The Chemistry of Chocolate Flavor

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- b) Ivory Coast
- c) Mexico
- d) Switzerland

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- b) Sugar cane becomes a cheap source of sugar
- c) Invention of the steam engine makes grinding cheap
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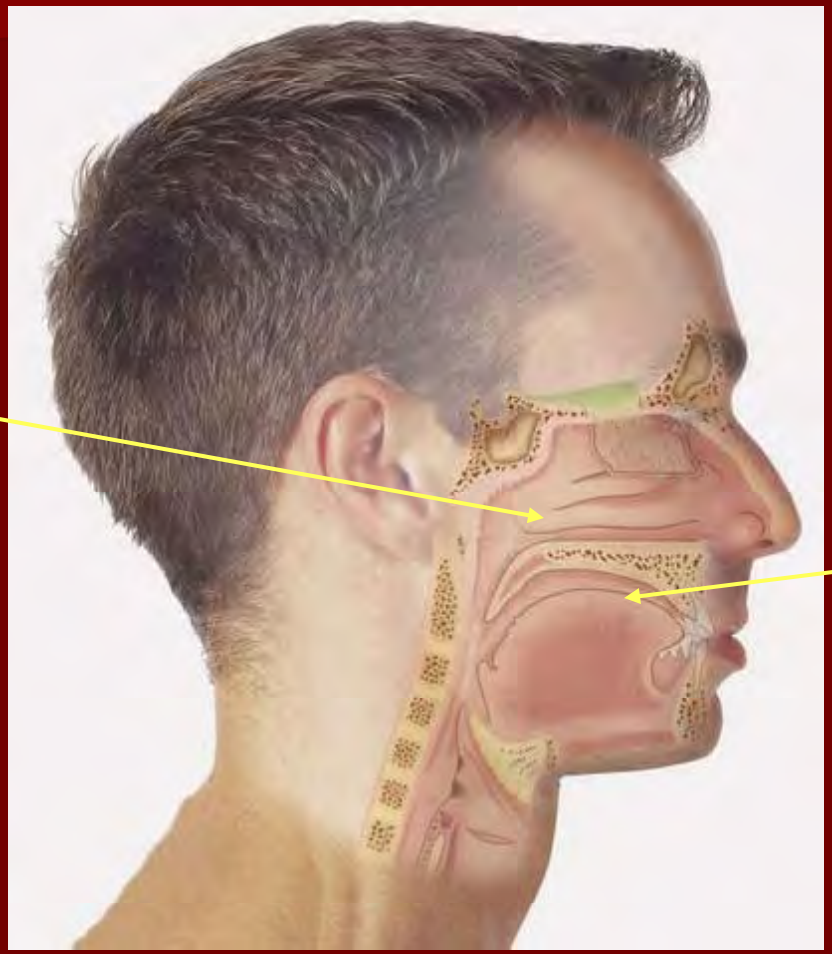
What is flavor?

- Flavor = taste + aroma
- Taste = sweet, salty, sour, bitter, umami
- Aroma = smell = volatiles

Taste + Smell



Complicated aroma

- Cherry – 1
- Chocolate – 200?

- 47 Hydrocarbons
- 28 Alcohols
- 24 Aldehydes
- 41 Ketones
- 57 Esters
- 21 Nitrogenous compounds
- 15 Sulfur compounds
- 53 Acids
- 7 Phenols
- 14 Pyrrols
- 9 Pyridines, chinoline
- 80 Pyrazines, chinoxalines
- 7 Thiazoles
- 11 Oxazoles
- 34 Furanes, pyrones, lactones

Ziegleder and Biehl 1988

Which volatiles are most important?

