Caramelisation

the source of malt flavour and colour

- We're talking about two sets of reactions:
  - Pyrolysis
    - Charring
    - "True" caramel

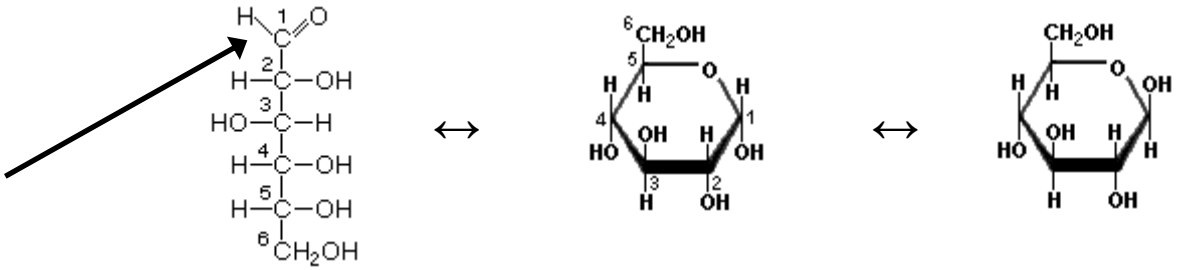
    These reactions do not involve nitrogen compounds
  - Maillard Reactions
    - "non-enzymatic browning"

    Reactions between some sugars and free amino nitrogen

First, let's meet the molecules

Sugars

Glucose is a simple, and relevant, example



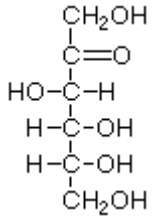
linear (0.25%) alpha ring beta ring

Three-dimensional structure is important, swap an H and OH and it's a different sugar, with different fermentability.

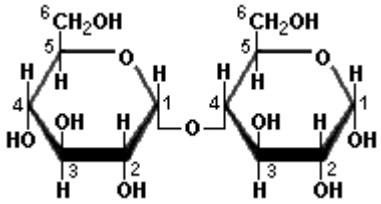
Also note the aldehyde group. If it's free it can be converted to an acid by mild oxidizers like Cu^{2+}.

$$2Cu^{2+} + RCHO + 2OH^{-} = 2Cu^{+} + RCOOH + H_2O$$

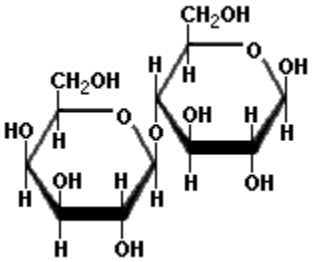
Other sugars



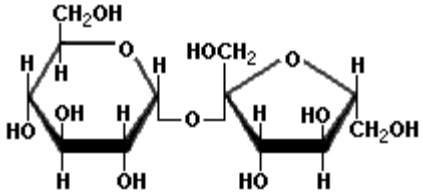
fructose



maltose



lactose

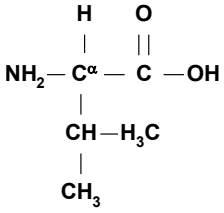


sucrose

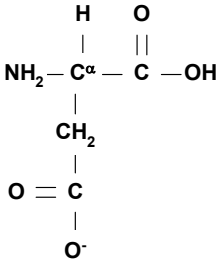
- In sucrose, the aldehyde and ketone are tied up and do not react with mild oxidizers

