American Craft Spirits Association

2017 DISTILLERS CONVENTION & VENDOR TRADE SHOW

FEBRUARY 16-17 | NASHVILLE, TN

More Continuous Chemistry: What has my making toast got to do with my favorite pour?

Gary Spedding, *Brewing and Distilling Analytical Services*

Who was Maillard & what has my making toast got to do with my favorite pour?

Gary Spedding, Ph.D.

Brewing and Distilling Analytical Services

Lexington, KY.

gspedding@alcbevtesting.com

www.alcbevtesting.com

ACSA-2017

A Frenchman

A yellow-brown sweet-savory reaction?

Toast starts the day & a steak may end it

Maillard chemistry

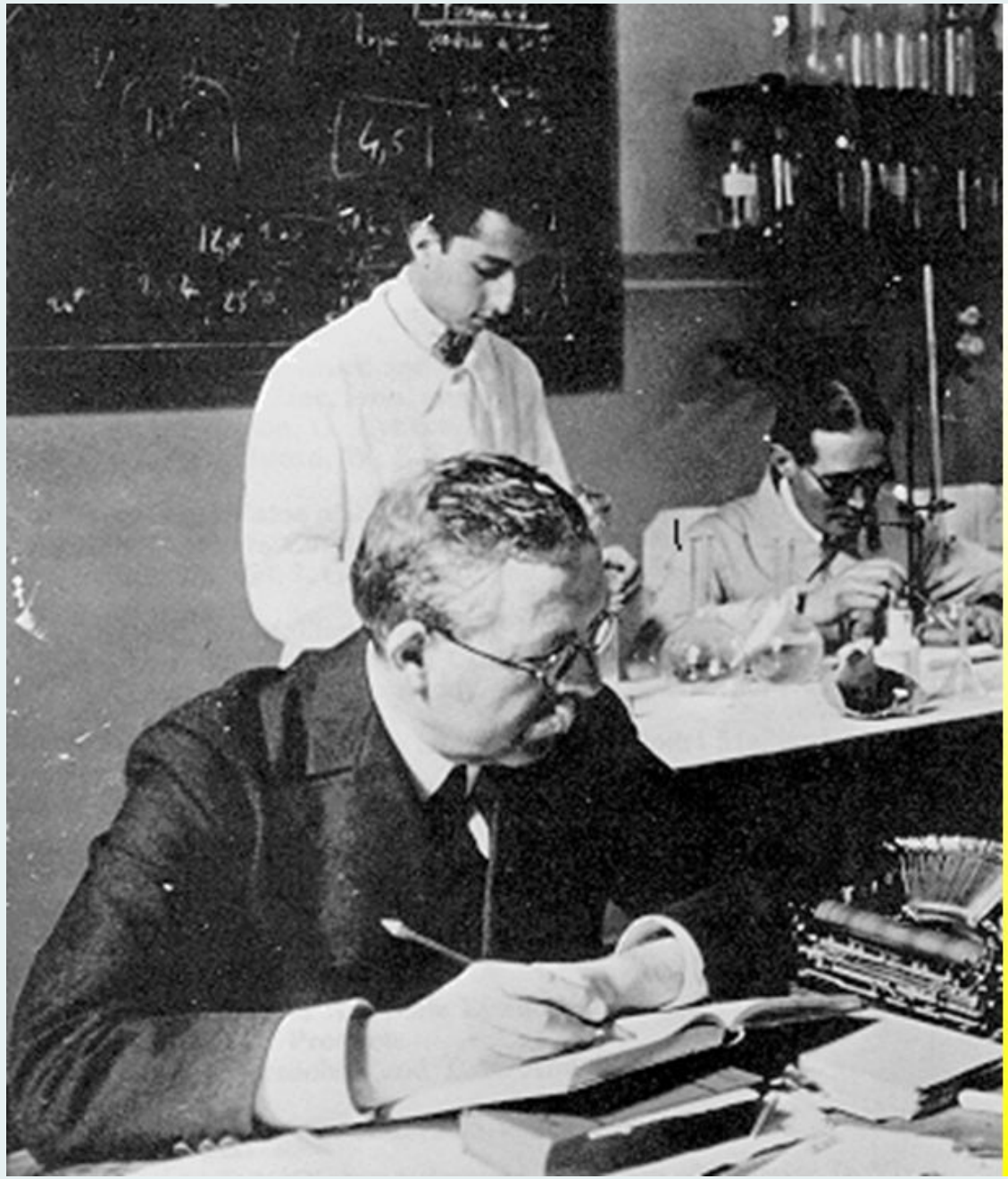
Distilled spirits production & Maillard chemistry

A coffee break

Million dollar question

Questions

Summary



Louis-Camille Maillard (1878 - 1936)

Photographed in his laboratory *ca* 1915

1912 - 1916:
He published 8 papers on his observations of colour changes on mixing amino acids and sugars.

No one else took much interest in the reaction until 1950s

Maillard – the Reactions

Maillard - The Basics

1912 – a simple browning reaction

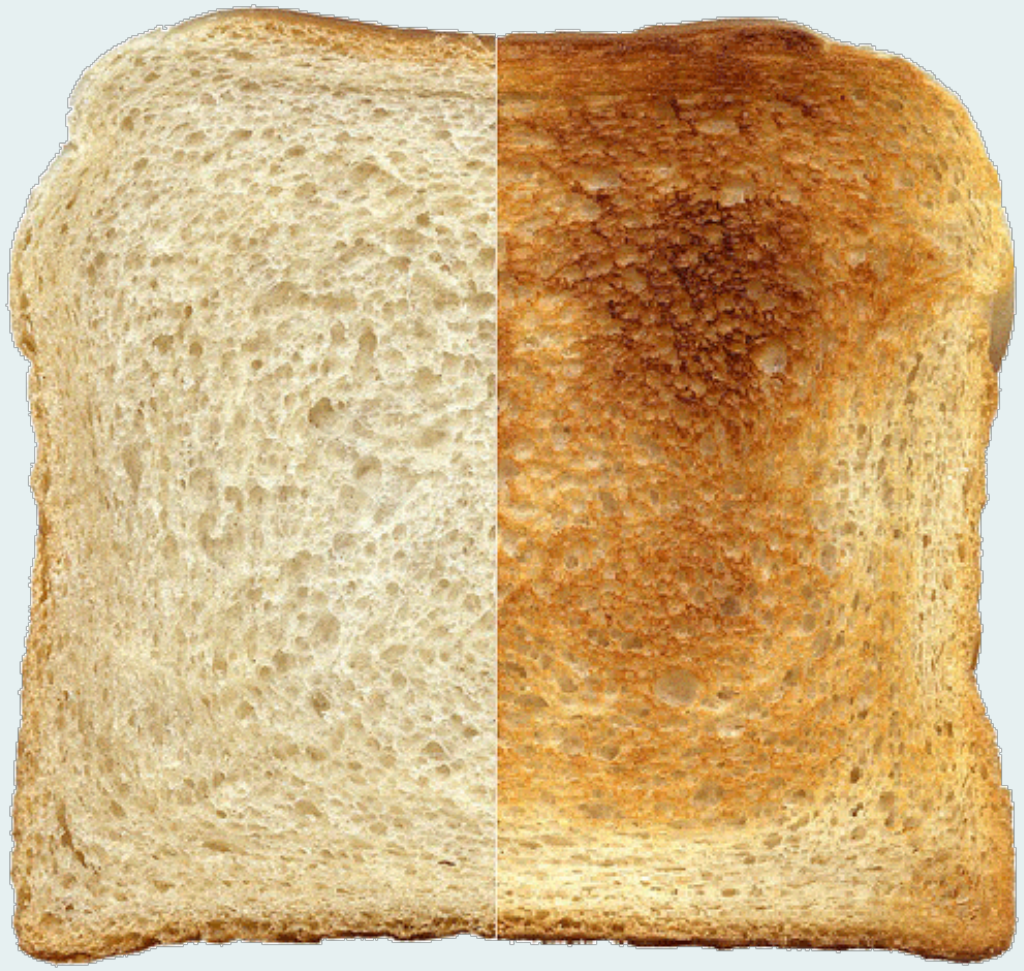
From disease to the taste of cooked onions