- Highest concentration
  - But thresholds vary
- CHARM –> flavor dilution
  - Gas Chromatograph
  - split detector, detection of odor, dilute, repeat

FD≥512 in milk chocolate

- Vanillin – vanilla
- 3-methylbutanal – malty
- 2-ethyl-3,5-dimethylpyrazine – potato chip
- 1-octen-3-one – mushroom
- 2-ethyl-3,6-dimethylpyrazine – nutty
- 2,3-diethyl-5-methylpyrazine – potato chip
- Z-2-nonenal – green
- E,E-2,4-decadienal – fatty
- E,E-2,4-nonadieanal – fatty
- Delta-decalactone – peach
- 2-methyl-3-methyldithiofuran - meaty
- 2 and 3-methylbutanoic acid – sweaty

Schnermann and Schieberle, 1997

The following steps are critical to the best chocolate flavor (choose all that apply):

- a) Choosing the best variety of beans
- b) Letting the beans rot on the ground for a few days
- c) Sun drying the beans
- d) Roasting the beans
- e) Grinding the beans
- f) Conching the cocoa liquor (mix for a day)
- g) Tempering the chocolate (heat-cool cycling before molding)

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Steps in chocolate manufacture that affect aroma

- Variety of tree
- Growing location
- Fermentation
- Drying
- Roasting
- Alkalinization (opt)
- (Winnowing)
- (Grinding)
- Additional ingredients
- Conching
- (Tempering)

Variety of tree

- Forestero (80-92%)
- Trinitario (5-10%)
- Criollo (0-10%)

The majority of today's cocoa beans are grown in:

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Cacao growing location

- Within 10° of equator
- Country differences, i.e.
  Brazil and Africa = base bean
  Ecuador, Venezuela, Trinidad, Sri Lanka = aromatic or flavor bean

Fermentation

- Succession of bacteria
- 3-5 days

Generation of aroma precursors

- Succession of bacteria:
- Yeast -> Lactic acid bacteria -> acetic acid bacteria -> spore formers -> mold
- Enzymes

- Source of volatiles: reducing sugars, free amino acids and oligopeptides

Gelatinous coating

- Sugars
- Pectin -> semi-anaerobic – encourages yeast
- citric acid -> pH 3.6 – encourages yeast

Yeasts

- Sucrose, glucose, fructose to ethanol and CO_2
- Pectinolytic enzymes – break down pectin "sweatings"
- Metabolize citric acid – pH rises
- Produce acetic, oxalic, phosphoric, succinic, malic acids – buffers pH

Lactic acid bacteria

- Glucose to lactic acid

(or ethanol, acetic acid, glycerol, mannitol)

- Produce citric acid then consume it

- Aeration and temperature increase

Acetic acid bacteria

- Decrease ethanol and lactic acid
- Oxidize ethanol to acetic acid to carbon dioxide and water
- Sugars to acetic acid
- Increase in acetic acid – kills seeds
- Hydrolyze proteins
- Temperature rises to 122 F

Assorted spore forming bacteria, esp Bacillus

- pH 5.0

- Mold, fungi – off flavors

Enzymes in beans

- Polyphenoloxidase: oxidizes bitter polyphenols
- Two proteases: aspartic endopeptidase and serine carboxy-(exo)peptidase on vicilin (7S)-class globulin storage proteins
- Roasting these peptides with reducing sugars produces chocolate aroma
- No aroma yet