Nitrogen compounds

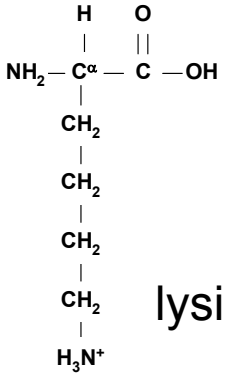
Amino acids



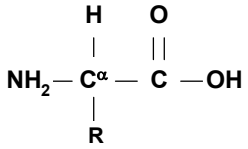
valine



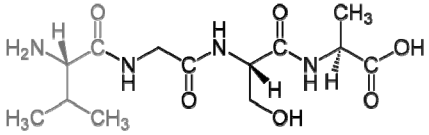
aspartic acid



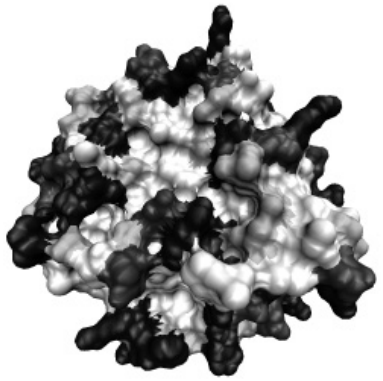
lysine



In general



peptide



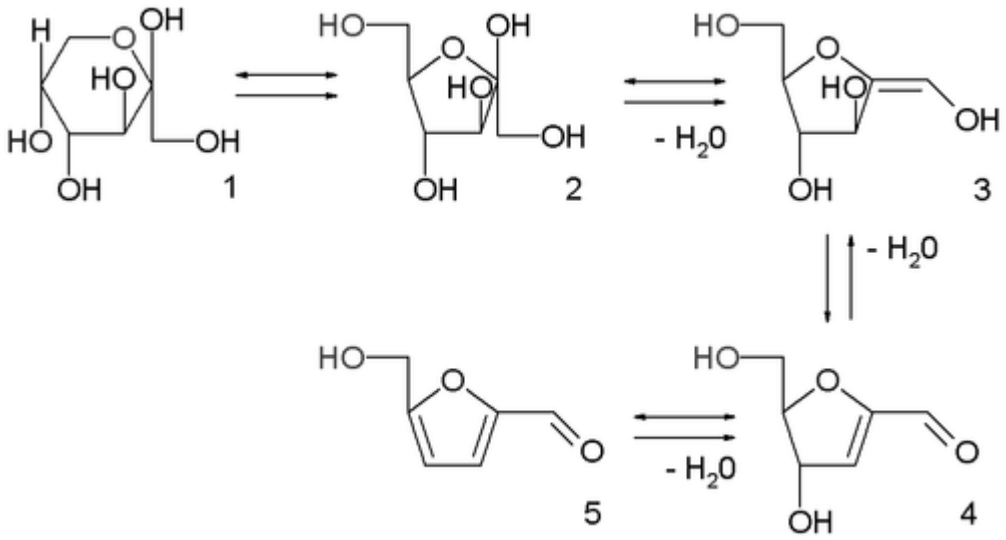
protein

("R" is the chemical symbol for "Rest of the molecule")

Pyrolysis

Hydrogen and oxygen <u>really</u> want to form water, just need enough heat to shake the atoms loose. They combine and give off a lot of energy to keep the reactions going.

$C_6H_{12}O_6$

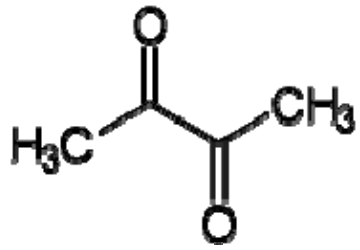


5-hydroxymethyl-2-furfural $C_6H_6O_3$

(13 ppm in dark beer)

- Forming water is the driving force for the reaction, but more happens:
  - Other bonds recombine
  - Molecules react with other molecules
  - $HO\cdot$ is a bull in a china shop - reacts with everything

$C_4H_6O_2$
(don't worry, it boils off)



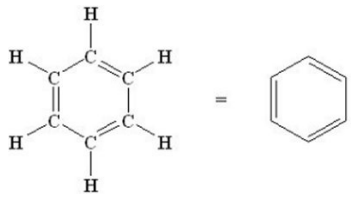
- Smaller molecules with less oxygen are more volatile so we can smell or "taste" them.

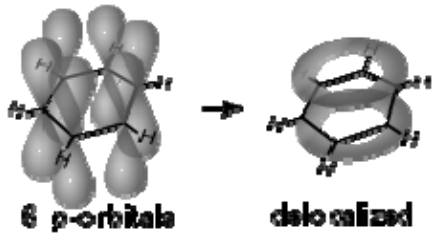
- Note that these molecules have lots of double bonds...

Colour formation

- When double bonds alternate, they act like one long bond.

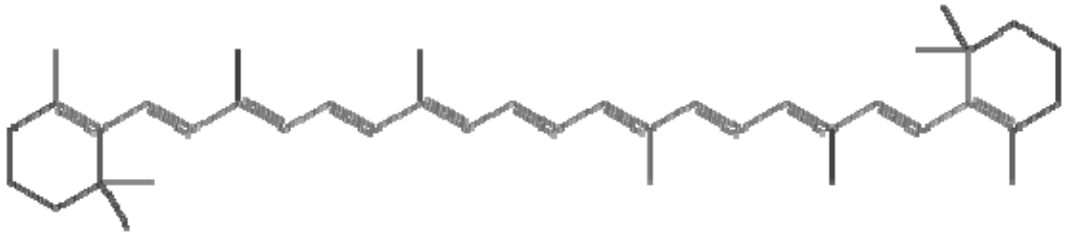
(benzene)





- Double bonds absorb UV light, but if the system is long enough the frequency drops into the visible range

