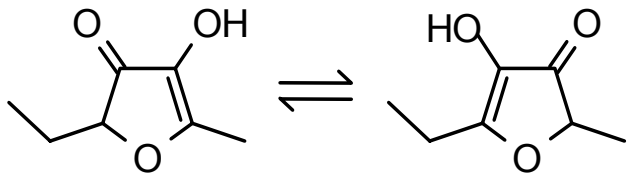
Typical reactions in the 'Maillard reaction':

- Amino/carbonyl reactions : basicity of α-NH_2, pK_a
- Aldol/retro-aldol reactions : 'alkaline' conditions
- Enolisation and elimination : 'alkaline/acidic' conditions
- Radical reactions : 'alkaline conditions
- Oxidation and reduction

Impact aroma compounds with caramel/sweet character: *O*-Heterocycles



(10)



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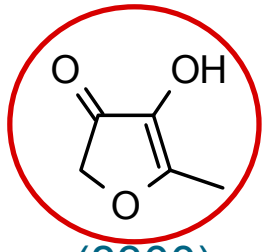
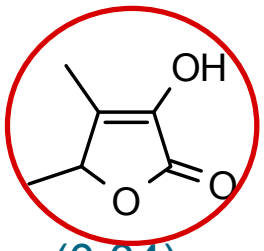
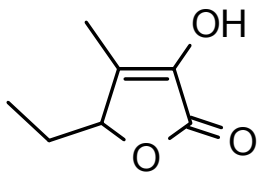


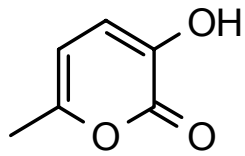
(8300)



(0.04)

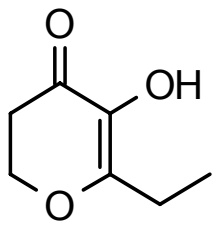


(0.02)

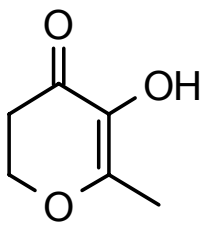


(n.d.)

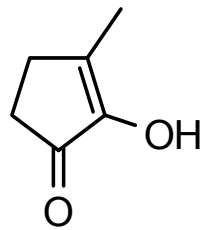
Odour thresholds in water (µg/L)



(44)



(2800)



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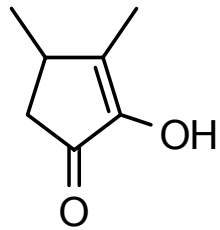
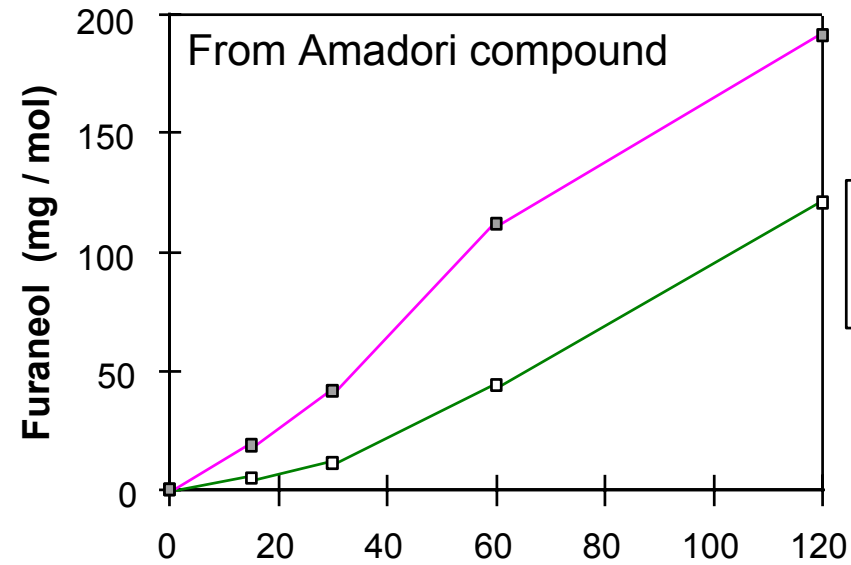
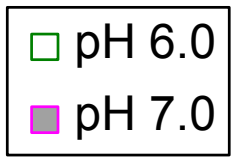


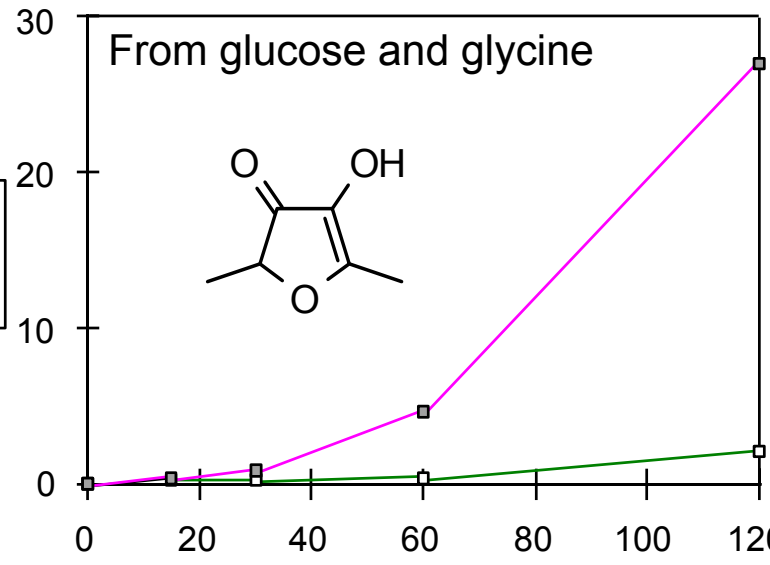
(17)

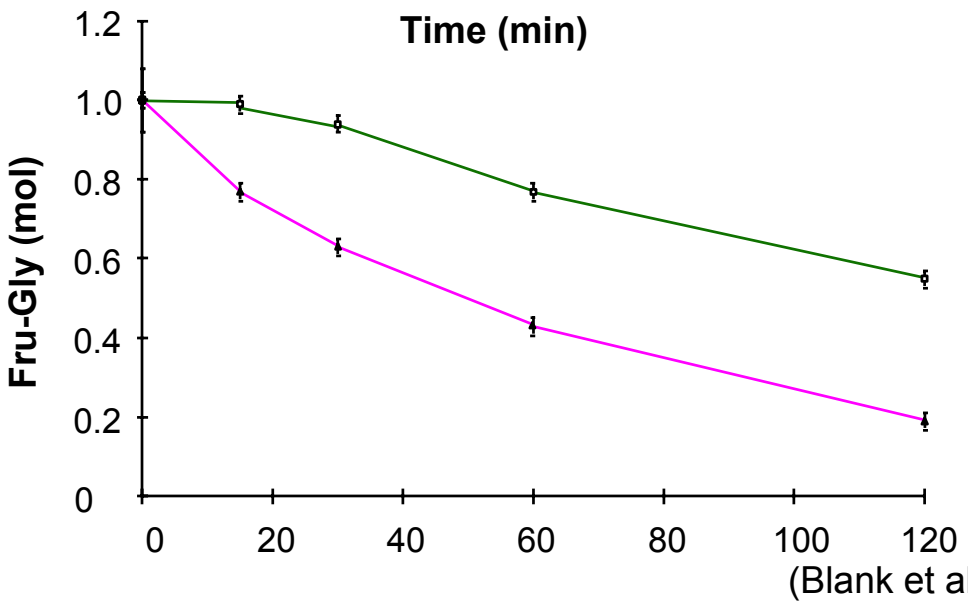
(Wild, 1988)

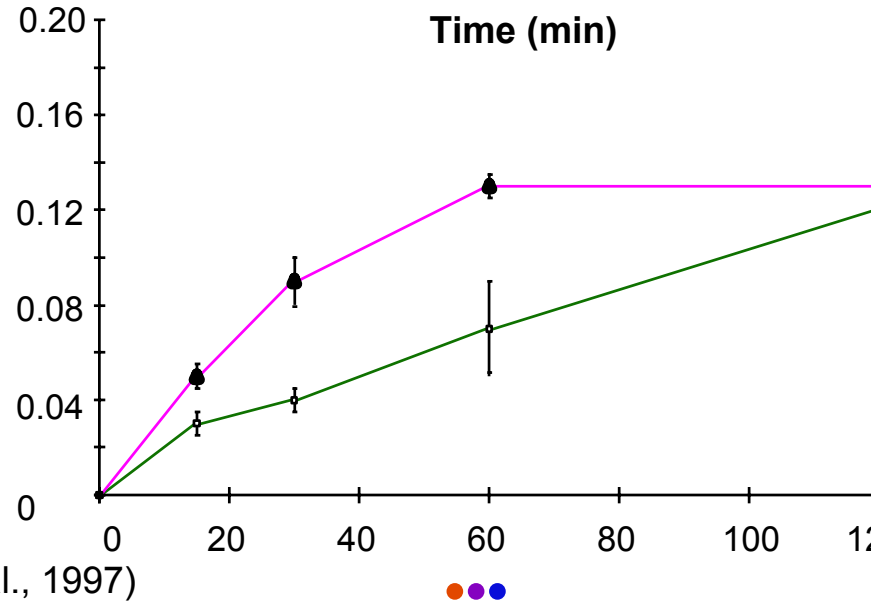
Formation of Furaneol (1 M aq. solution, no buffer, pH= const., T= 90°C)