Drying

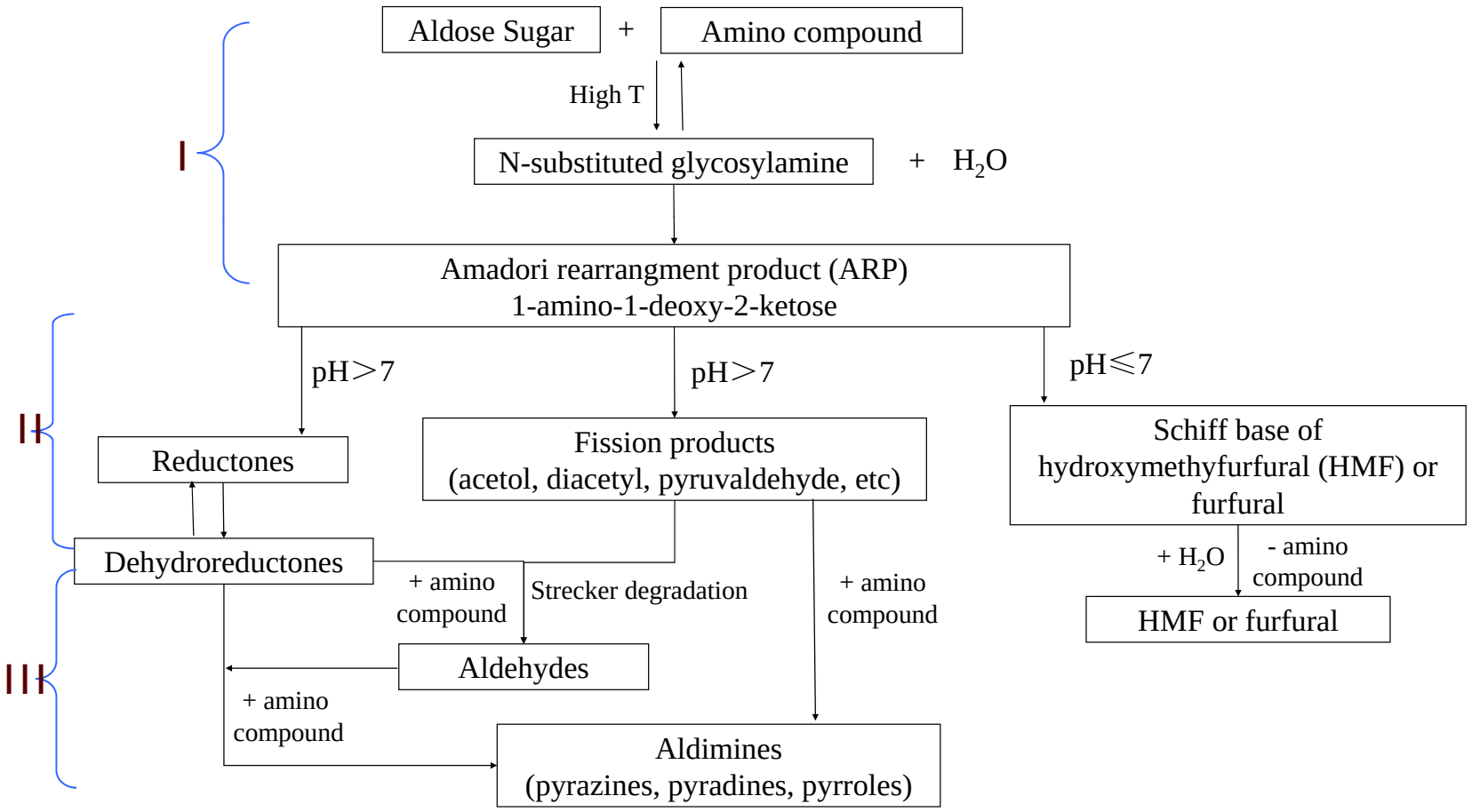
- Stop fermentation

- Off flavors:
- Smoke, from wood fires
- Hammy, from short chain fatty acids by bacilli and fungi

Roasting

- No cystine nor cysteine is present, and methionine at low concentration
- Maillard reaction, especially Strecker degradation
- Reducing sugars are the limiting factor

Simplified Maillard reaction (pyrazines and aldehydes)

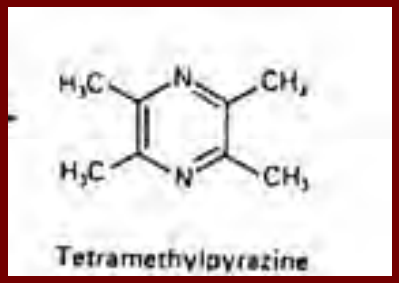


Volatiles present:

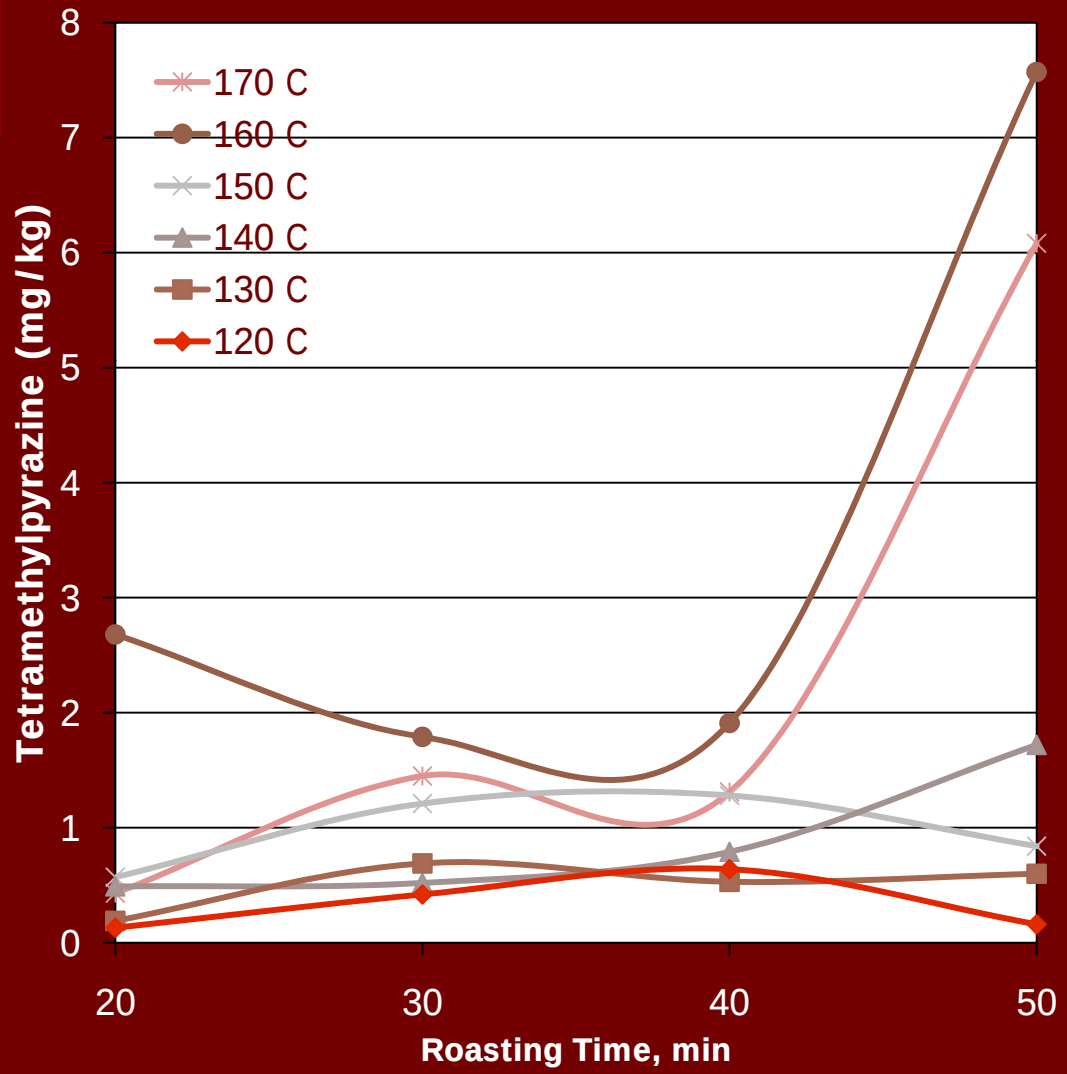
- Pyrazines – roasted notes
- Aldehydes
- Alcohols
- Esters
  - flowery, green

Tetramethylpyrazine

- 90% of pyrazines in chocolate
- Nutty, grassy, pungent, persistent chocolate note
- Maillard reaction



Tetramethylpyrazine formation



Adapted from
Ramli et al. 2006

The “Dutch process” involves soaking the beans in alkali, making the chocolate (choose all that apply):

- a) Taste sour
- b) Taste less bitter
- c) Have a fuller, rounder flavor
- d) Dissolve in water
- e) Turn brown