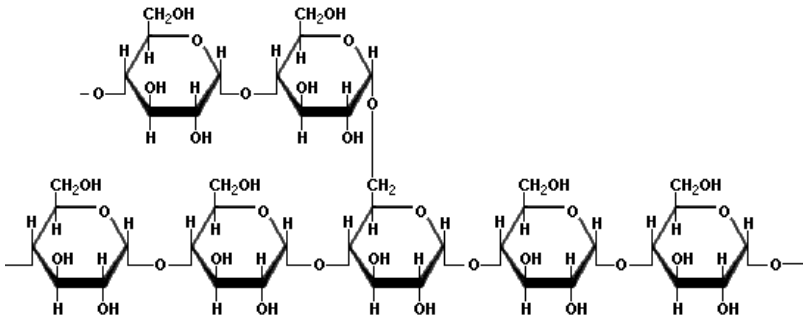
(carotene)



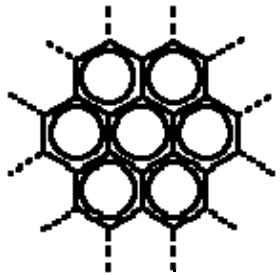
- If you have a random mixture of chemicals all absorbing different wavelengths of light you get....

Pyrolysis

- What happens if we heat starch?



  - it doesn't melt, so it's solid
    - non-uniform charring
  - don't get as many medium-sized molecules
    - toasted rather than caramel flavours
    - a lot of small molecules evaporate
  - eliminate all water, you get graphite (well, charcoal)
    - charcoal can adsorb some of the small molecules



The Maillard Reactions

Louis Camille Maillard

PhD thesis 1912

A reaction between a reducing sugar and free amino nitrogen

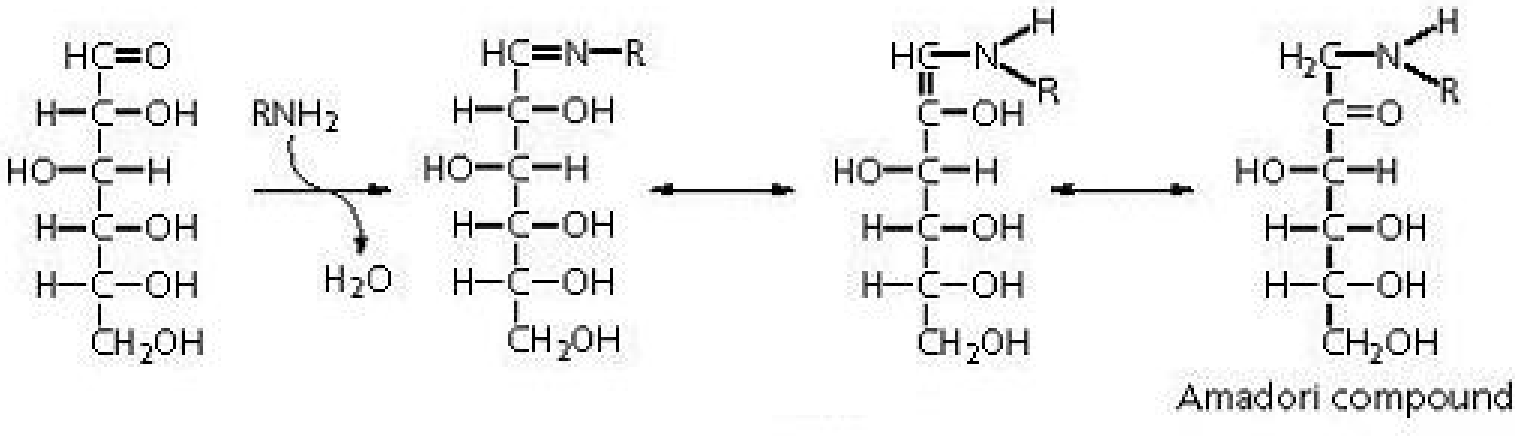
- Reducing sugars
  - glucose, fructose, lactose, maltose are reducing sugars
  - sucrose is <u>not</u> a reducing sugar
    - but it can be hydrolyzed into glucose and fructose
- Free amino nitrogen (FAN)