Maillard reaction & cooking

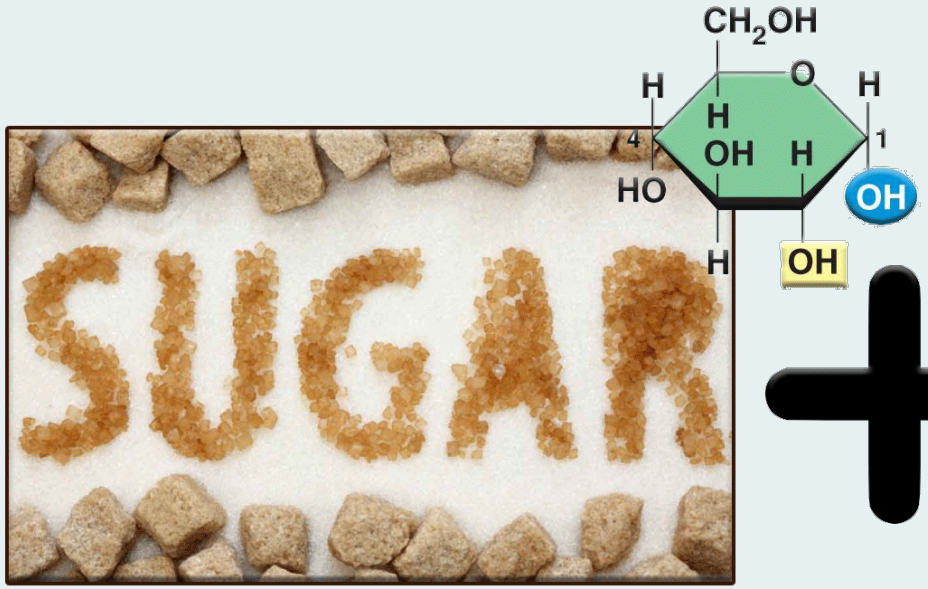
Non-enzymatic browning

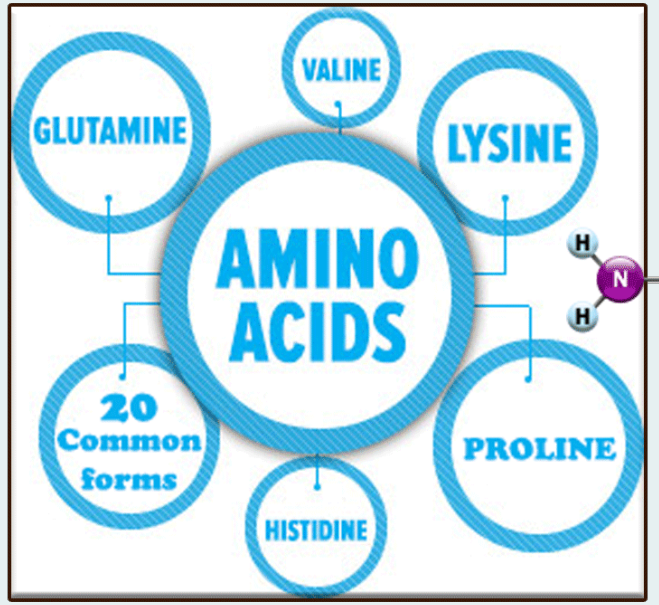
Hodge 1973

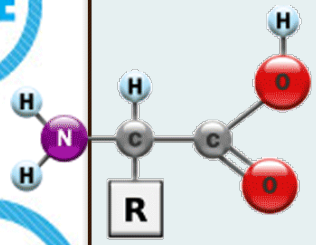
Many reactions - 3 main stages



Maillard –Simply Defined

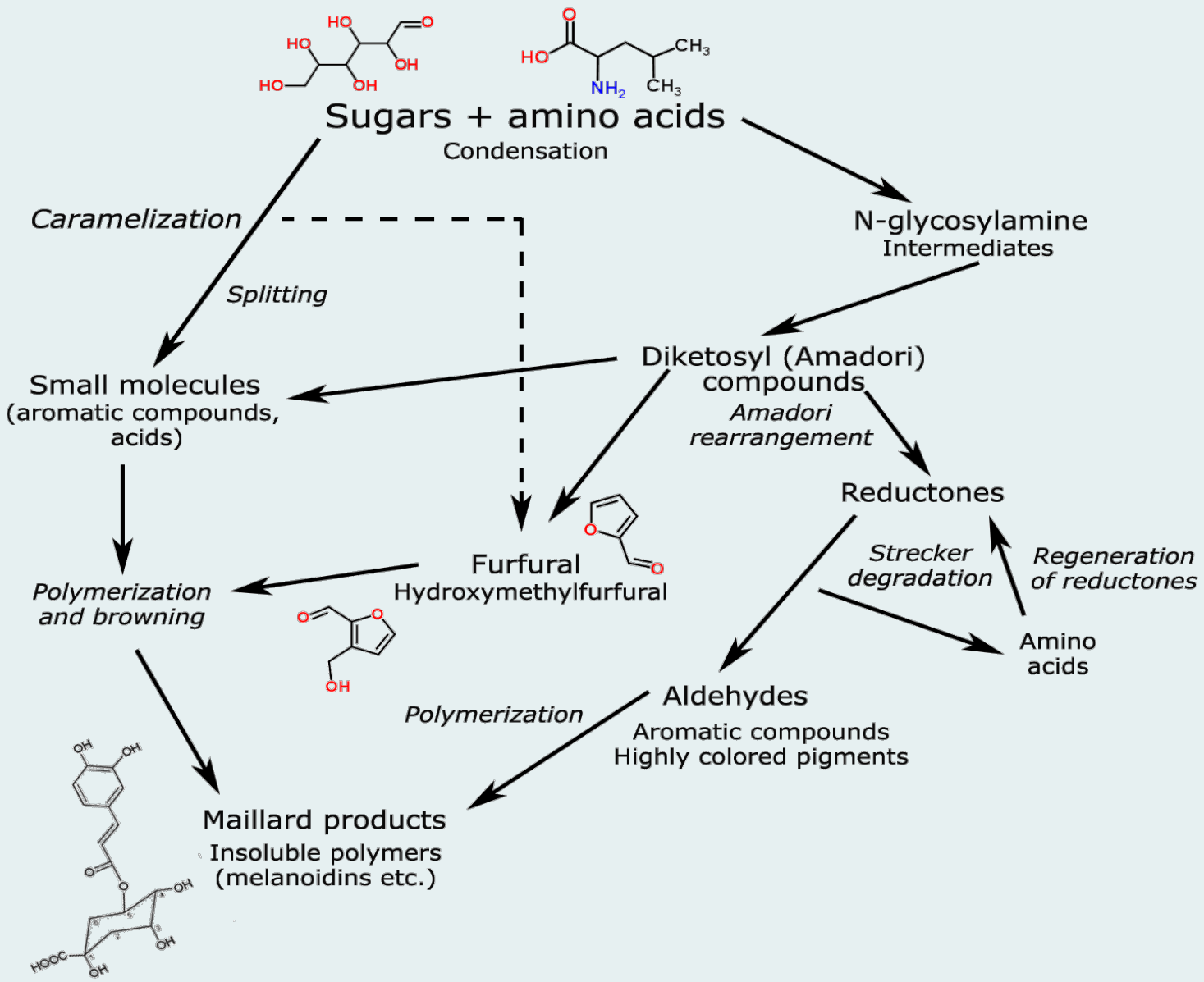






+ High temperature = Range of dark pigmented products & flavor


maillard
a cascade
of reactions


Sugars + amino acids
Condensation
Caramelization
Splitting
N-glycosylamine
Intermediates
Small molecules
(aromatic compounds,
acids)
Diketosyl (Amadori)
compounds
Amadori
rearrangement
Reductones
Furfural
Hydroxymethylfurfural
Polymerization
and browning
Strecker
degradation
Regeneration
of reductones
Amino
acids
Aldehydes
Aromatic compounds
Highly colored pigments
Polymerization
Maillard products
Insoluble polymers
(melanoidins etc.)