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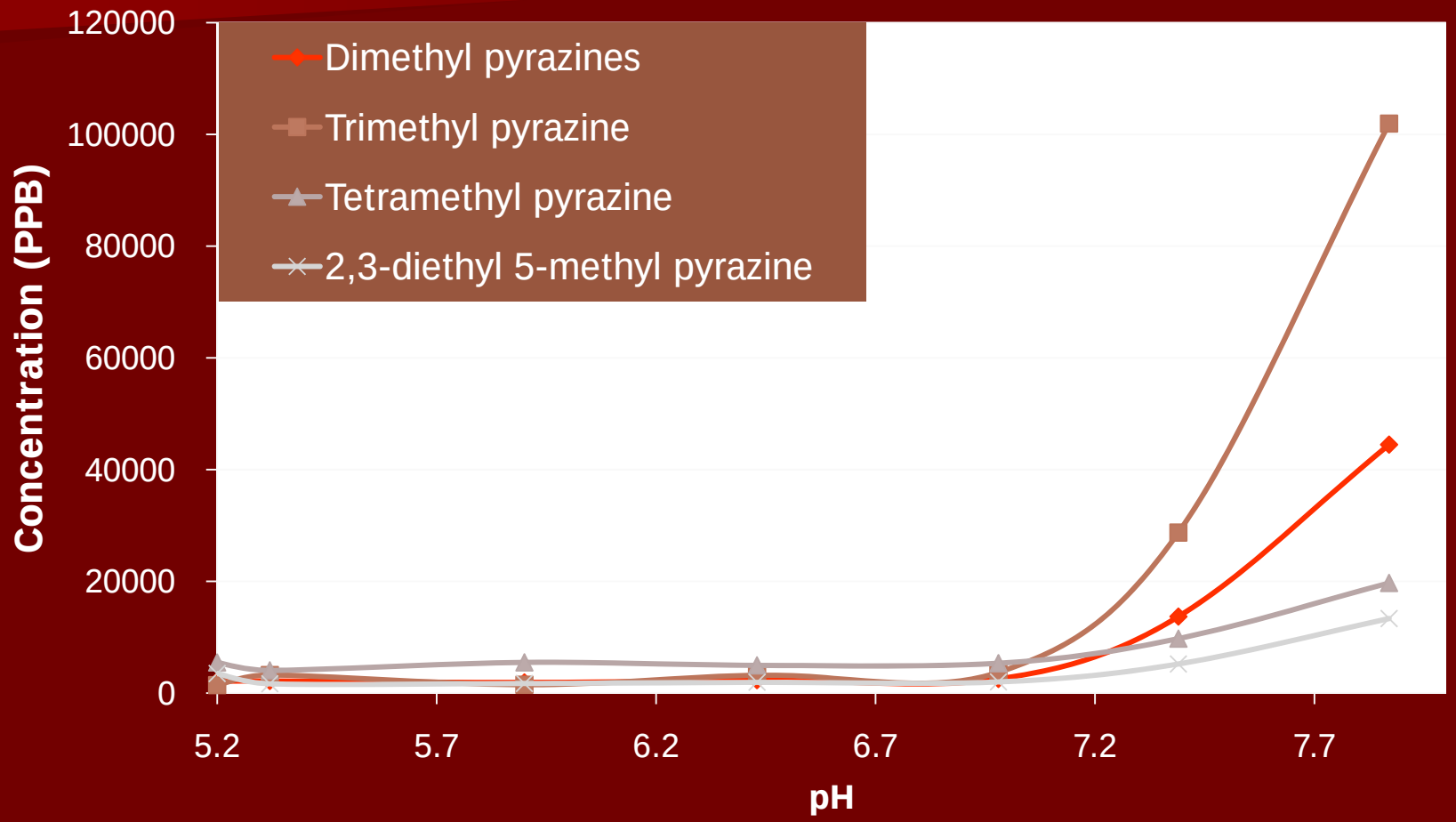
Alkalinization

- Make cocoa powder (hot chocolate)

- Water soluble
- Darker
- Changes flavor

pH 5 ←----------→ pH 8

Effect of alkalinization on pyrazines



Little effect on aroma:

- Winnow (remove shells)
- Grind to liquor

The three most common ingredients, by weight, mixed to make dark chocolate are:

- a) Caffeine
- b) Cocoa liquor
- c) Cocoa butter
- d) Lecithin
- e) Salt
- f) Sugar
- g) Vegetable oil
- h) Vanilla

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Dark chocolate typically is about (one from each column):