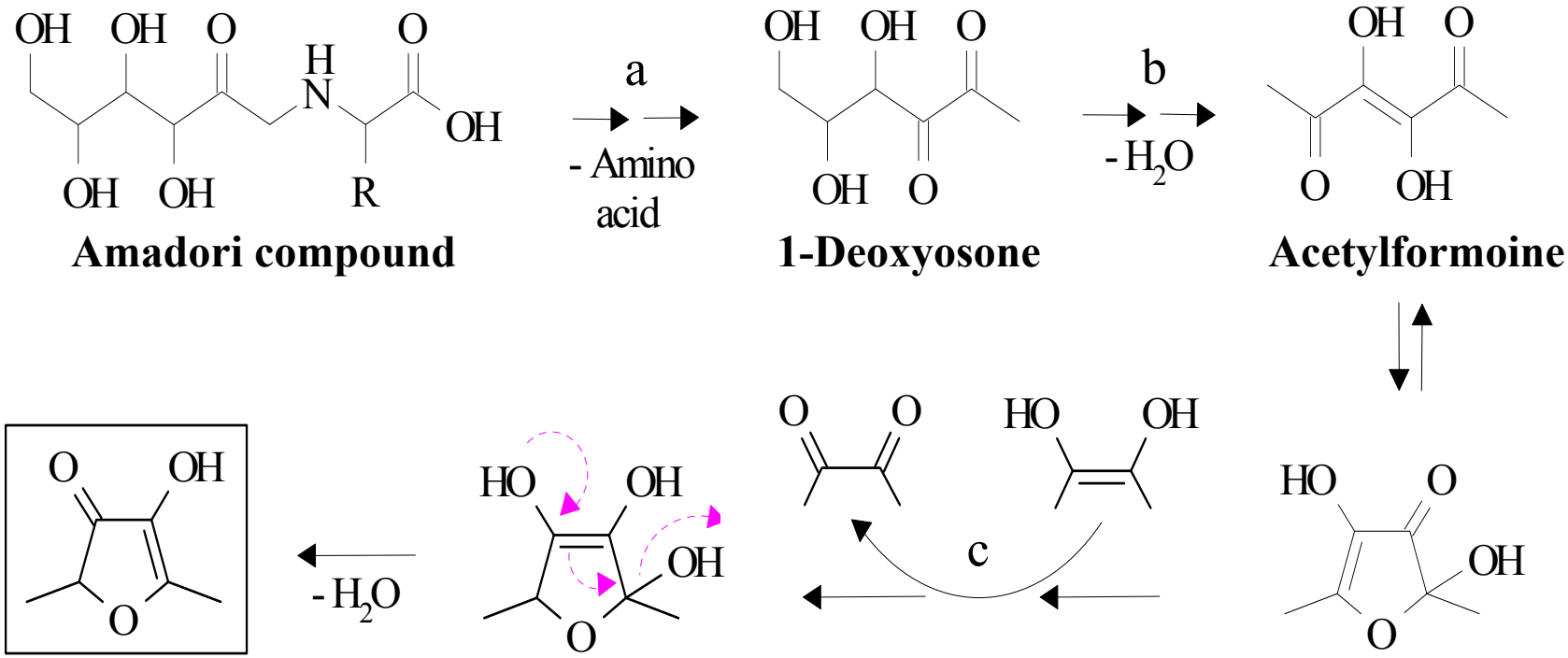






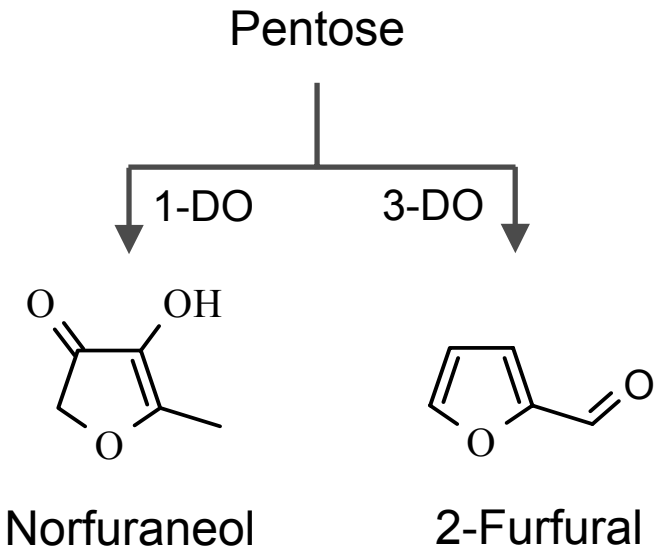
(Blank et al., 1997)

Formation of furaneol from Amadori compounds *via* acetylformoine



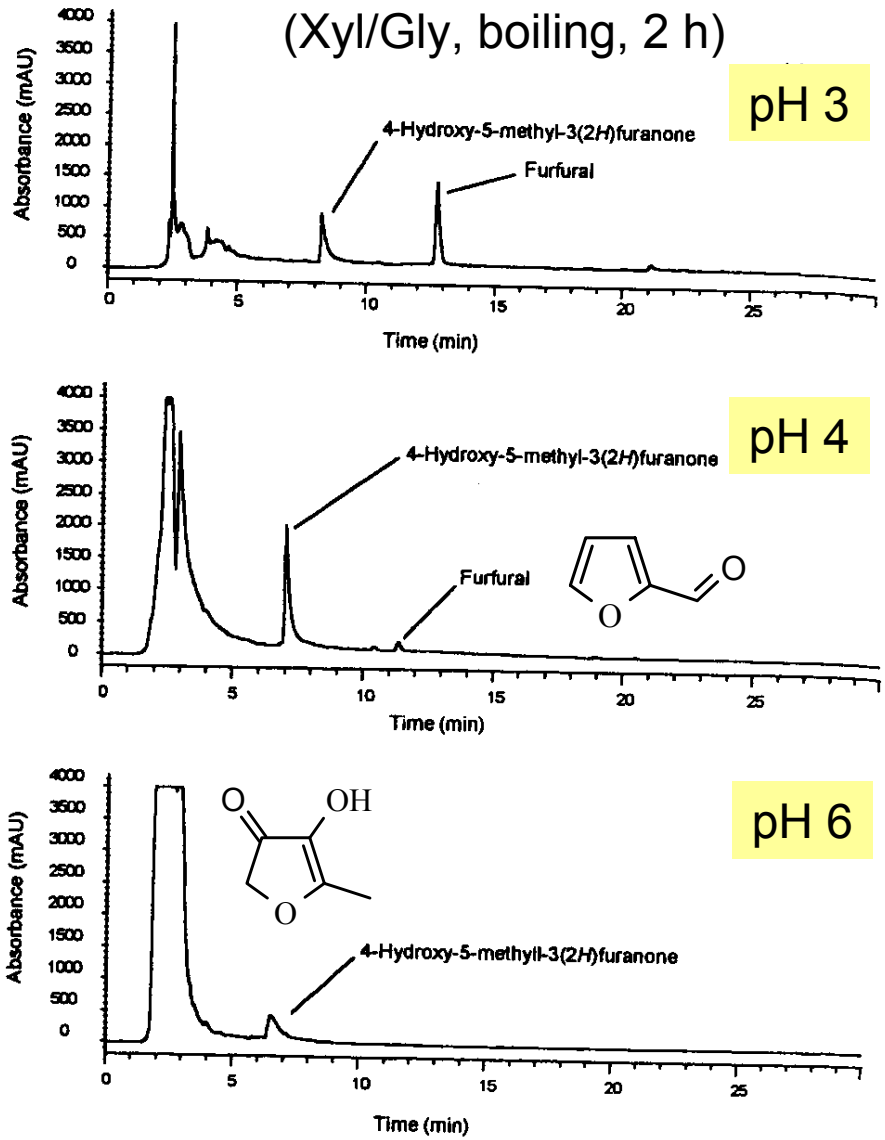
(Blank et al., 1997)