$R\text{-}NH_2$

ammonia NH_3 amino acids

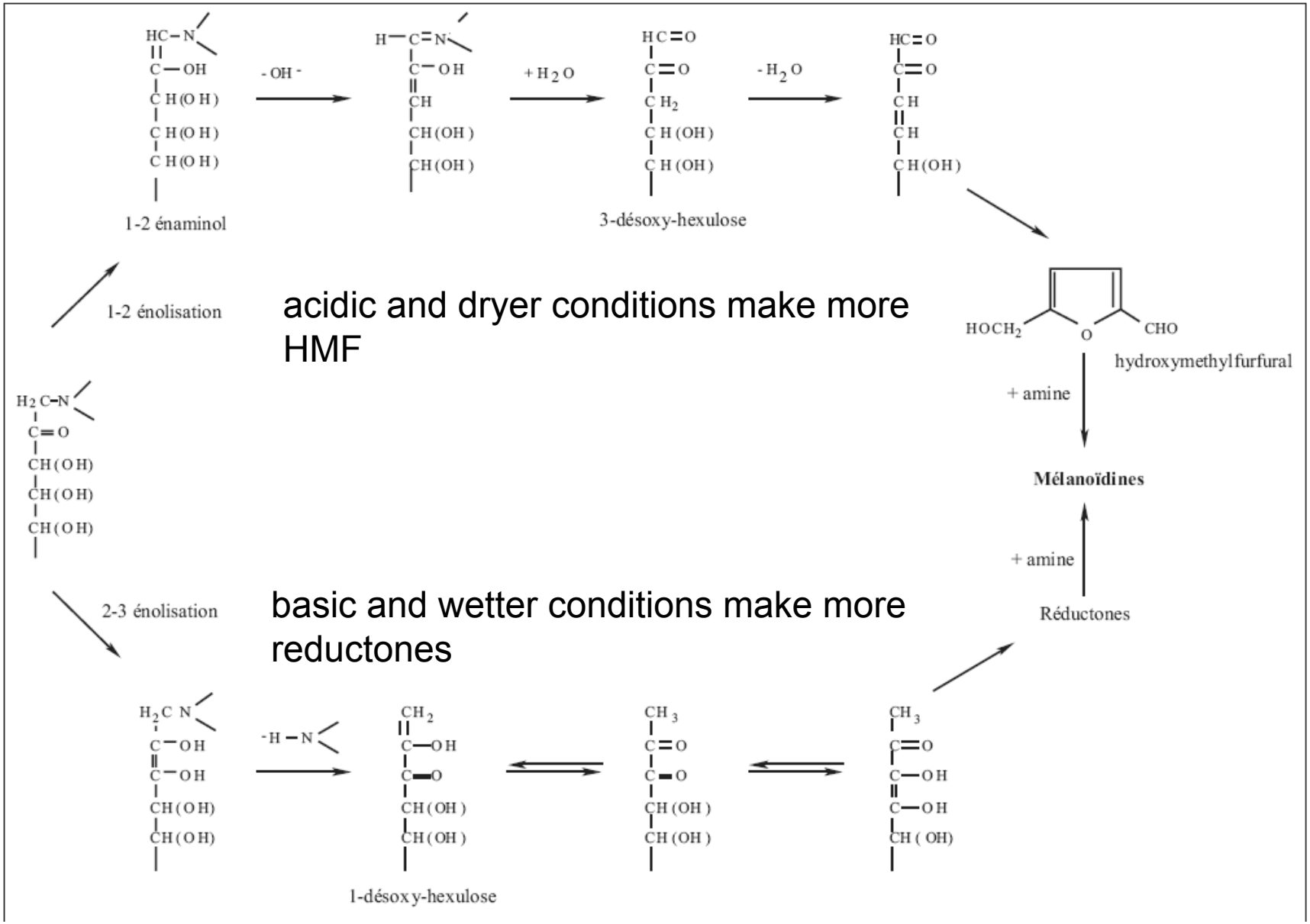
small proteins

First steps

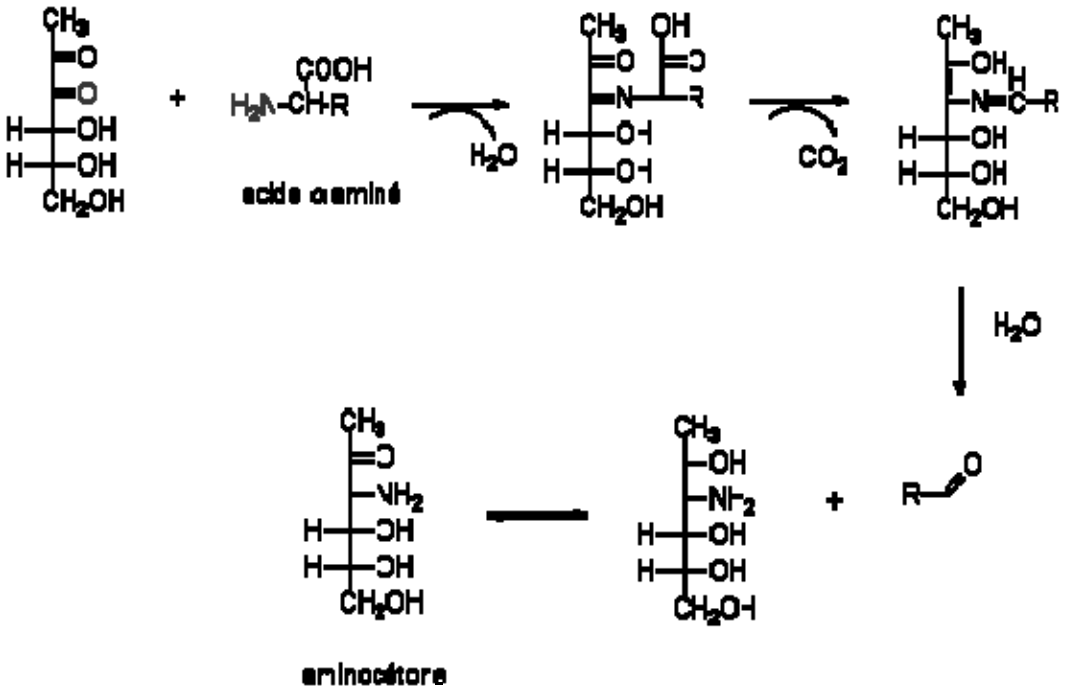


FAN reacts with aldehyde group

Reaction is favoured by acidic conditions


1-2 énaminol
- OH -
+ H2O
3-désoxy-hexulose
- H2O
1-2 énolisation
acidic and dryer conditions make more HMF
HOCH2
O
CHO
hydroxymethylfurfural
+ amine
Mélanoïdines
+ amine
Réductones
2-3 énolisation
basic and wetter conditions make more reductones
-H-N
1-désoxy-hexulose

Strecker degradation



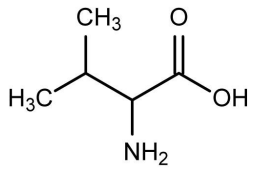
1-desoxyhexulose reacts with another amino acid

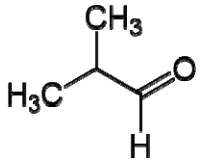
FOLLOW THE "R"

Aldehydes react with each other to form random colour and flavour compounds

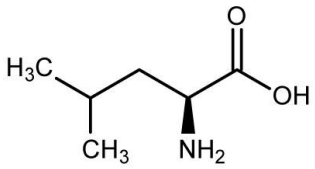
Also have distincts aromas of their own

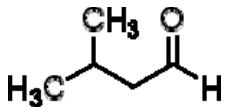
Strecker aldehydes



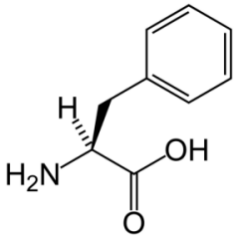


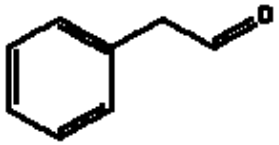
Valine produces isobutyraldehyde (malty)





Leucine produces isovaleraldehyde (cocoa)