- a) ¼ sugar
- b) 1/3 sugar
- c) ½ sugar
- d) ¾ sugar
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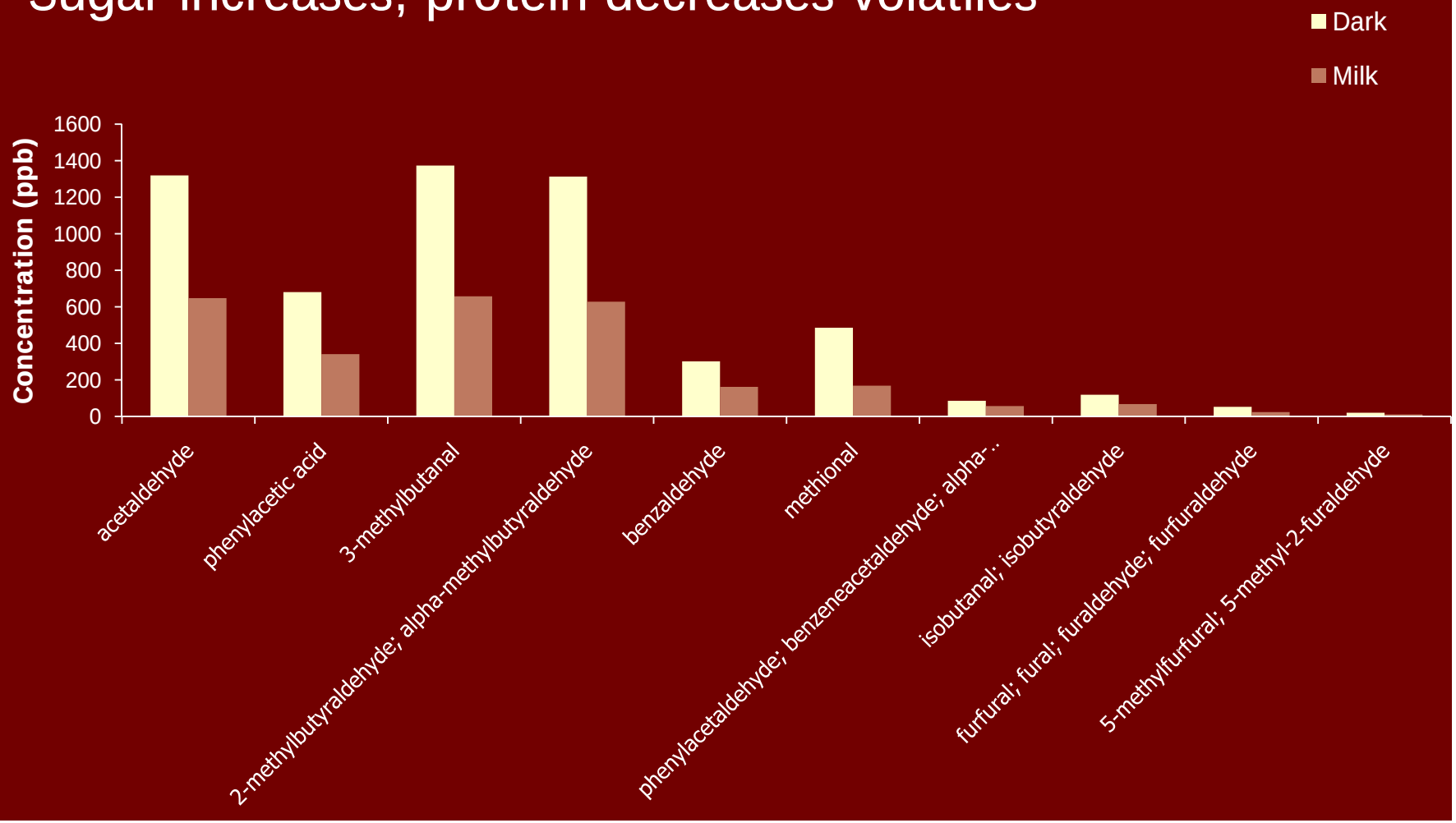
Addition of ingredients

- Vanilla – vanillin
- Sugar
- Cocoa butter
- Lecithin
- Milk -> caramel, milky, “sour”