Degradation of pentose sugars *via* the Maillard reaction

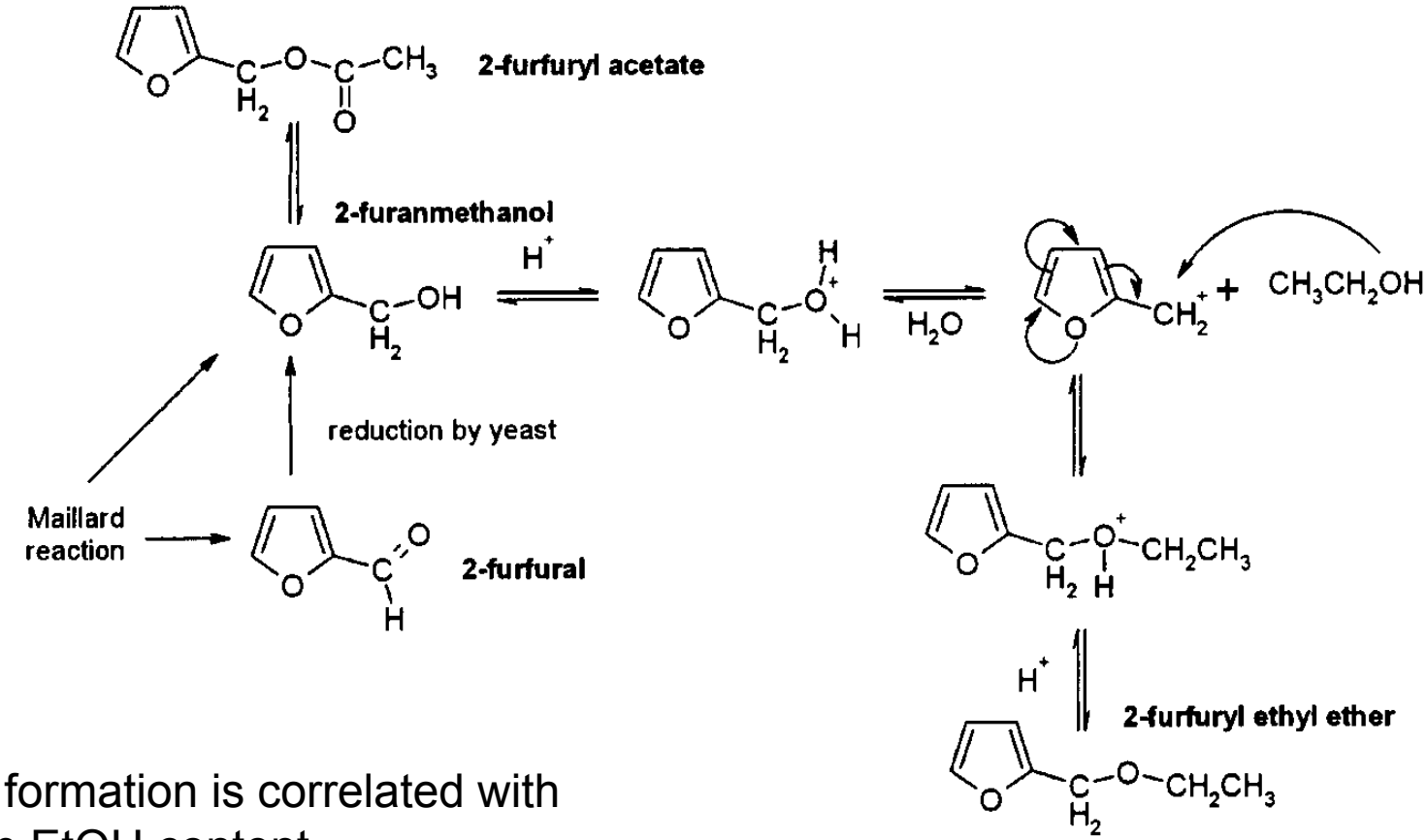


Norfuraneol 2-Furfural

(Monti



Formation of furylethylether indicating aging flavour of beer

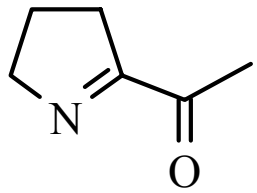


FEE formation is correlated with
- high EtOH content,
- darker colour,
- lower pH.

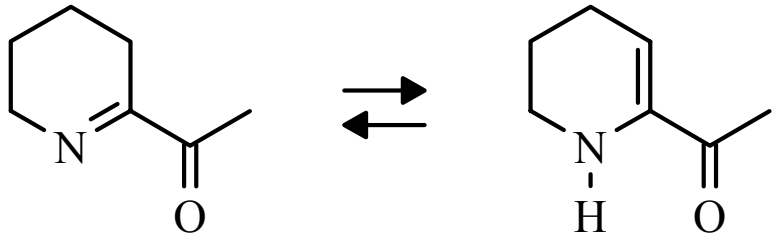
FEE
(Flavour threshold: 6 µg/L beer)

(Vanderhaegen et al., 2003, 2004)

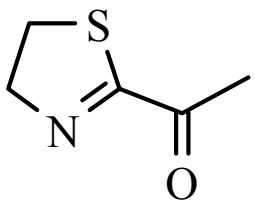
Impact aroma compounds with roasty/sweet character: *N*-Heterocycles



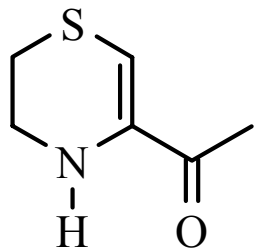
2-Acetyl-1-pyrroline (roasty, 0.02)



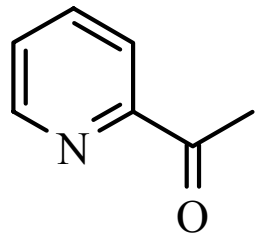
2-Acetyltetrahydropyridine (roasty, 0.06)



2-Acetyl-2-thiazoline (roasty, 0.05)



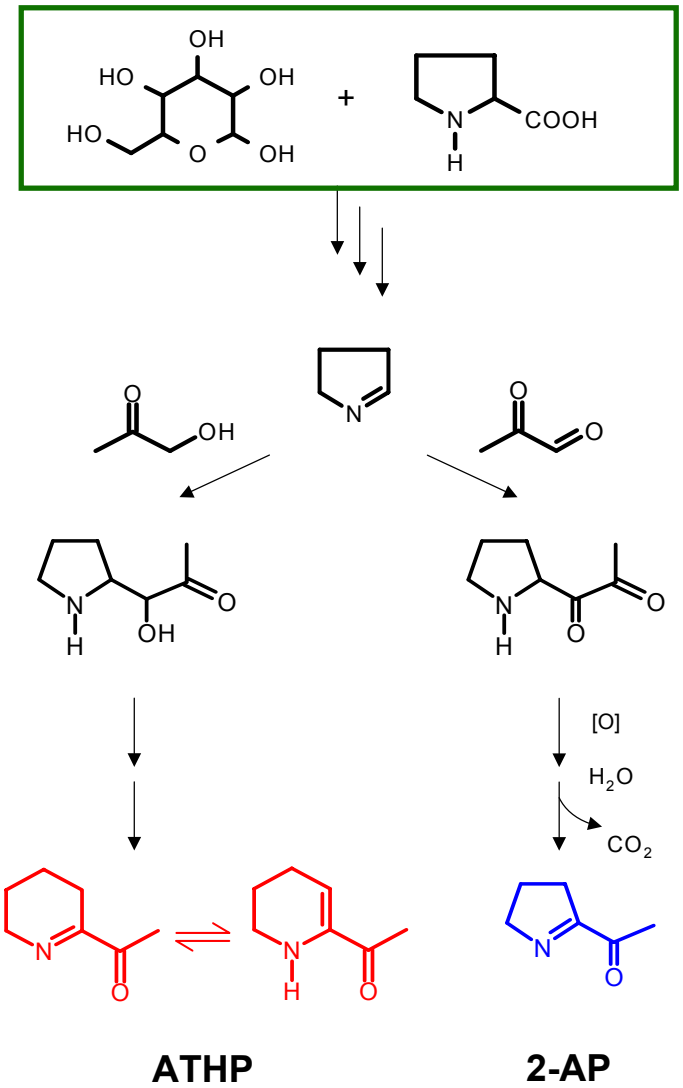
(roasty, 0.06)



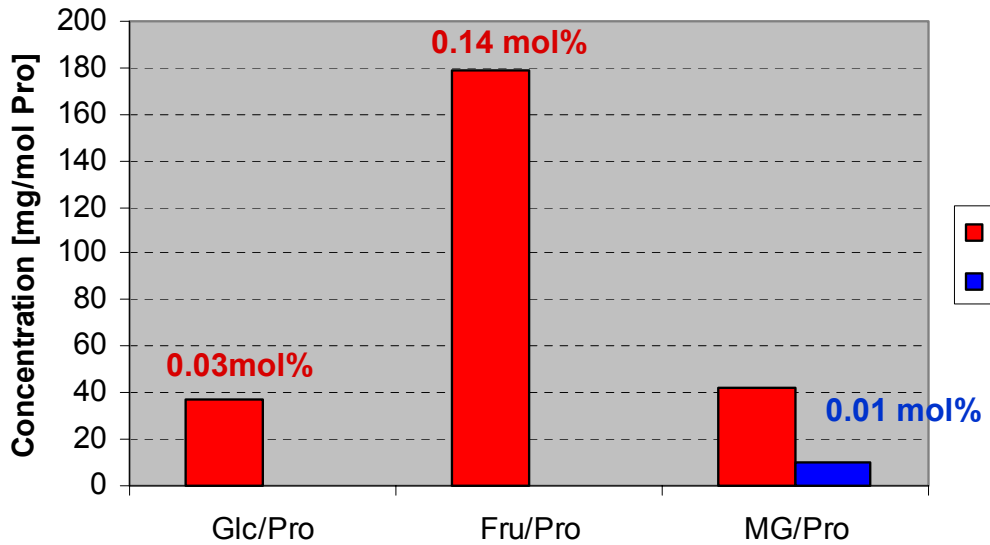
2-Acetylpyrazine (roasty, 0.4)

(Threshold values in ng/L air)