The CASCADE leads to a POOL of compounds

Early products rearranged then...

Degradation

Elimination

Cyclization

Dehydration

Fission

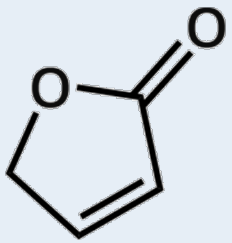
Fragmentation

....Reactions lead to

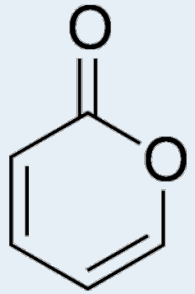
many flavor and color compounds

Strecker Degradation products & flavors

Amino acid	→ Strecker aldehyde	Odor description	
Valine	2-Methylpropanal	Green, overripe fruit	
Leucine	3-Methylbutanal	Malty, fruity, toasted bread	
Isoleucine	2-Methylbutanal	Fruity, sweet, roasted	
Phenylalanine	Phenylacetaldehyde	Green, floral, hyacinths	
Methionine	Methional, methanethiol, 2-propenal	Vegetable-like aromas	
Proline	Pyrrolidine, 1-pyrroline NO STRECKER ALDEHYDE	Important intermediates for bread-like aromas	
Cysteine	Mercaptoacetaldehyde, acetaldehyde, H_2S, ammonia	Important intermediates for meat-like aromas	



FURANONES
sweet
caramel
burnt

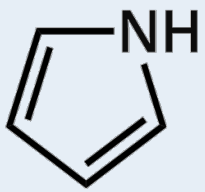


PYRANONES
maple-like
vanillin-like
warm, spicy
fruity, jam-like

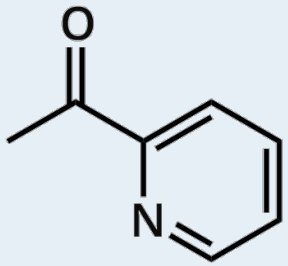
Reductones+ dehydroreductones

NH_3 H_2S

- Furanones
- Pyranones
- Pyrroles
- Thiophenes



PYRROLES
cereal-like
nutty



ACYLPYRIDINES
cracker-like
cereal

amino acid

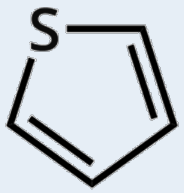
Strecker reaction

Aldehydes + aminoketones

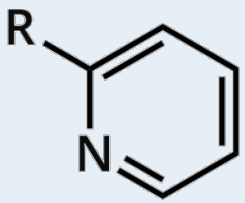
acetoin

heterocyclization

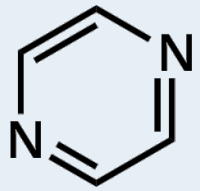
- Pyridines
- Pyrazines
- Oxazoles
- Thiazoles
- Pyrroles
- Imidazoles



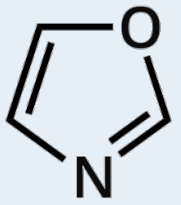
THIOPHENES
meaty
roasted



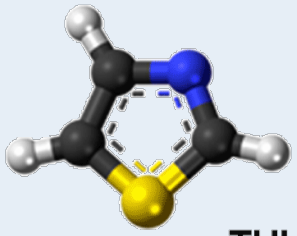
ALKYLPYRIDINES
bitter
burnt
astringent



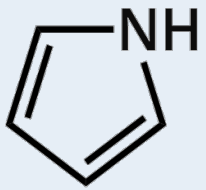
PYRAZINES
cooked
roasted
toasted



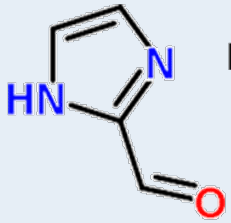
OXAZOLES
green
nutty
sweet



THIAZOLES
nutty



PYRROLES
cereal-like
nutty

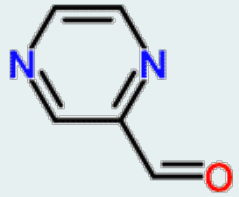


IMIDAZOLES
chocolate
nutty
bitter

Maillard – color, aroma & flavor

1000's products > flavor & aroma

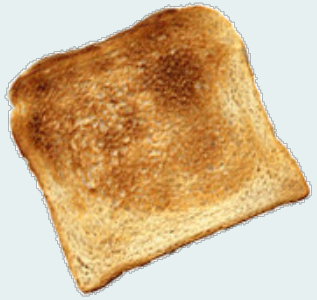
Melanoidins > complex = brown polymers > contribute color