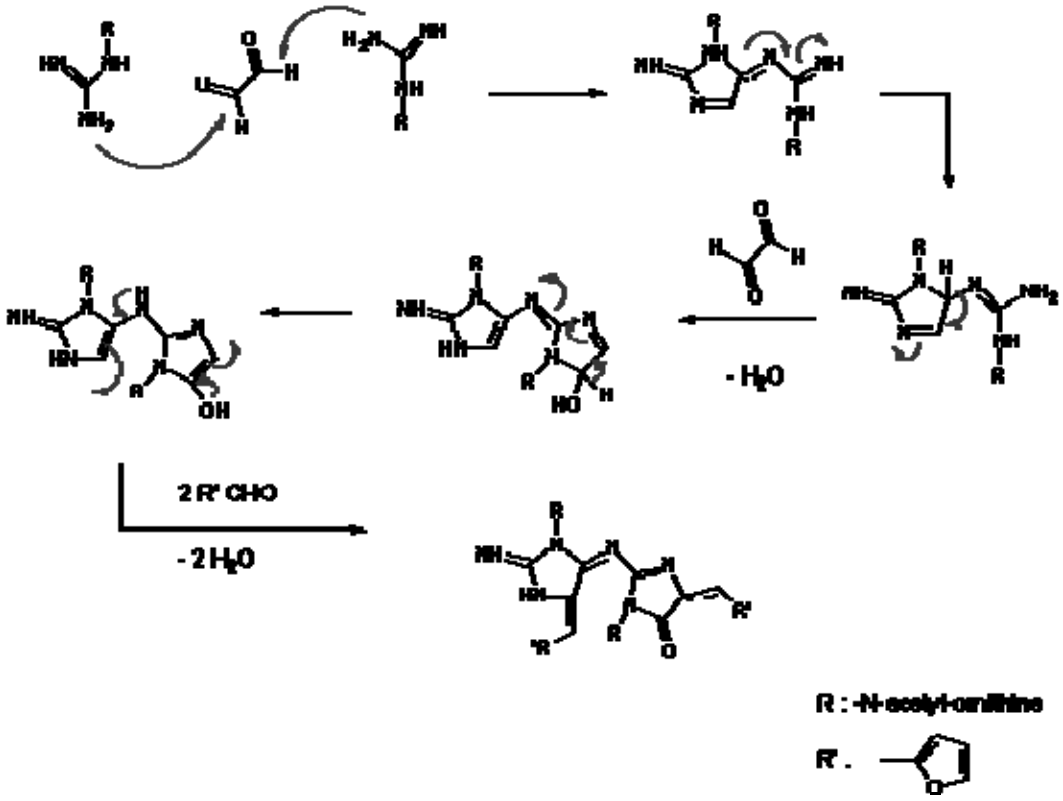




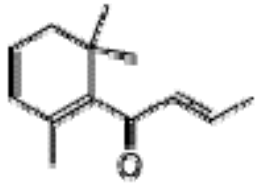
Phenylalanine produces 2-phenylethanal (honey, daffodils)

Melanoidin formation

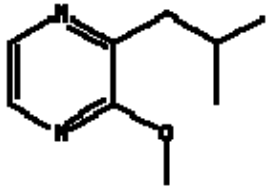
Big brown miscellaneous molecules formed by reactions of all the above reaction products



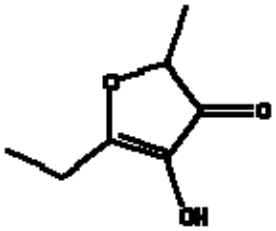
Various products



(E)-ß-Damascenone
(honey, fruit)

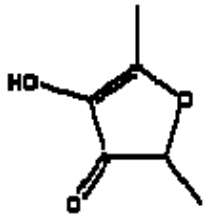


2-Isobutyl-3-methoxypyrazine
(earthy)

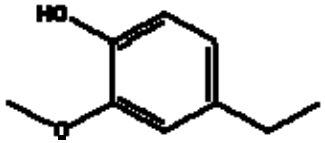


5-Ethyl-4-hydroxy-
2-methyl-3(2H)-
furanone

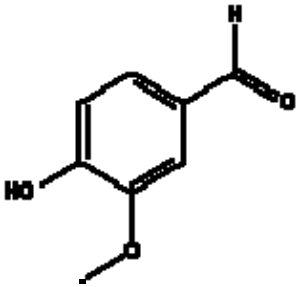
Methional
(potato, sweet)



4-Hydroxy-2,5-dimethyl-
3(2H)-furanone
(Furaneol)
(caramel)