Formation of impact odorants from proline/sugar mixtures at pH 7



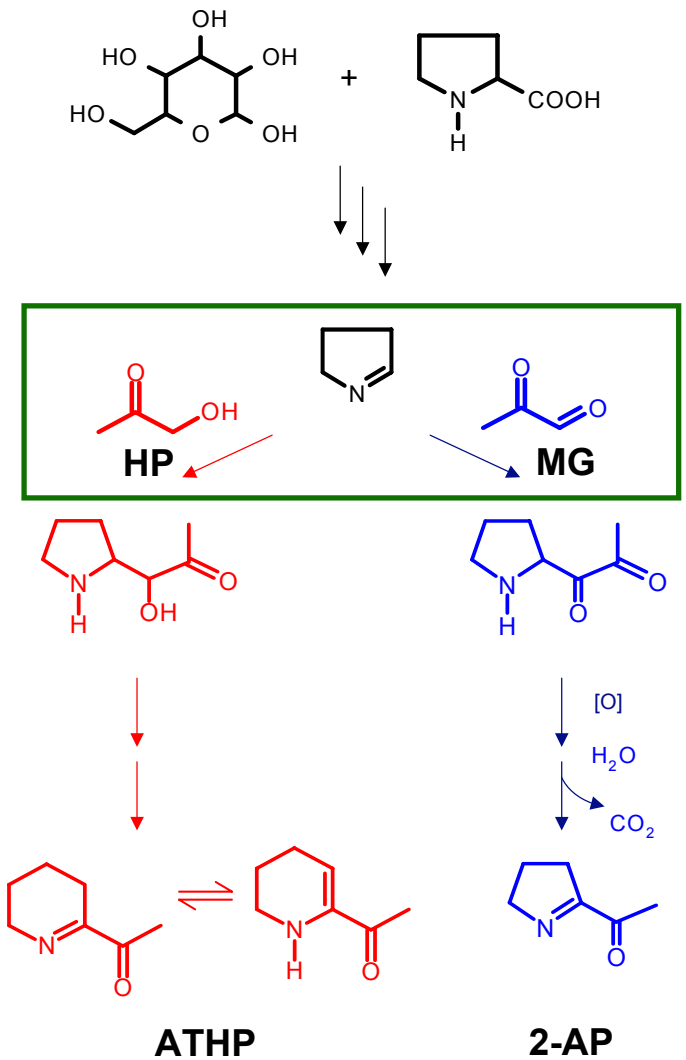
ATHP **2-AP**

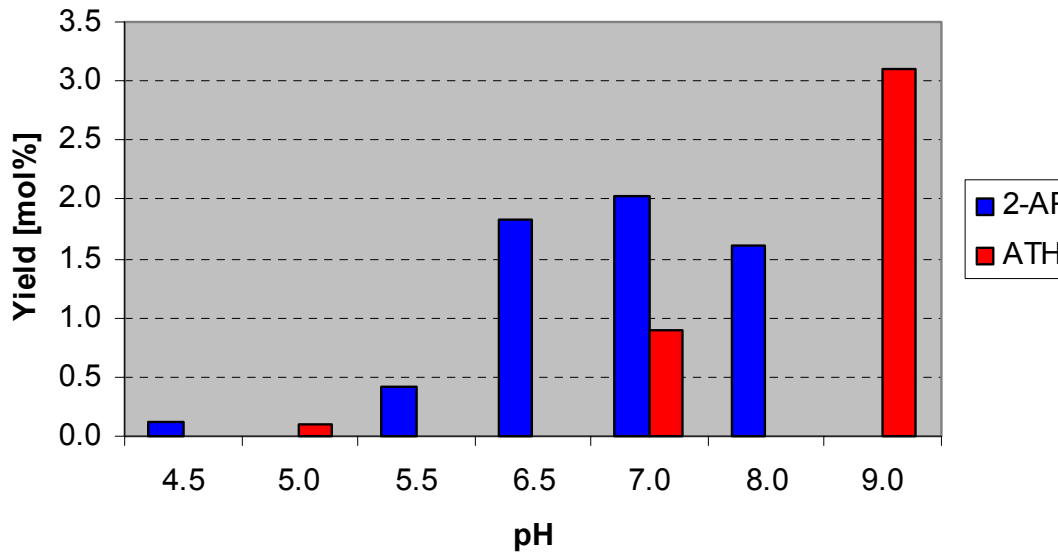


Reaction conditions:
Pro (4 mmol) + 'sugar' (2 or 0.1 mmol)
Phosphate buffer (pH 7.0, 0.1 mol/L)
Reflux, 2 h

(Schieberle et al., 1995, 1998, 2000)

Increased yields of roasty odorants: Reaction of secondary degradation products





Reaction conditions:

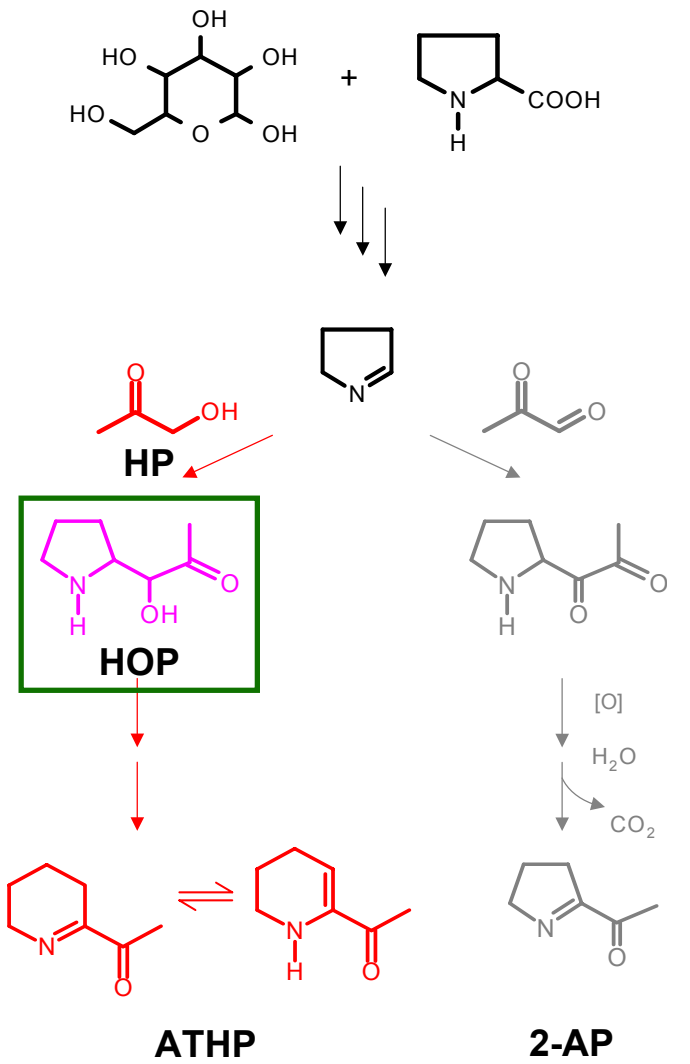
1-Pyrroline (10 µmol) + MG or HP (10 µmol)

Phosphate buffer (pH 7.0, 0.5 mol/L)

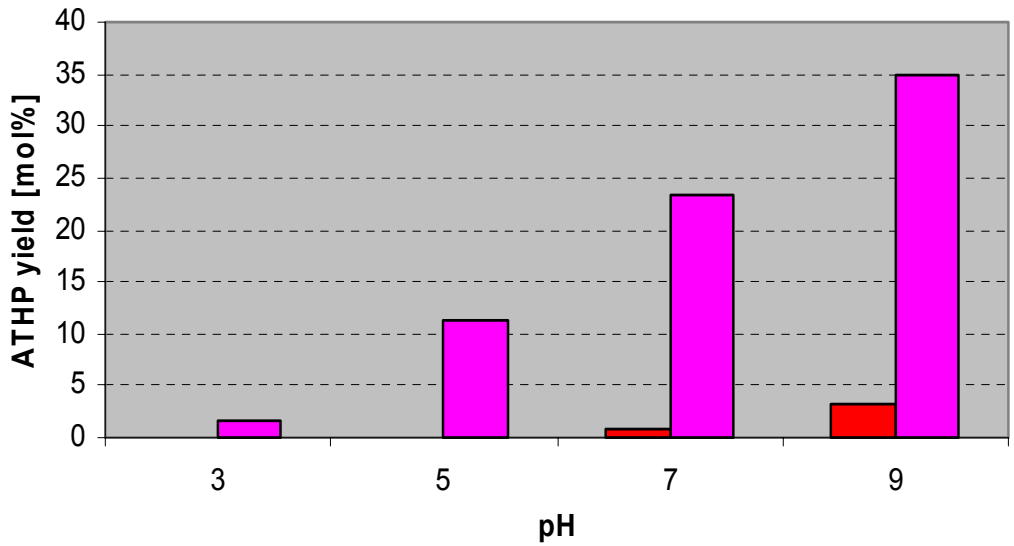
Reflux, 30 min

(Schieberle et al., 1995, 1998)

Increased yields of roasty odorants from key intermediates: ATHP from HOP

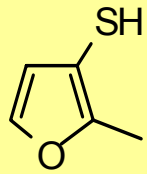


Reaction conditions:
HOP (1 µmol)
Phosphate buffer (pH 7.0, 0.5 mol/L)
Reflux, 30 min



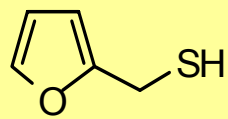
(Schieberle et al., 1995, 1998)

Impact aroma compounds with roasty / savoury character: *S*-containing odorants



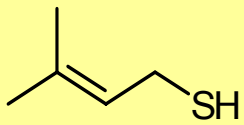
Meat, coffee
Sulfury, meaty
O_x= 0.007 µg/L H_2O

2-Methyl-3-furanthiol (MFT)



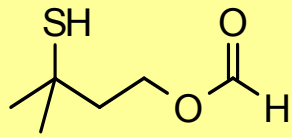
Coffee, meat
Sulfury, coffee-like
O_x= 0.01 µg/L H_2O

2-Furfurylthiol (FFT)



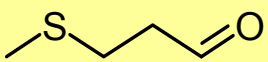
Beer, coffee
Sulfury, catty
O_x= 0.0003 µg/L H_2O

3-Methyl-2-buten-1-thiol



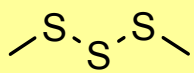
Coffee, beer
Sulfury, catty
O_x= 0.003 µg/L H_2O

3-Mercapto-3-methylbutyl formate



Potato, beer
Cooked potato-like
O_x= 0.2 µg/L H_2O

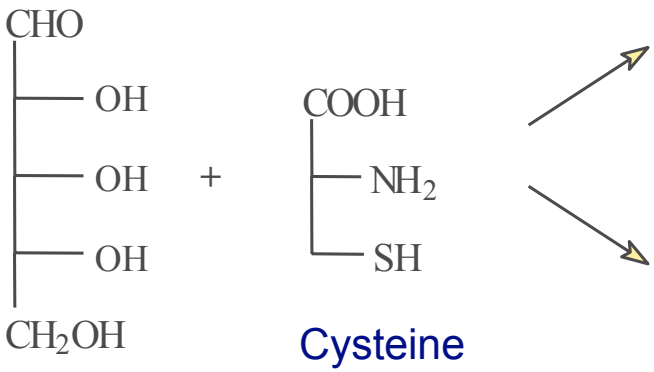
Methional



Cabbage, beer
Sulfury, cabbage-like
O_x= 0.006 µg/L H_2O

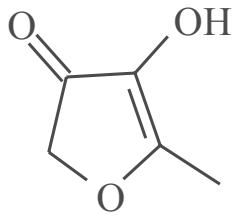
Dimethyltrisulfide (DMTS)