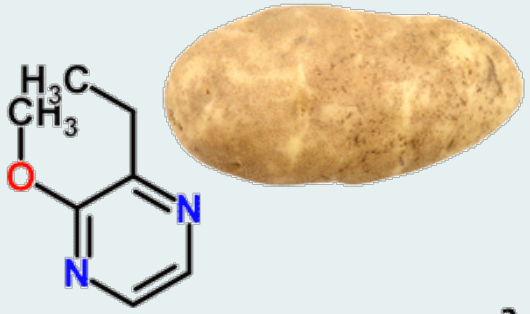


Pyrazinecarbaldehyde

or formylpyrazine

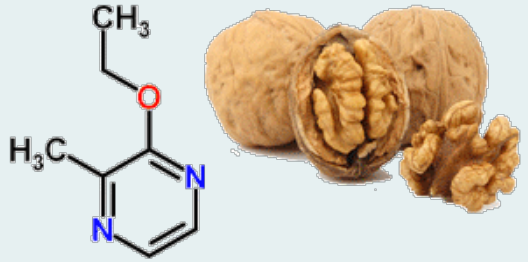
Toasted aroma





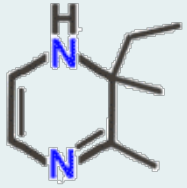
2-ethyl-3-methoxypyrazine

Potatoes

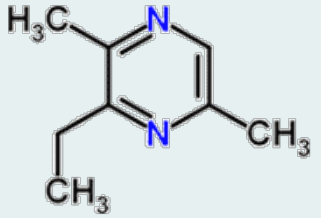


2-ethoxy-3-methylpyrazine

Roasted Walnut



2-ethyl-2,3-dimethyl-1,2-dihydropyrazine



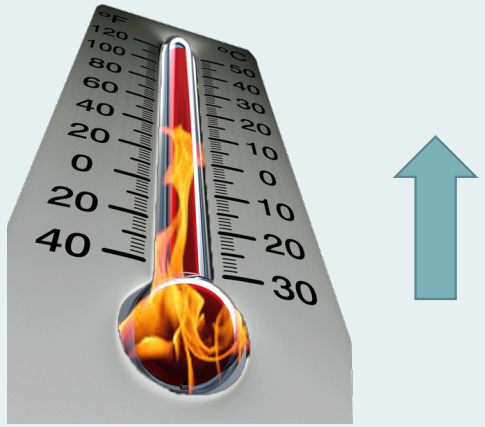
2-ethyl-3,6-dimethyl-pyrazine

Hazlenut

Roasted Almond

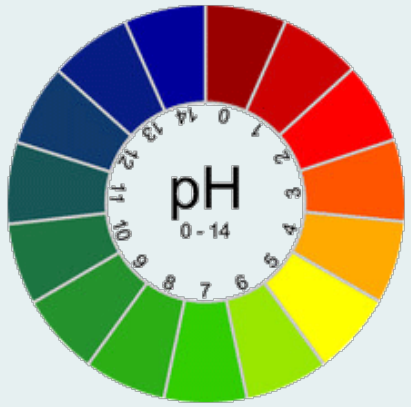
Maillard Conditions

Increase in Temp



Heat time

pH (esp. above 7.0)



< 55°C (130°F): Days, months, years

55-100°C (130-212°F): Water [High Protein] [High Sugar] & alkaline – hours, days

100-150°C (212-300°F): Hours when close to BPt. of Water

150-165°C (300-330°F): Fast – browning in mins.

165-200°C (330-400°F): Inc. in caramelization – Maillard inhibited

200+°C (400+°F): Caramelization and burning

Let’s add some color to the mix!

DL-Pheala + Cys	Control	L-Glutathione+Gly+Lys
pH 5.0 SRM 9 (0.56)	pH 5.37 SRM 16 (1.0)	pH 5.22 SRM 20 (1.25)

On to Distilled Spirits Production

Where will Maillard reactions occur?

Malting/kilning

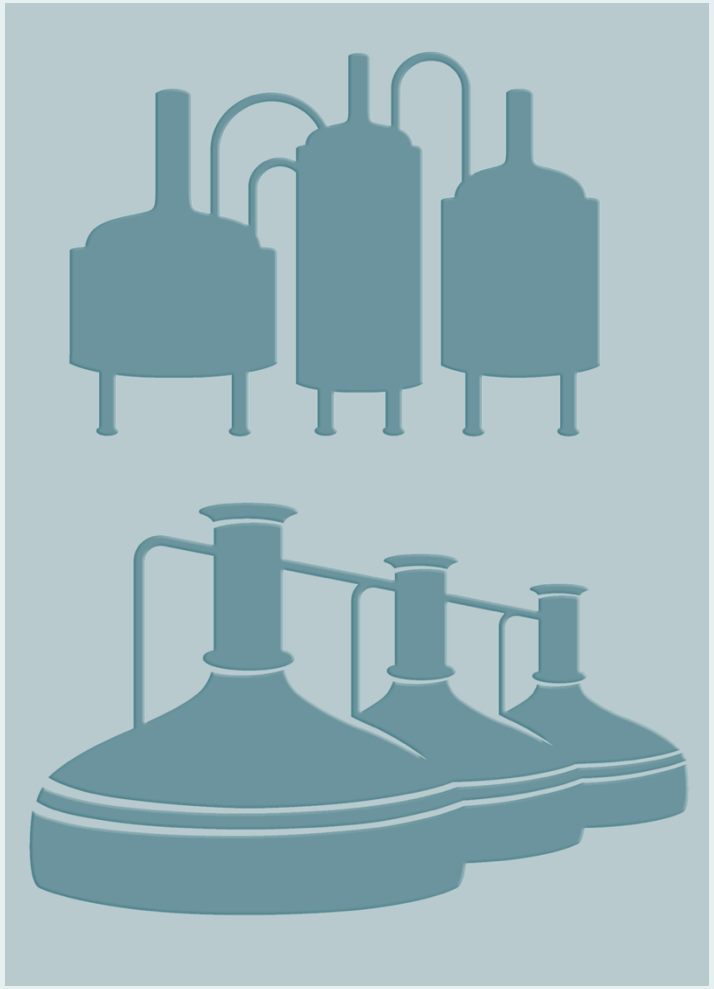
Cooking

Mashing

Distilling

Spent grain drying

Cask toasting/ charring



Malting and kilning

Malt & grains > initial input
Maillard reaction components

Distillers malts not cured like ale malts - choose grains for desired flavor

Brewer’s malts: High temperature kilning & roasting > develops flavor compounds

Cereals

Chemical formation - aroma components from free amino acids & reducing sugars

Amino acids in green malt transformed → Strecker aldehydes – pH dependent!

Model Maillard reactions > cereal, corny, bready flavors

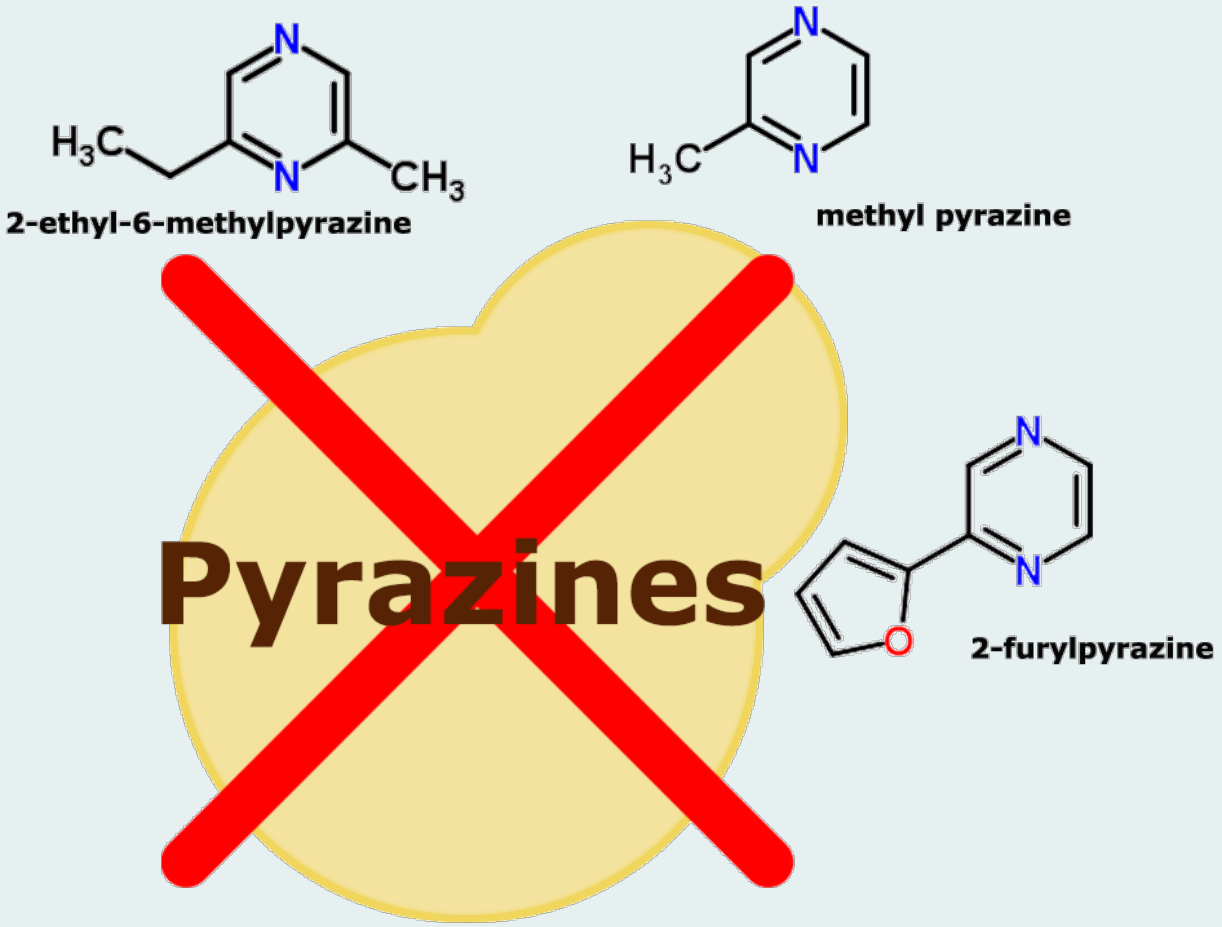
Cereals & Pyrazines

Kilning/roasting: Strecker degradation free amino acids → Pyrazines

“Green, nutty roasted, coffee”