Dark Chocolate vs. Milk Chocolate Aldehydes

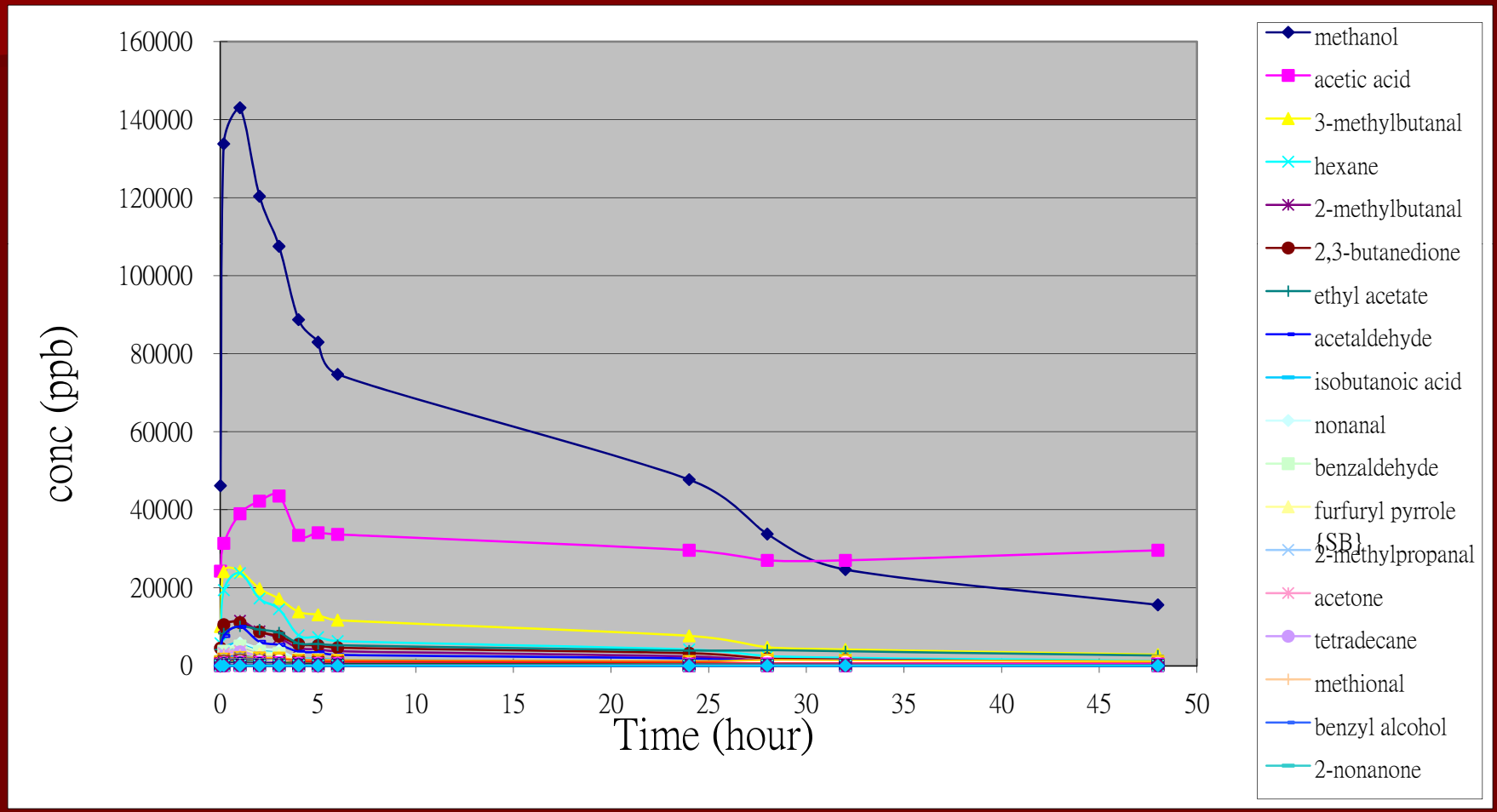
- 40% cocoa mass, 10% cocoa butter, sugar & milk varied
- Sugar increases, protein decreases volatiles



Conching

- 24 hours of mixing
- Lose ½ to ¾ of all volatiles
  - Methanol
  - Acetic acid
- Noticeable change in odor
  - No preference

Changes during conching



Old chocolate will develop white spots, or bloom, caused by:

- a) Drying out
- b) Fading
- c) Fat recrystallizing
- d) Mold growth

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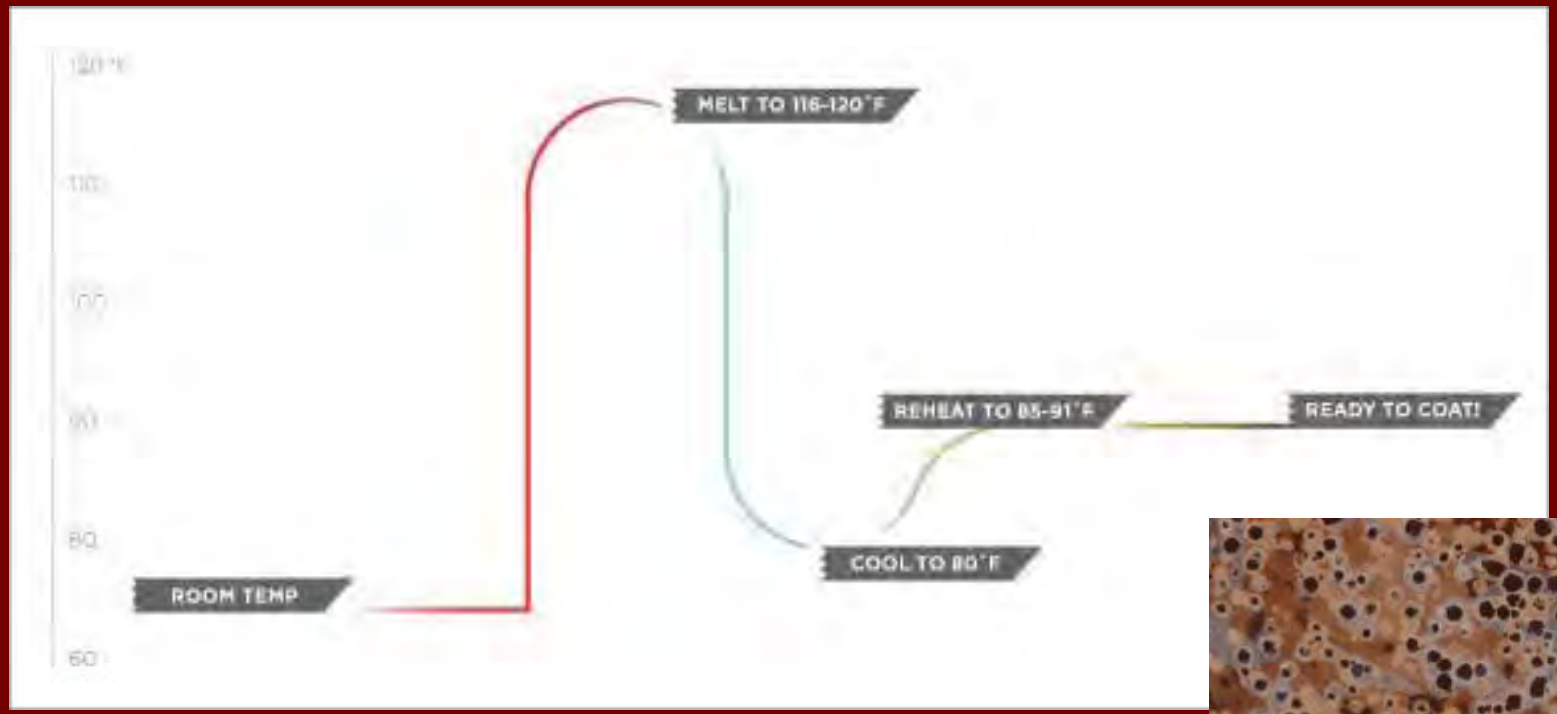
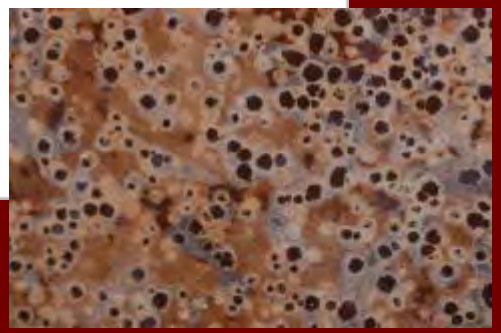
Tempering

- Texture
  - Heat, cool, heat, cool





Conclusion

- Variety of tree
- Growing location
- Fermentation
- Drying
- Roasting
- Alkalinization (opt)
- (Winnowing)
- (Grinding)
- Additional ingredients
- Conching
- (Tempering)

Chocolate is considered an aphrodisiac because:

- a) Montezuma II was known for the size of his harem
- b) Casanova ate large amounts of chocolate
- c) The Bishop of Chiapas, Mexico forbade the drinking of chocolate
- d) Serotonin and phenylethylamine in chocolate produce a feeling like falling in love

Thank you
Any questions?