Cysteine and pentose sugars are important precursors for thiols

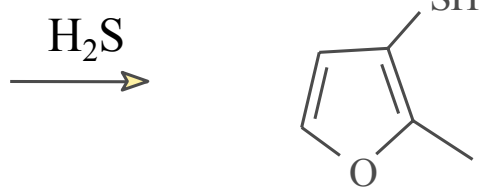


Ribose

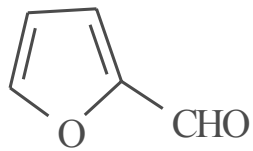
Cysteine



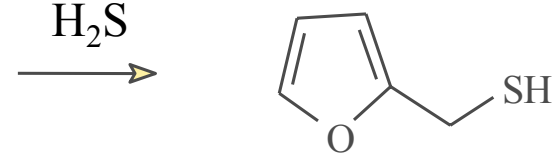
Norfuraneol



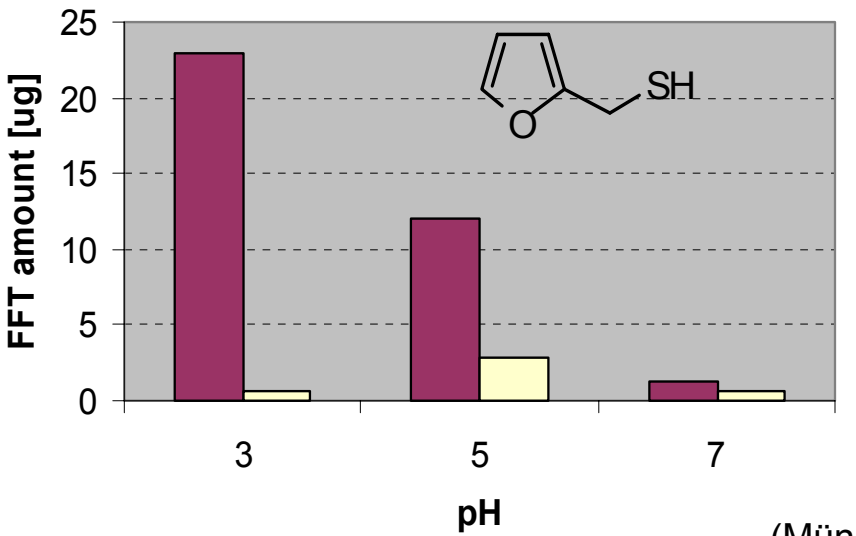
2-Methyl-3-furanthiol

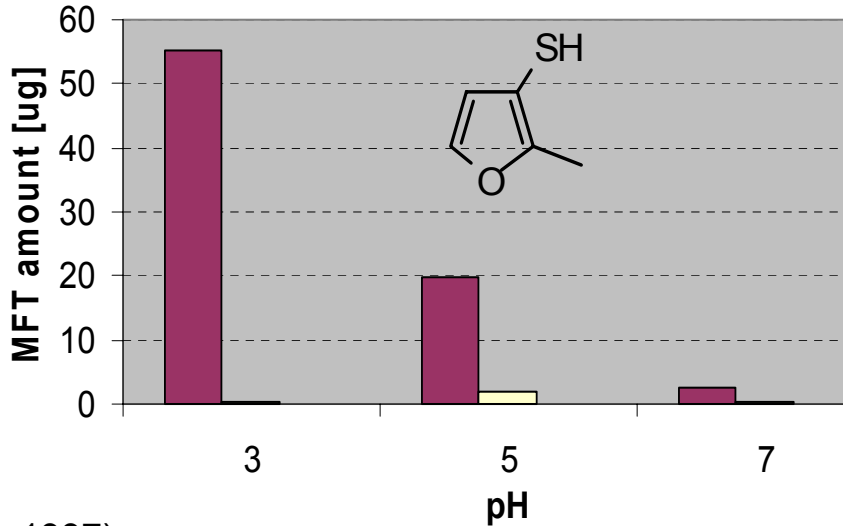


2-Furfural



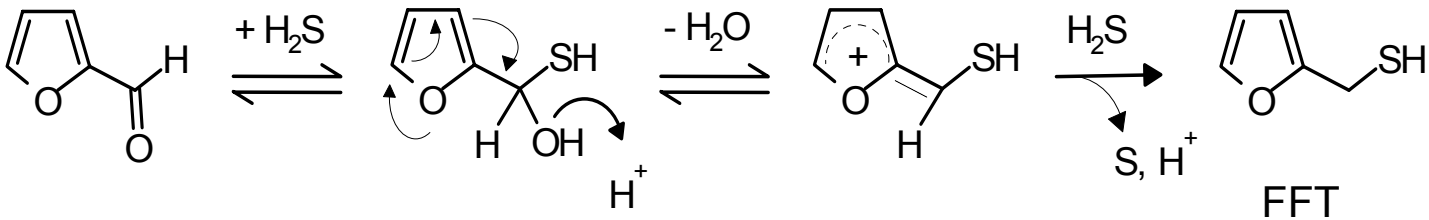
2-Furfurylthiol





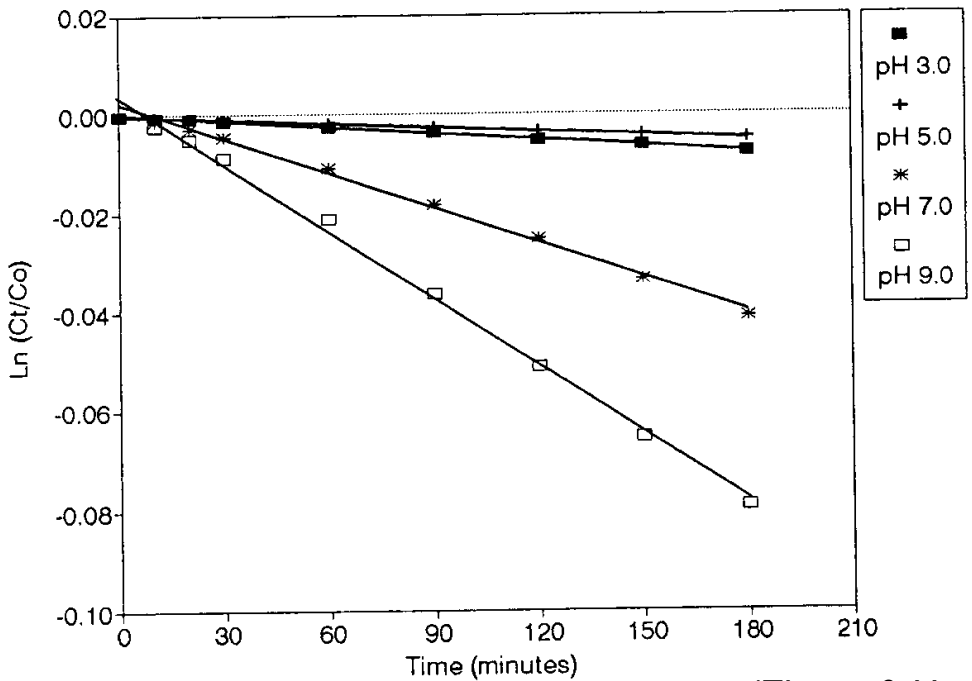
(Münch et al., 1997)

Formation of 2-furfurylthiol (FFT) from 2-furfural in the presence of H_2S



(1 mmol each) Thiosemiacetal FFT (550 µg, 0.5 mol%) (25 µg, 0.02 mol%) H_2S Cysteine

(Münch et al., 1997)