End up in wash or beer

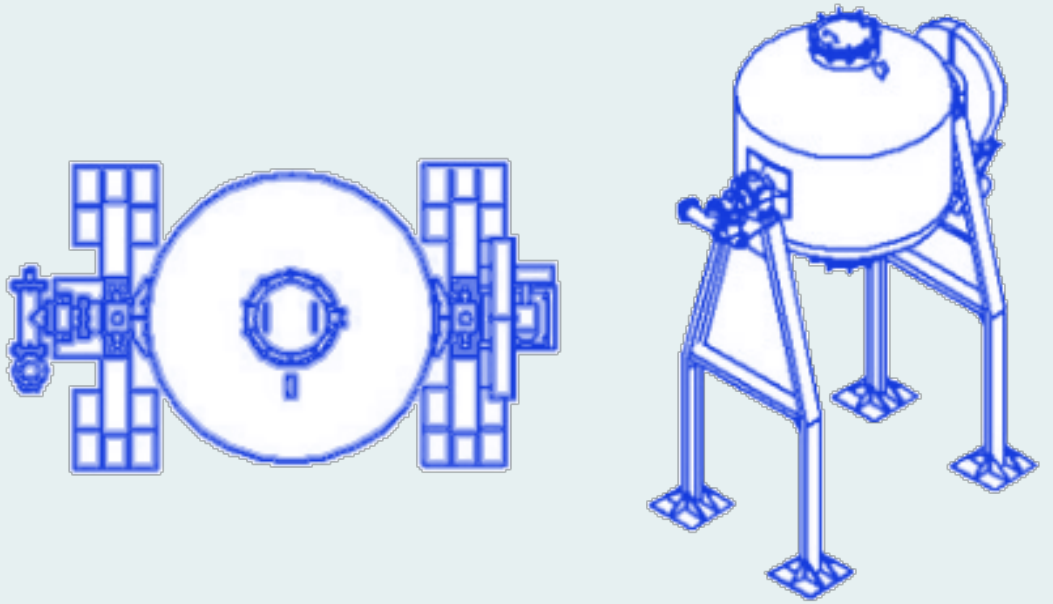
Dozen + pyrazine derivatives > notable flavors



Cooking

Different cooking systems

Degradation of fermentable carbohydrates & amino acids – impact spirit yield!



Mashing

Mashing operations & Maillard:

Flavor & Yield

FAN and fermentation?

Distilling

Changing distillation temperature/protocols

Saving energy

Direct firing (hot spots)/ indirect heat more uniform

Distilling – Thermal issues

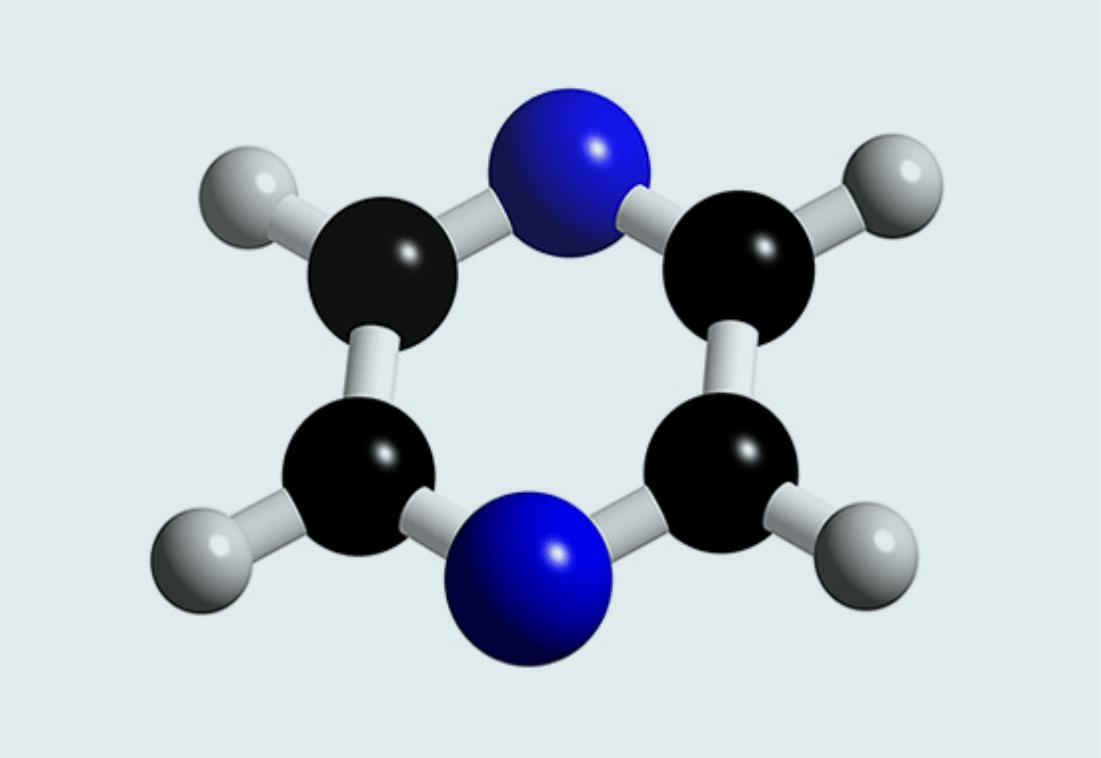
Decrease still operation time – higher temperature & increased distillation rate

or

Insulate still

= changes in temperature profile through the distillation

Some Experiments



Thermal issues - SWRI - Frances Jack

Mimic still surface temp.

Heat wash: 60, 80, 100, 120°C

Hold under reflux 1 hr.

Vacuum distilled 57°C [Low thermal stress]

The results....?

Thermal issues - SWRI – F. Jack - Results

Sensory results:

Each 20°C rise > significant change in aroma

= Heavy cereal & sulfury notes

Note: Cu(I), Cu (II) and Fe increases Maillard reactions

Cereal and feinty notes?