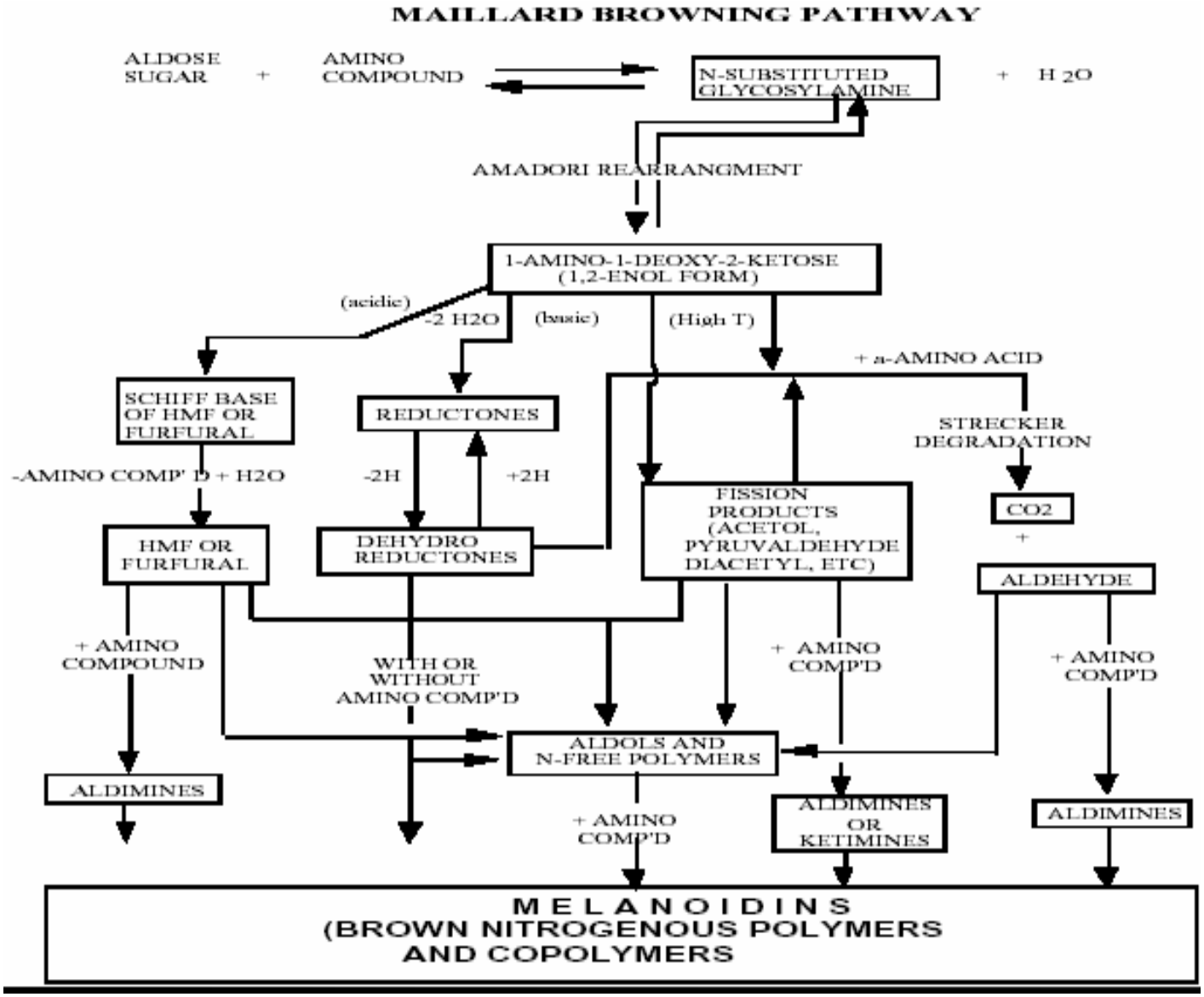


4-Ethylguaiacol
(spicy)