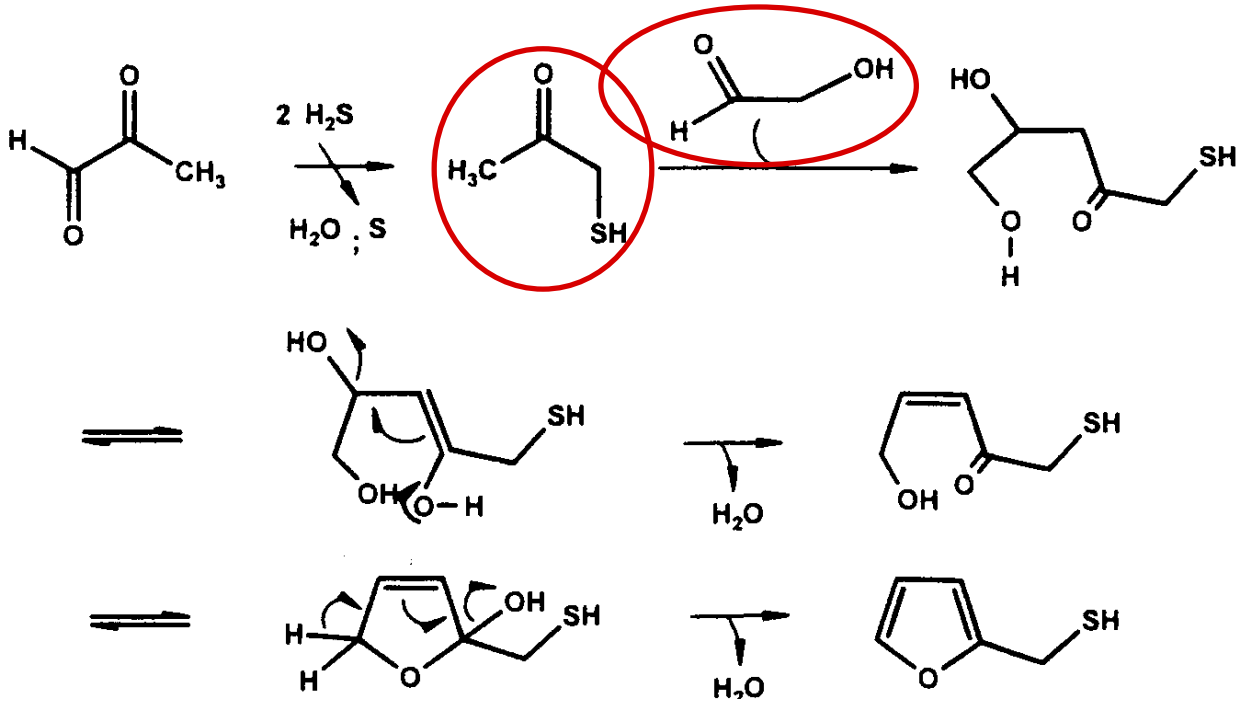


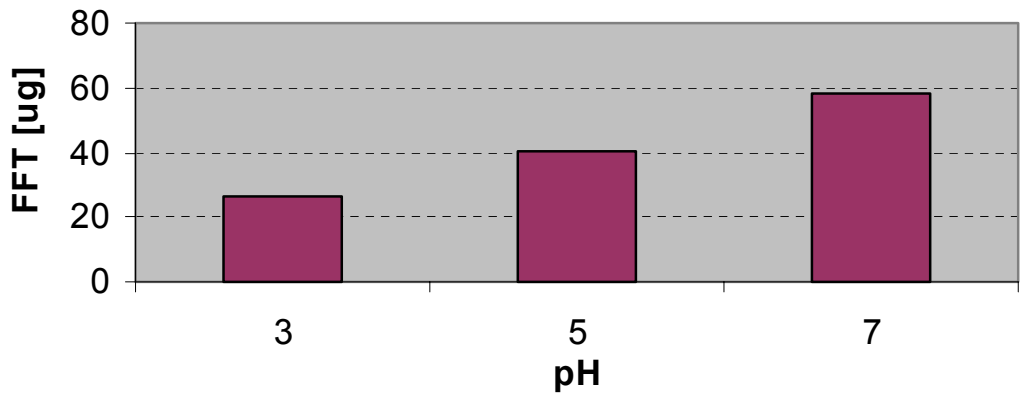
(Zheng & Ho, 1994)

First-order kinetics of H_2S release from cysteine

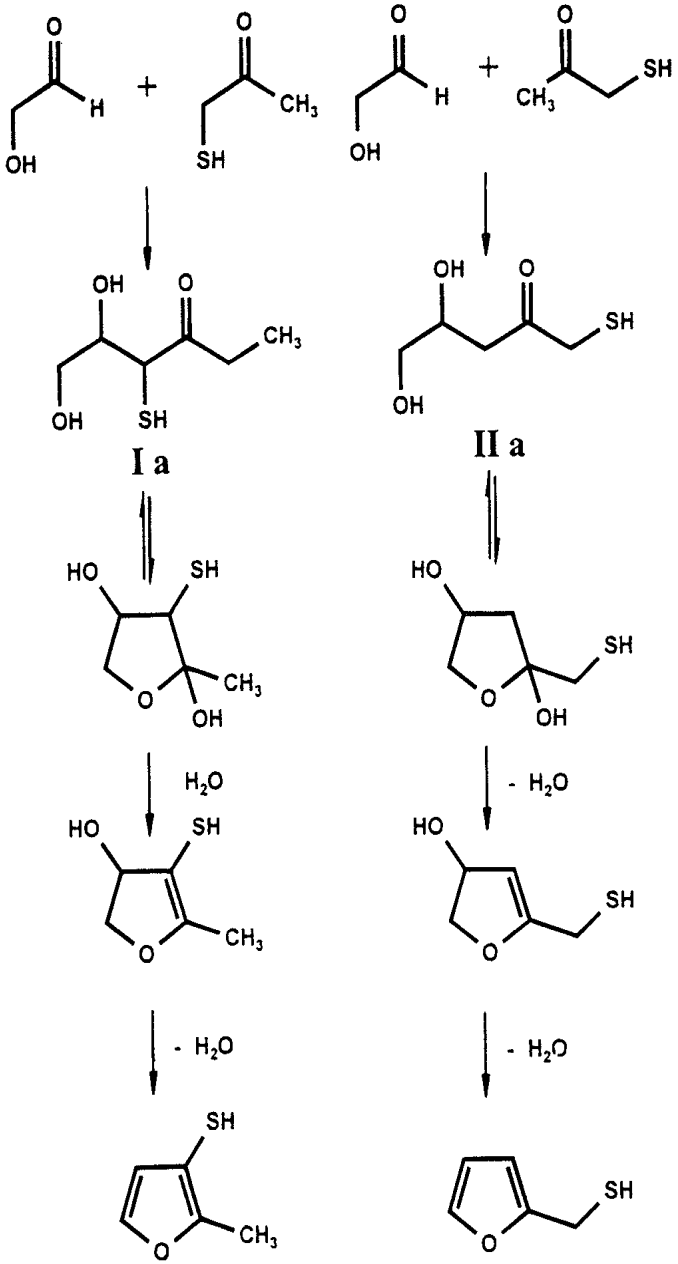
Conditions:
0.1 M Cys, buffer, 100 °C
Detection:
Sulfide/silver ion selective electrode

Formation of 2-furfurylthiol (FFT) from sugar fragments and H_2S





(Münch et al., 1997)



Reaction conditions:

Precursors (each 1 mmol)

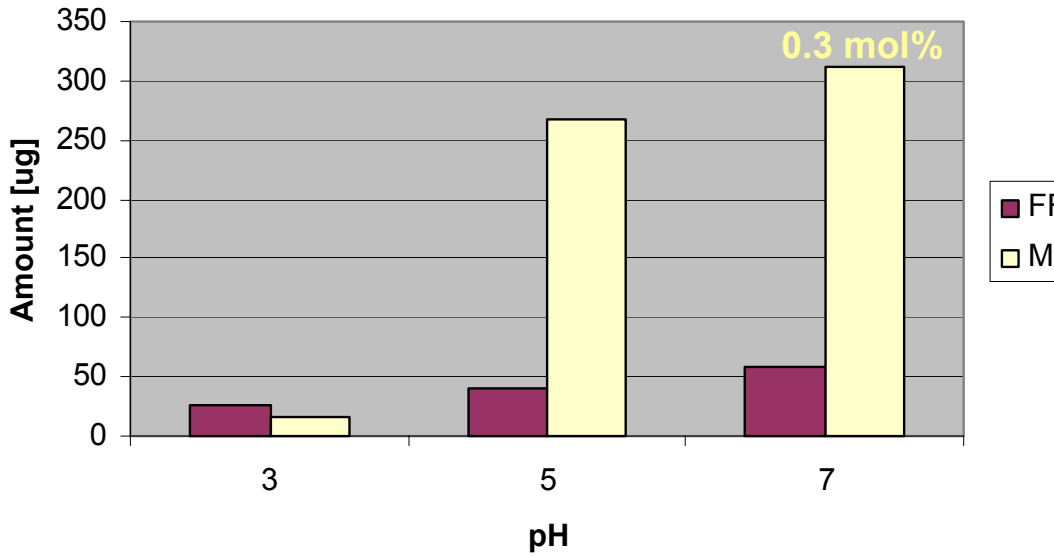
Phosphate buffer (50 mL, 0.5 mol/L)

Autoclave (145 °, 20 min)

Mechanism:

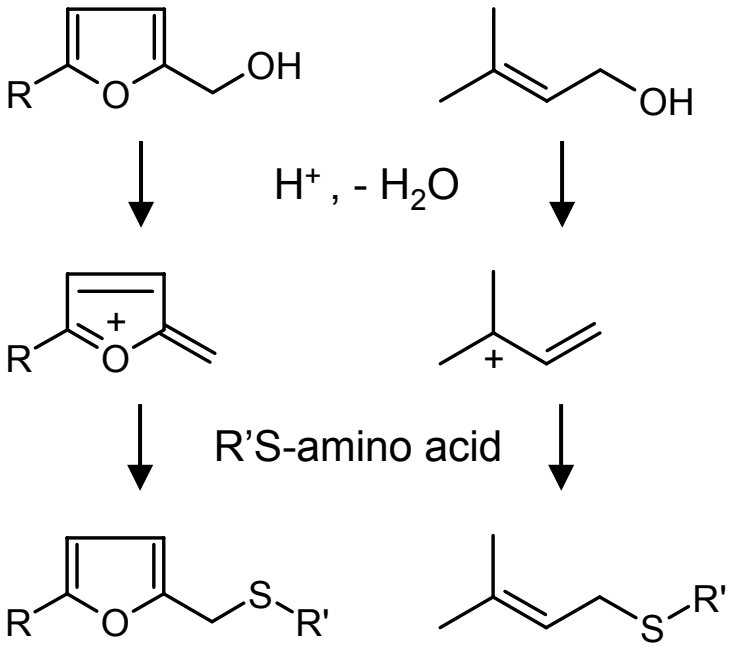
Aldol-type condensation

Cyclisation, dehydration



(Hofmann & Schieberle, 1998)

Formation of S-containing odorants from alcohols under acidic conditions



(Rizzi, 2000)

Reaction conditions:

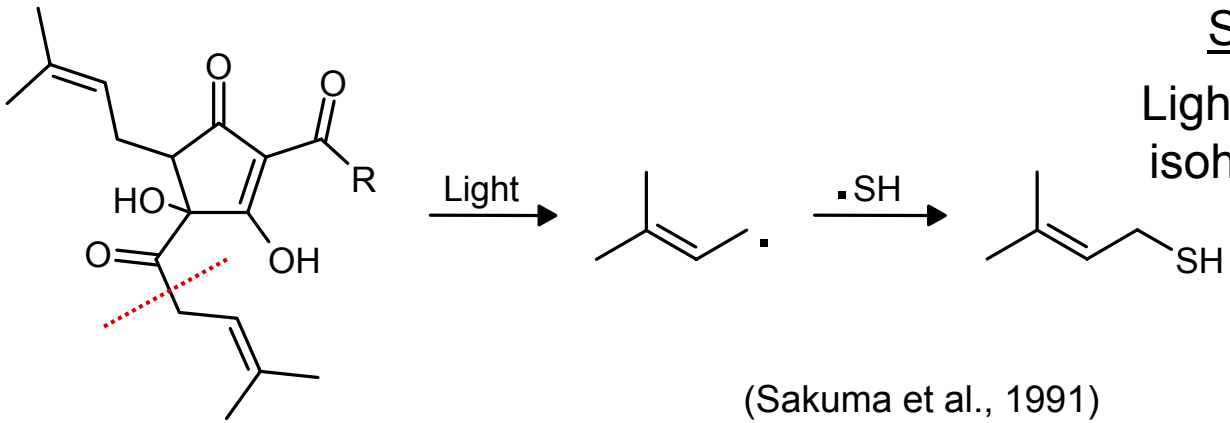
Alcohol, acetate buffer, pH 4.0, 100 °C

Mechanism:

Acid-catalysed alkylation of amino acid S-atom *via* cationic intermediates.