Likely Maillard notes

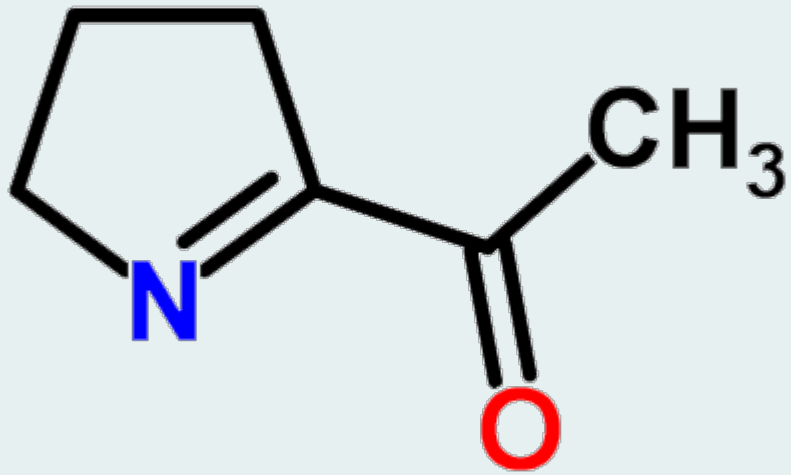
Remember:

Amino acids + sugars + HEAT = Flavor Active Congeners

Try simple heat steps with wash (or wort) & compare flavors - alter conditions accordingly!

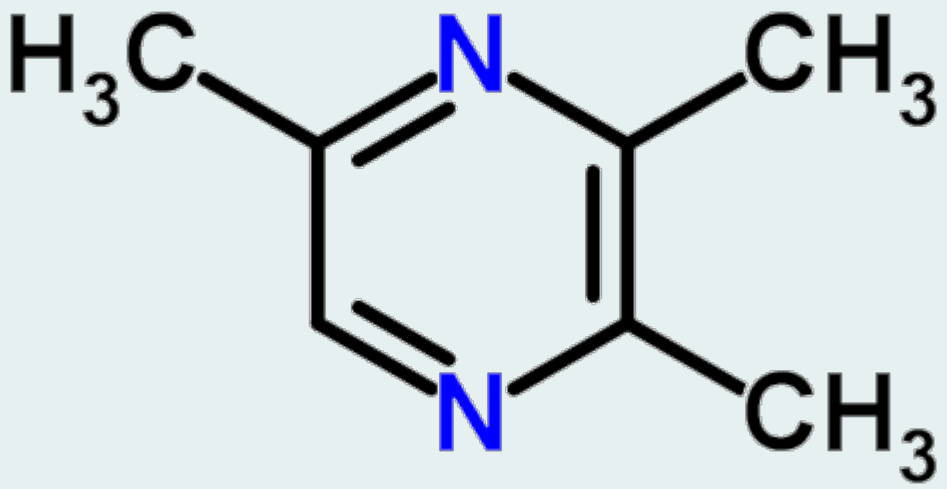
What SWRI found:

2-Acetyl-pyrroline (cereal, white bread, jasmine & basmati rice, hot buttered popcorn)



What SWRI found:

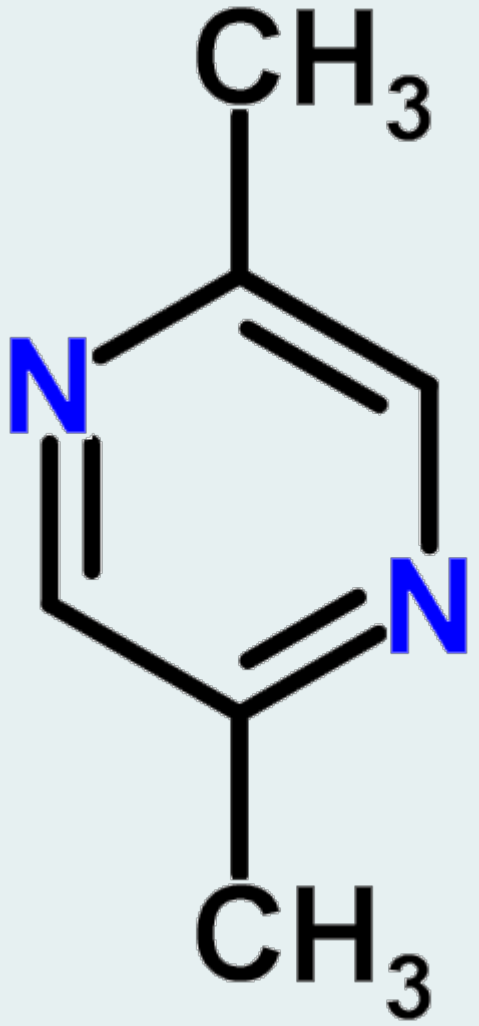
Tri-methyl pyrazine (nutty, peanut, potato)



What SWRI found:

2,5-dimethyl pyrazine

(nutty, roasted nuts, meaty, roast beef, potato chips, woody & grassy)



Flavors produced via Maillard reactions between wash amino acids & sugars during distillation

Aldehydic	Cooked potatoes	Grassy/green	Sweetcorn
Biscuity	Cooked vegetables	Malty	Sour
Burnt	Damp wool	Meaty	Stale
Buttery	Dead roses	Metallic	Sulfury
Cereal	Fecal/manure	Musty	Sweaty
Cheesy	Farmyard	Nutty	Sweet
Chlorine	Floral	Oily	Toasty
Chocolatey	Fruity	Rubbery	Toffee


1,000,000
UNITED STATES OF AMERICA
1M
US1002633H
ONE
MILLION
1M
1,000,000
US1002633H
1M
ONE MILLION DOLLARS
1,000,000
1,000,000

Will they distill over – that is the question!

SWRI showed under lab reduced vacuum – yes!

+ Spirits taste of the raw materials used

Conditions:

Heat Boiling Points

pH Hydrogen bonding (?)

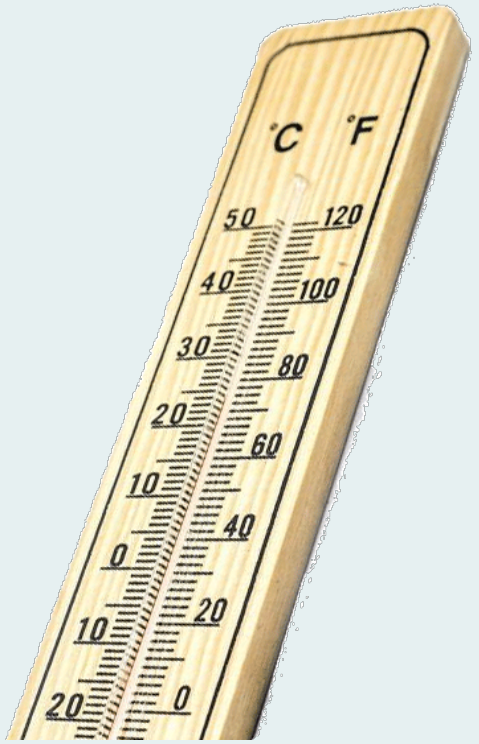
Lower proof distillation > grain notes carryover?

Will they distill over – that is the question!

Furan – BPt. 31.3°C (88.3°F)

Oxazole – BPt. 69.5°C (157.1°F)

Pyridine (alkylpyridine) – BPt. 128-130°C (262.4-266.0°F)

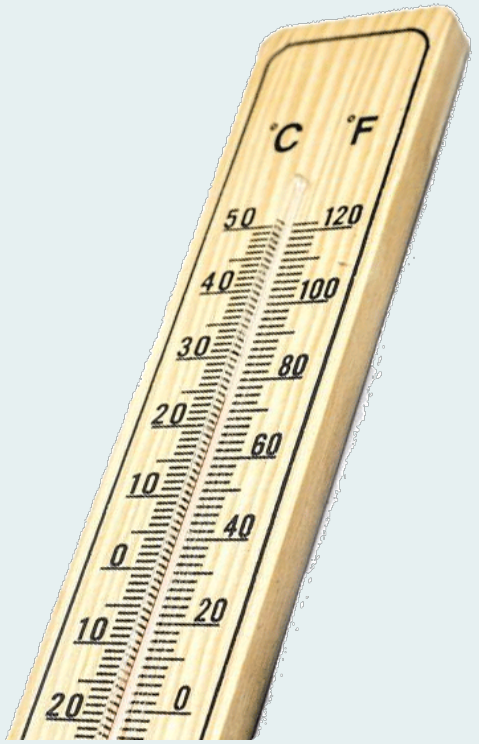


Will they distill over – that is the question!