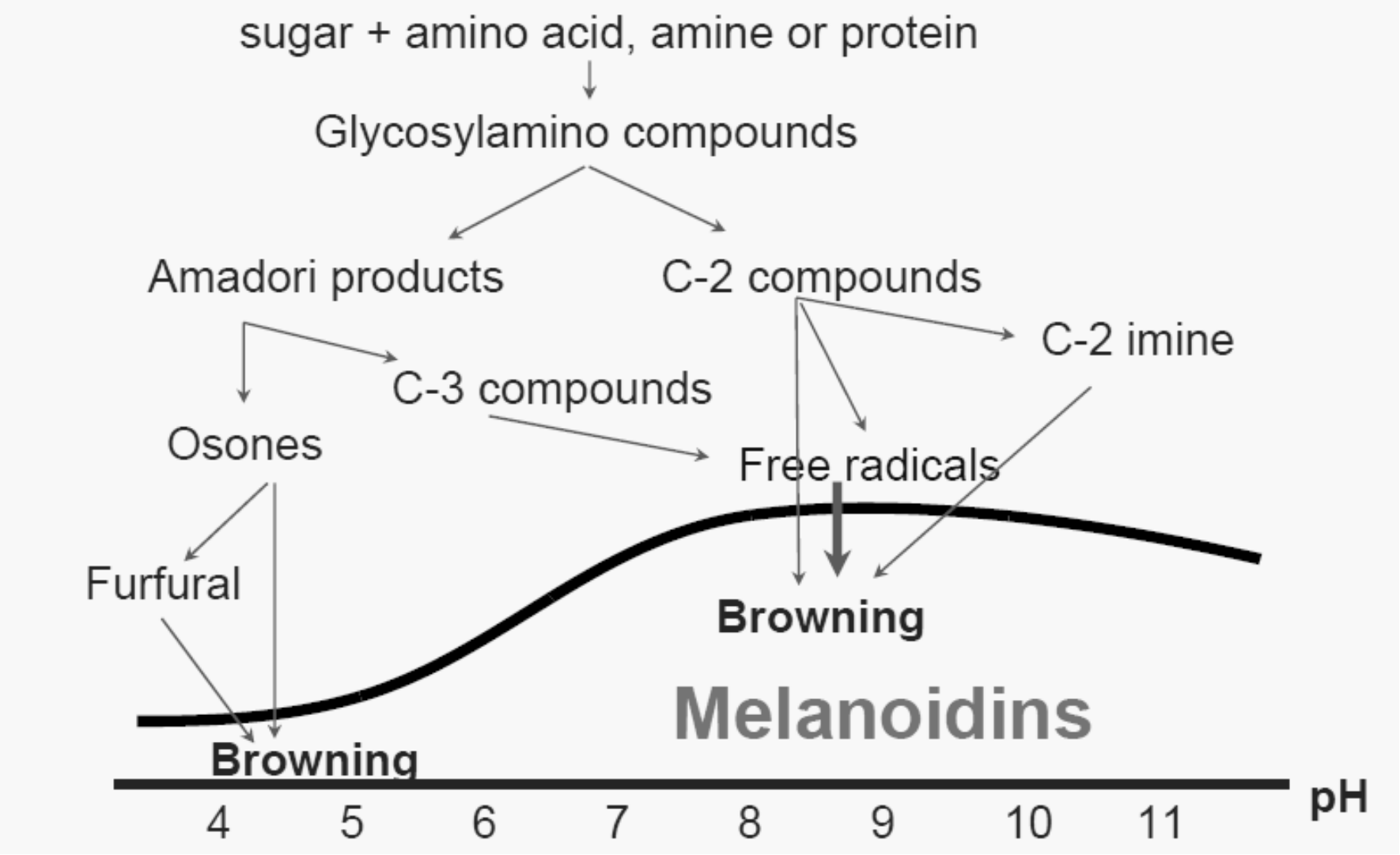


Vanillin

Summary


MAILLARD BROWNING PATHWAY
ALDOSE SUGAR
+
AMINO COMPOUND
N-SUBSTITUTED GLYCOSYLAMINE
+ H 2O
AMADORI REARRANGMENT
1-AMINO-1-DEOXY-2-KETOSE (1,2-ENOL FORM)
(acidic)
-2 H2O
(basic)
(High T)
+ a-AMINO ACID
SCHIFF BASE OF HMF OR FURFURAL
REDUCTONES
STRECKER DEGRADATION
-AMINO COMP' D + H2O
-2H
+2H
FISSION PRODUCTS (ACETOL, PYRUVALDEHYDE DIACETYL, ETC)
CO2
+
HMF OR FURFURAL
DEHYDRO REDUCTONES
ALDEHYDE
+ AMINO COMPOUND
WITH OR WITHOUT AMINO COMP'D
+ AMINO COMP'D
+ AMINO COMP'D
ALDOLS AND N-FREE POLYMERS
ALDIMINES
+ AMINO COMP'D
ALDIMINES OR KETIMINES
ALDIMINES
MELANOIDINS
(BROWN NITROGENOUS POLYMERS AND COPOLYMERS

Effect of pH


sugar + amino acid, amine or protein
Glycosylamino compounds
Amadori products
C-2 compounds
C-2 imine
C-3 compounds
Osones
Free radicals
Furfural
Browning
Melanoidins
Browning
4
5
6
7
8
9
10
11
pH

Other controls

- Higher moisture content:
  - malty, nutty, chocolate aromas
- Drier conditions:
  - bready aromas
- Level of FAN, type of amino acid
  - lysine has two -NH_2 groups

But what about malting and brewing?

- You can make true caramel, check cooking websites for instructions
  - be careful, the burns can be nasty
- "Brewer's caramel", like cola colouring, is actually made with a bit of ammonia. Different grades are available in the trade with various flavours (or none) and colours.

- Heating starch under dry conditions forms pyrolysis products
  - barley has low FAN (about 0.024% by weight)
    - roast barley is almost entirely pyrolysis flavoured
  - malting liberates sugars and amino acids, (FAN is 0.14%)
    - black malt and chocolate malt have some Maillard products as well

- Moisture content
  - Munich malt is dried just enough to save the enzymes then finished hot to give melanoidin and toasty flavours
  - Crystal malt has lots of free sugars and amino acids to react during toasting
    - raisin aromas are a dehydration product
- The modern specialty malts are all about manipulating the Maillard reactions to get novel combinations of sugars, amino acids, temperature and humidity, and sequences of those combinations
  - Melanoidin, Victory, Abbey, Special, CaraMunich, etc.

- Mild reaction conditions don't form significant amounts of flavour, but slightly degrade the sugars.
  - damaged starches are less digested by amylases, leave big dextrins
  - Cara-pils, toasted malt
- Long boils for Scotch ales and strong beers (old ales, bocks) produce a range of Maillard products
- Reductones act as anti-oxidants.
  - Dark beers have longer shelf life, hop aromas preserved
- Other impacts
  - storage of malt extract - relatively dry conditions, long enough at room temperature produces caramel flavours
  - long fermentations

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