Unsaturated alcohols form electrophilic species in acidic media reacting with ambient nucleophilic sites.

(R, R': H, Me)

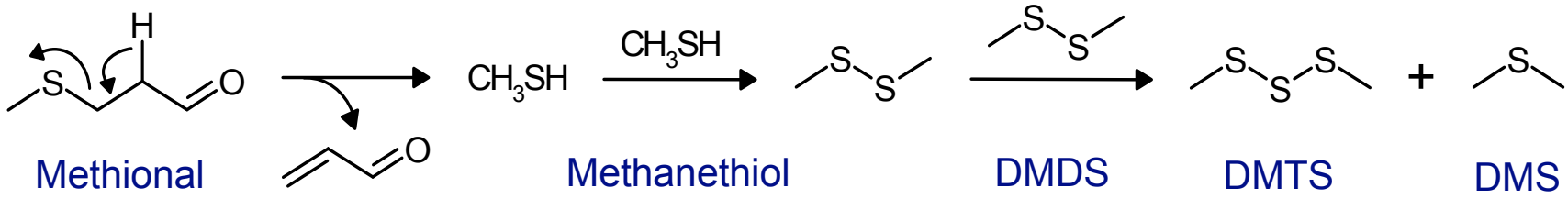


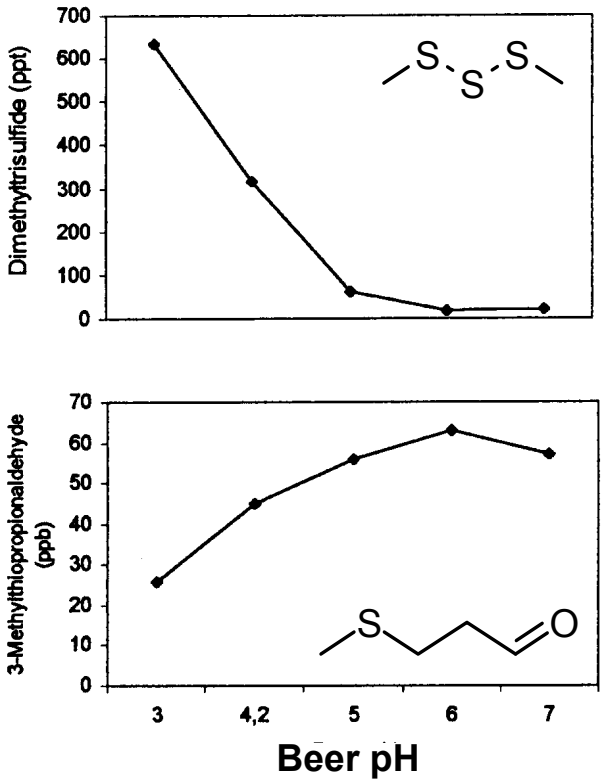
(Sakuma et al., 1991)

Sunstruck off-flavour in beer

Light-induced radical reaction of isohumulone and an SH-source (riboflavin-photosensitized reaction)

Formation of methional and DMTS during accelerated aging of beer





Reaction conditions:

Storage for 5 days at 40 °C

Mechanism:

Strecker degradation of methionine to form methional.

Formation of sulfite/aldehyde adducts trapping methional.

→ Higher DMTS amounts at lower pH

via disproportionation of DMDS

(Gijs et al, 2002)

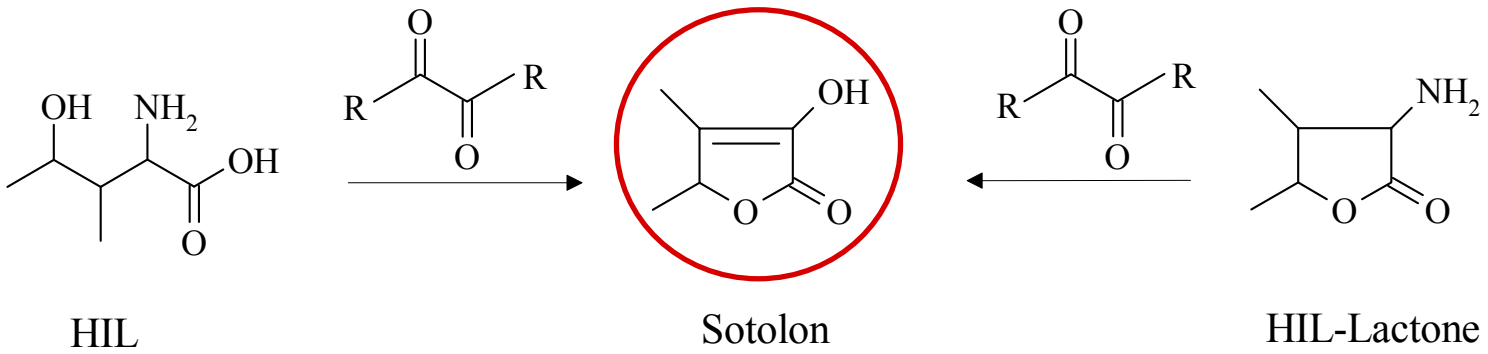
The role of pH in the Maillard reaction: Conclusions

- Many steps in the Maillard cascade are affected by the pH
- pH effect can be different, favouring reactions under acidic or alkaline conditions
- Buffer may have various tasks: i.e. constant pH (reaction control), catalytic effect (increasing reaction rate)
- Neutral pH (6-7) is often the best compromise for flavour formation
- Final amounts depend on formation & degradation, both of them are influenced by pH and may lead to off-notes

Thanks for your attention

Back-up slides

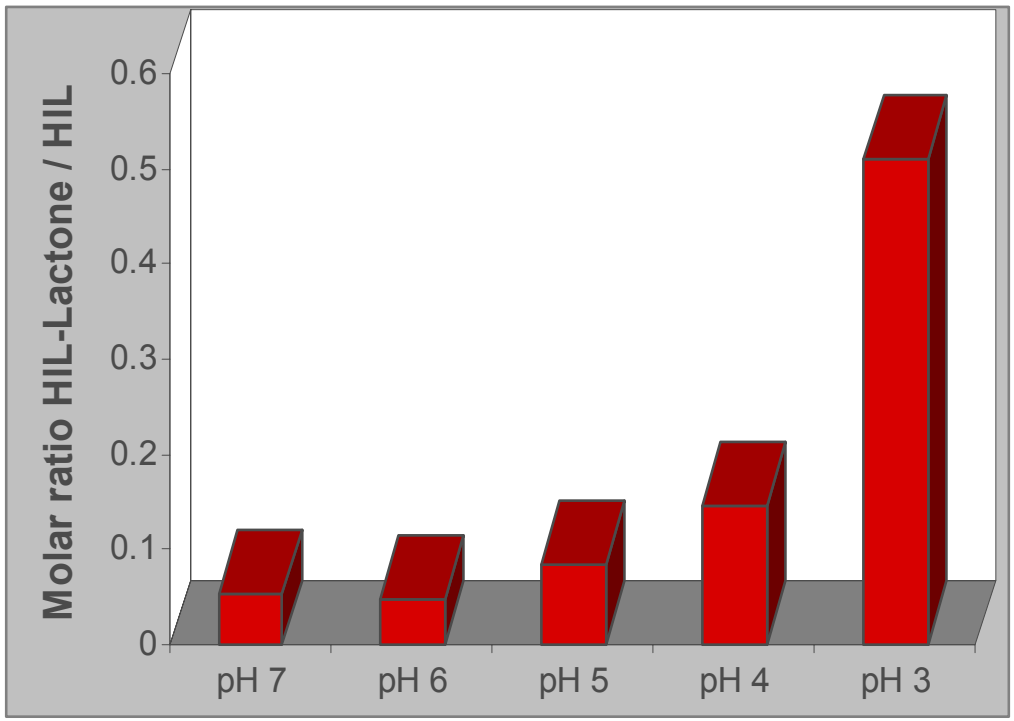
Formation of sotolon from 4-hydroxy-L-isoleucine (HIL) and its lactone

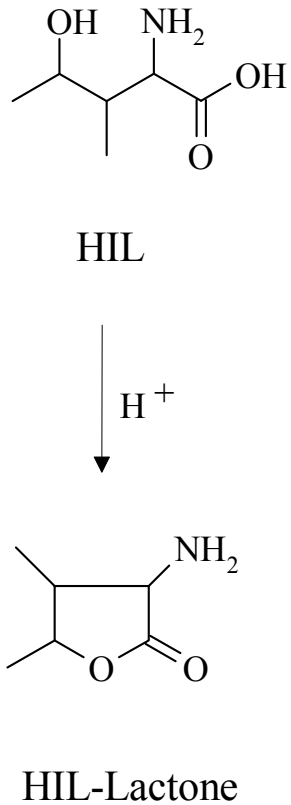


Carbonyl compound	Sotolon yield (mol%) (from HIL-Lactone)	Sotolon yield (mol%) (from HIL)
Methylglyoxal	35.9	7.4
2,3-Butanedione	0.3	<0.1