Pyrazine – BPt. 115°C (239°F)

Pyrrolle – BPt. 129°C (264.2°F)

Thiophenes – BPt. 84°C (183.2°F)



After Distillation & Maillard Reactions

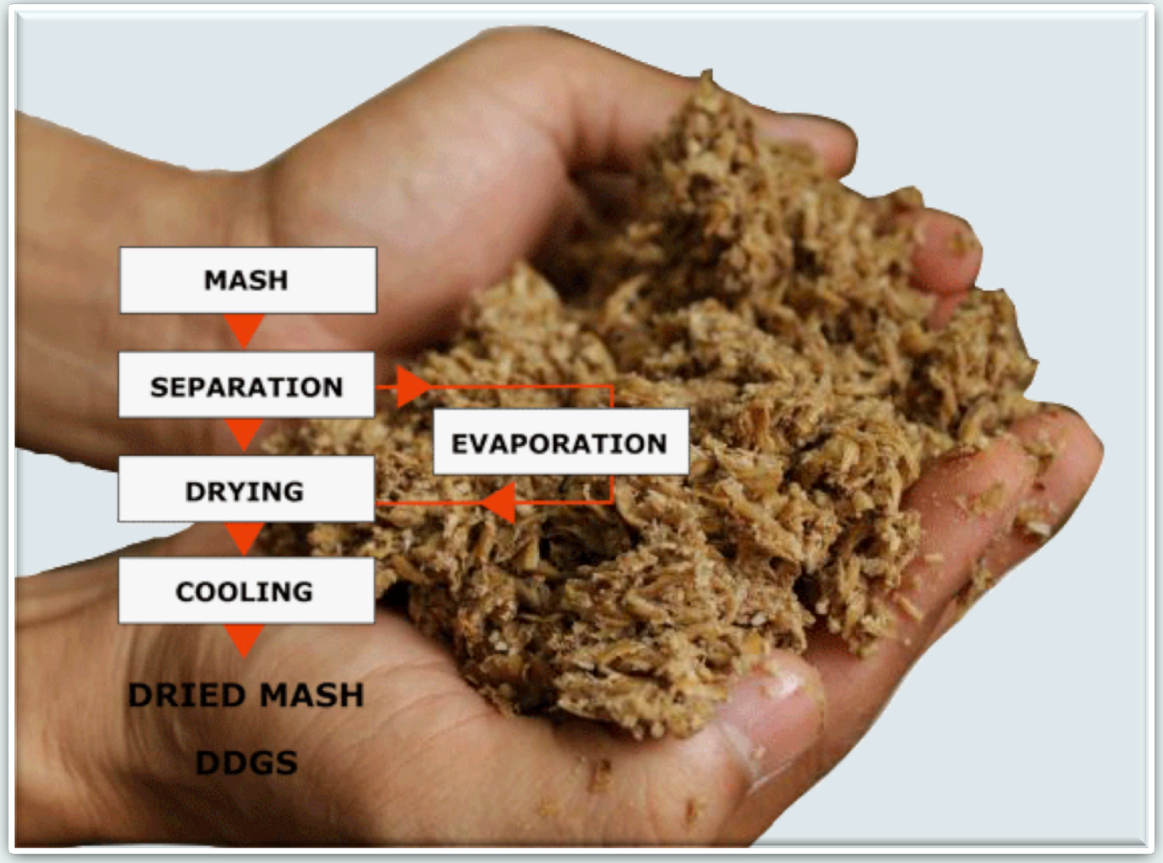
Spent Grain

Distillers Dry Grains with Solubles

Quality protein in spent grains imp. poultry & swine diets

Overcooked DDGS in drying: amino acids combine with CHO's – rendered undigestible

Amino acid deficiencies!



Casks

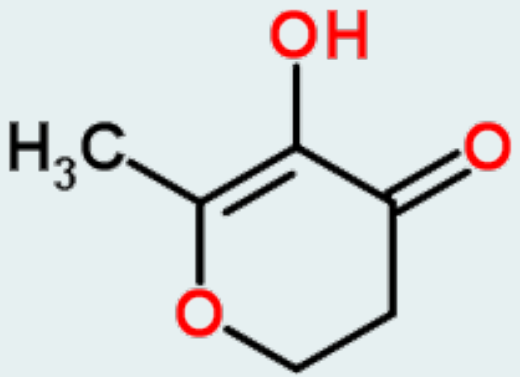
Many sugars generated/developed in charring & toasting

Charring: Caramelization overrides Maillard

Toasted Oak

Extracts have shown the Maillard compound:

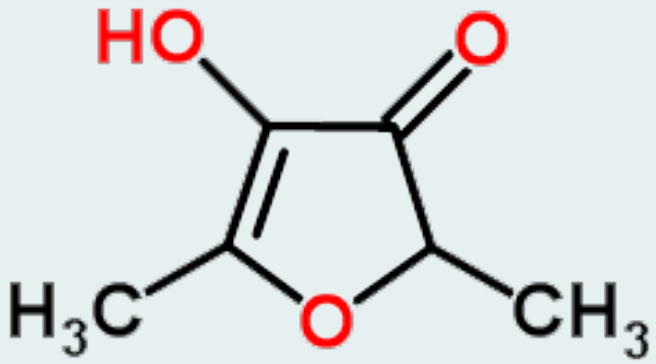
2,3-dihydromaltol [aka. 5-Hydroxy-6-methyl-2,3-dihydro-4H-pyran-4-one. PYRANONE!]



Toasted Oak

Extracts have shown:

Furaneol

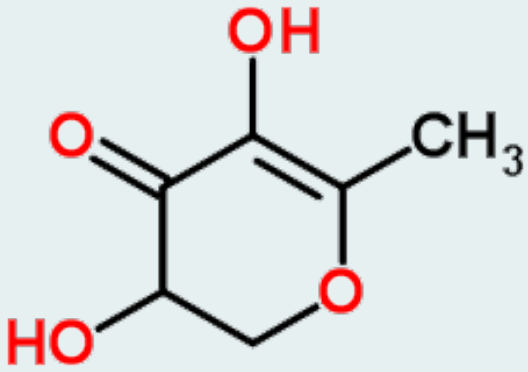


[aka.4-hydroxy-2,5-dimethyl-3(2H) FURANONE]

Toasted Oak

Extracts have shown:

2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one [aka. 3,5-Dihydroxy-6-methyl-2,3-dihydro-4H-pyran-4-one. PYRANONE!]



Questions?