(Blank et al., 1996)

Lactonisation of 4-hydroxy-L-isoleucine (HIL) is favoured under acidic conditions

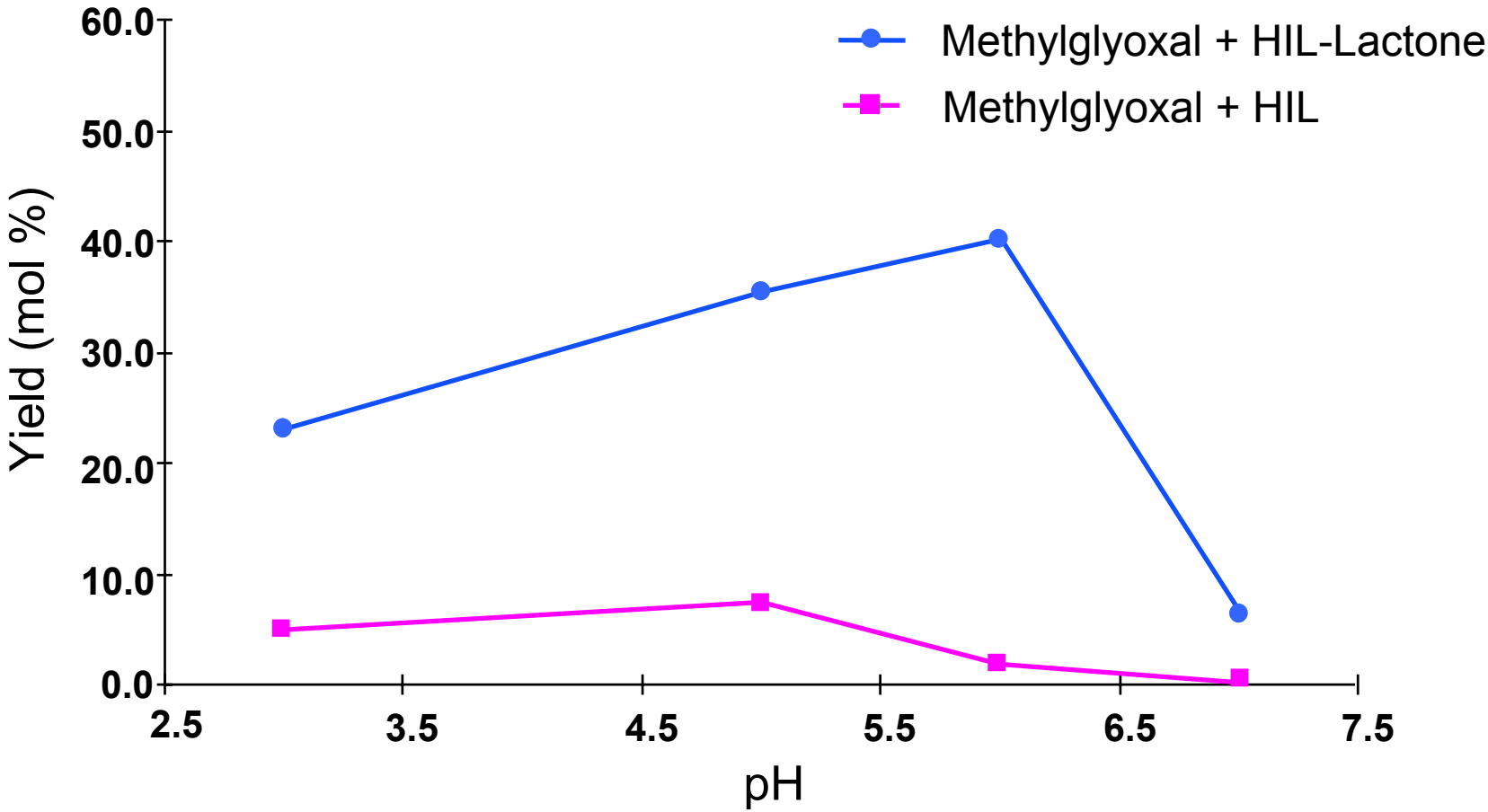




Reaction conditions : 100°C, 1 h, phosphate buffer
Analytical technique : FAB-MS

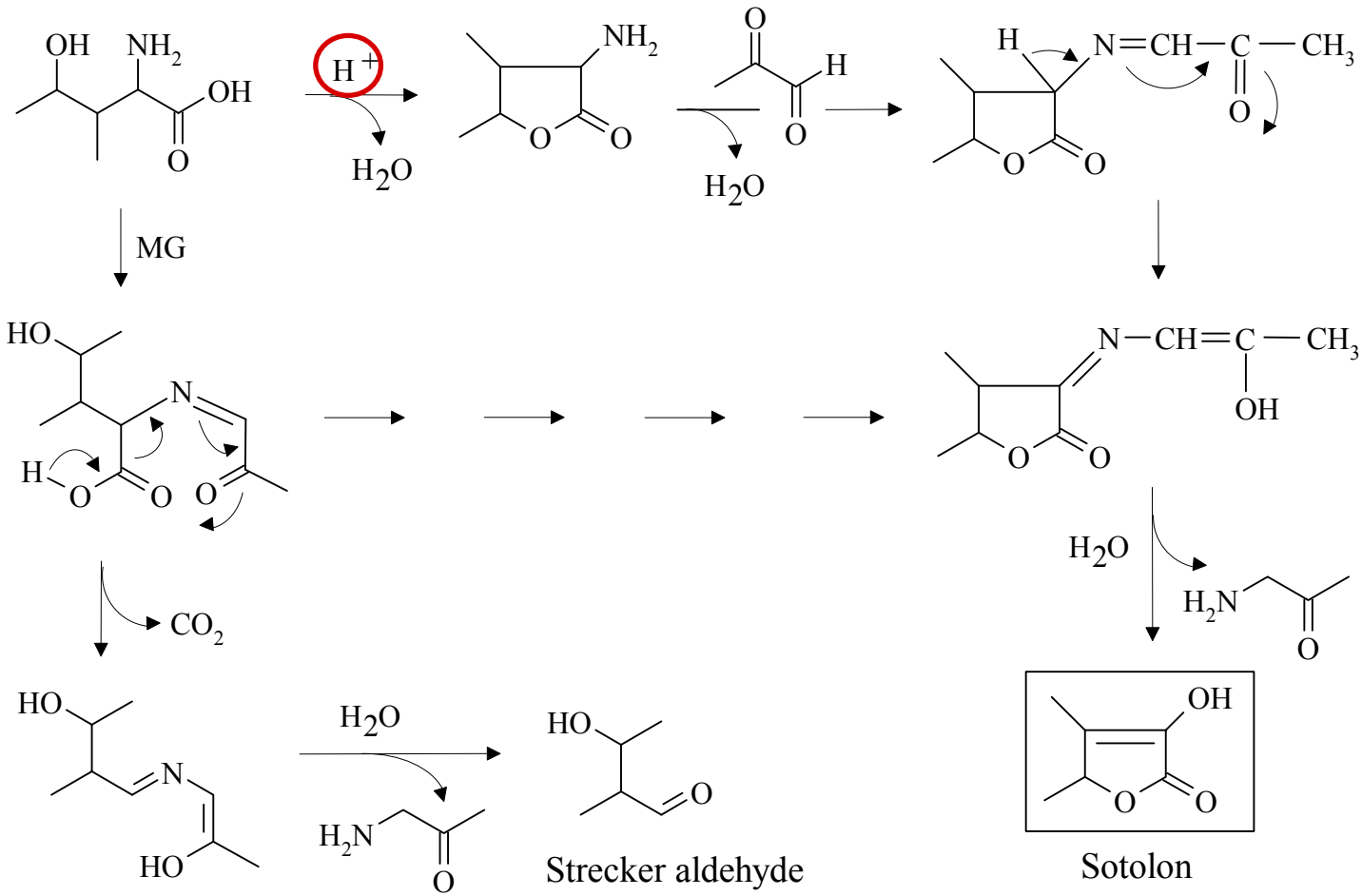
(Blank et al., 1997)

Formation of sotolon from hydroxyisoleucine (HIL) and its lactone: Influence of the pH



→ **Optimum: pH 5-6**

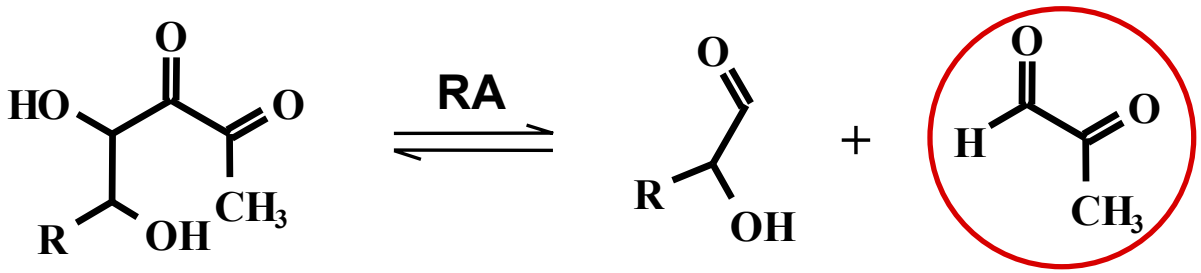
Sotolon formed from 4-hydroxy-L-isoleucine by thermally induced oxidative deamination



(Blank et al., 1997)

Formation of secondary degradation products: 1-Pyrroline and methylglyoxal

Retro-aldol reaction



Strecker reaction