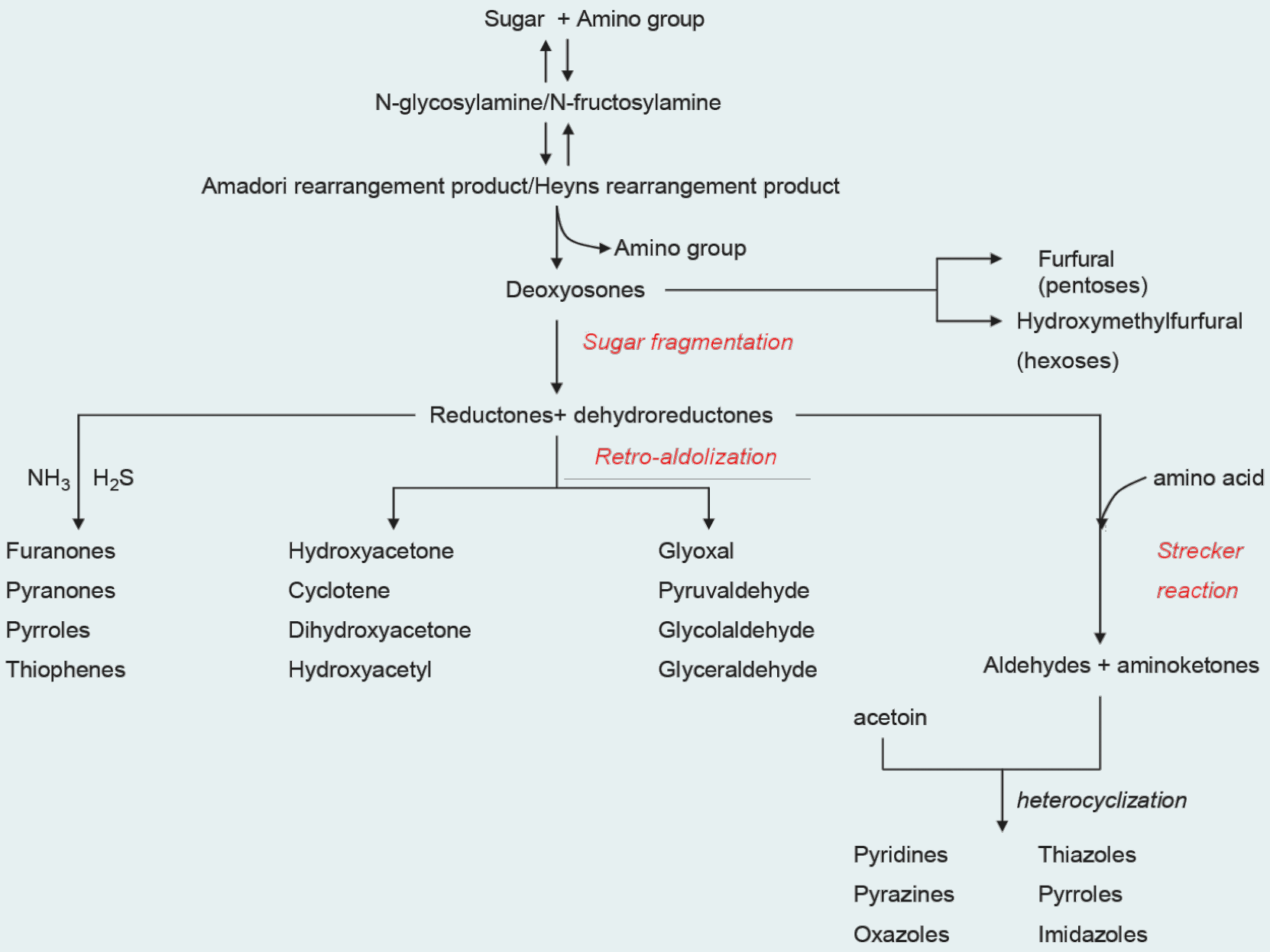
Summary/Conclusions

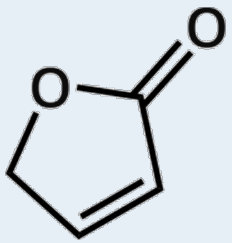
Summary

Simple concept

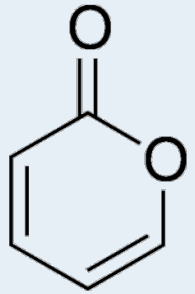
Sugars & amino acids

Complex reactions


Sugar + Amino group
N-glycosylamine/N-fructosylamine
Amadori rearrangement product/Heyns rearrangement product
Amino group
Deoxyosones
Furfural
(pentoses)
Hydroxymethylfurfural
(hexoses)
Sugar fragmentation
Reductones+ dehydroreductones
Retro-aldolization
NH3
H2S
amino acid
Strecker
reaction
Furanones
Pyranones
Pyrroles
Thiophenes
Hydroxyacetone
Cyclotene
Dihydroxyacetone
Hydroxyacetyl
Glyoxal
Pyruvaldehyde
Glycolaldehyde
Glyceraldehyde
Aldehydes + aminoketones
acetoin
heterocyclization
Pyridines
Pyrazines
Oxazoles
Thiazoles
Pyrroles
Imidazoles



FURANONES
sweet
caramel
burnt

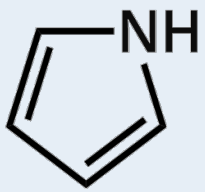


PYRANONES
maple-like
vanillin-like
warm, spicy
fruity, jam-like

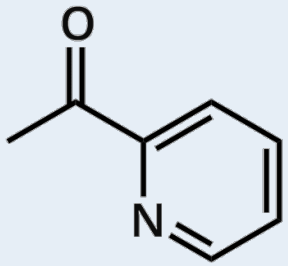
Reductones+ dehydroreductones

NH_3 H_2S

- Furanones
- Pyranones
- Pyrroles
- Thiophenes



PYRROLES
cereal-like
nutty



ACYLPYRIDINES
cracker-like
cereal

amino acid

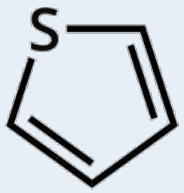
Strecker reaction

Aldehydes + aminoketones

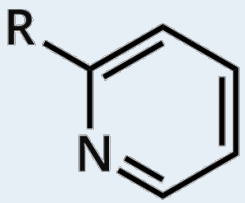
acetoin

heterocyclization

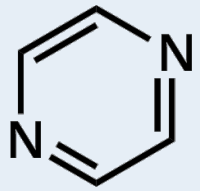
- Pyridines
- Pyrazines
- Oxazoles
- Thiazoles
- Pyrroles
- Imidazoles



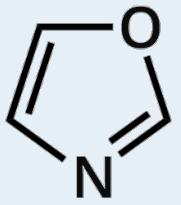
THIOPHENES
meaty
roasted



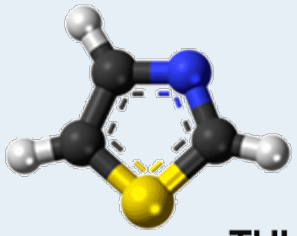
ALKYLPYRIDINES
bitter
burnt
astringent



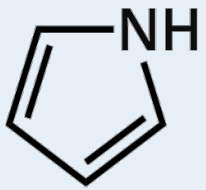
PYRAZINES
cooked
roasted
toasted



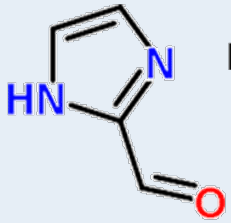
OXAZOLES
green
nutty
sweet



THIAZOLES
nutty



PYRROLES
cereal-like
nutty



IMIDAZOLES
chocolate
nutty
bitter

Occurrence – many heating stages of process

Affects: Yields, Flavor & Quality Spent Grain

Many points of control!

Control

Choice of Grains – kilning & preparation

Milling operations (→ cloudy or clear wash, mash or wort)

Heat - cooking & mashing steps

Heat & time course – distillation

Final words

A key understanding of flavor changes can allow ultimate control of spirit quality

It started with a yellow-brown colored product & a French chemist back in 1912

Now it is up to you.....

Ask yourself what can browning do for you.

But.....

Thank you,

Gary Spedding, ***Brewing and Distilling Analytical Services***

Please complete the evaluations!