# Zat Kimia Karsinogen Yang Terbentuk Selama Pengolahan Pangan

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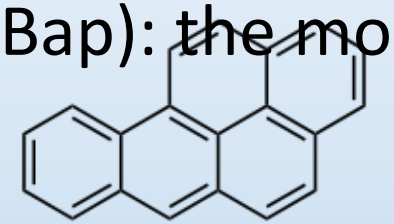
# Toxic substances formed from thermal processing

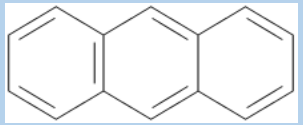
# Polycyclic aromatic hydrocarbon (PAH)

- Burning of organic materials (wood, coal or fuel oil) → pyrolytic by pyrolysis of hydrocarbons between 500 and 800°C in zone of flame with insufficient $O_2$ → various types of polycyclic aromatic hydrocarbons (ca 250 have been identified) with more than three linearly or angularly fused benzene rings, that are carcinogenic to varying extents
- Highly lipophilic → accumulated in fatty tissue
- Contamination of food :
  - fall-out from the atmosphere (contaminating fruit and leafy vegetables in industrial districts)
  - smoking or roasting of food (barbecuing or charcoal broiling; smoking of sausage, ham or fish; roasting of coffee).

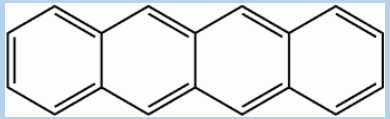
- Example: Benzo[a]pyrene (Bap): the most common, most dangerous



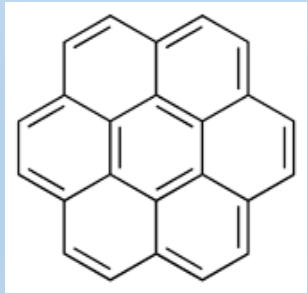
- Meat and processed meat products < 1 µg/kg end-product measured as Bap. A maximum of 5 µg/kg Bap is tolerated in smoked fish.
- Others



anthracene



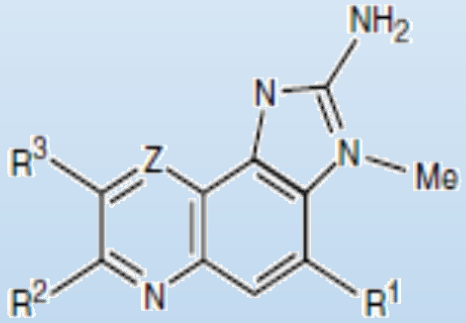
naphthacene



anthracene

# Heterocylic aromatic amines

- Heating proteinaceous food products (e.g. meat) may induce the formation of traces of heterocyclic aromatic amines, especially aminoimidazoazaarenes (AIA), which are potent mutagens




| Abbreviation | Z | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|---|
| IQ | C | H | H | H |
| MeIQ | C | Me | H | H |
| MeIQx | N | H | H | Me |
| 4,8-DiMeIQx | N | Me | H | Me |

GURE 12.21 Structures of commonly occurred aminoimidazoazaarenes (AIAs).

(1) IQ = 2-Amino-3-methylimidazo[4,5-*f* ]quinoline
(2) MeIQ = 2-amino-3,4-dimethylimidazo[4,5-*f* ]quinoline
(1) and (2) isolated from boiled, sun-dried sardines

(3) 4,8-DiMeIQ = 2-Amino-3,8-dimethylimidazo-[4,5-*f* ]quinoxaline
(4) 2-amino-3,4,8-trimethylimidazo[4,5-*f* ]quinoxaline)
(1), (2), (3), (4) have been isolated from dried meat products

# Heterocylic aromatic amines

- The exact mechanism for heterocyclic aromatic amines formation in food has not been clearly elucidated
  - 2-aminoimidazo part of the molecules may originate from naturally occurring creatine in muscle
  - quinoline and quinoxaline parts are believed to be formed from Maillard reaction products, especially precursors of pyrazines or pyridines and aldehydes

Heterocyclic aminoamines formation from Maillard reactions (see figure)

- Maillard reaction:

  - reducing sugar + amino acids → reactive dicarbonyl compounds (e.g. pyruvaldehyde)

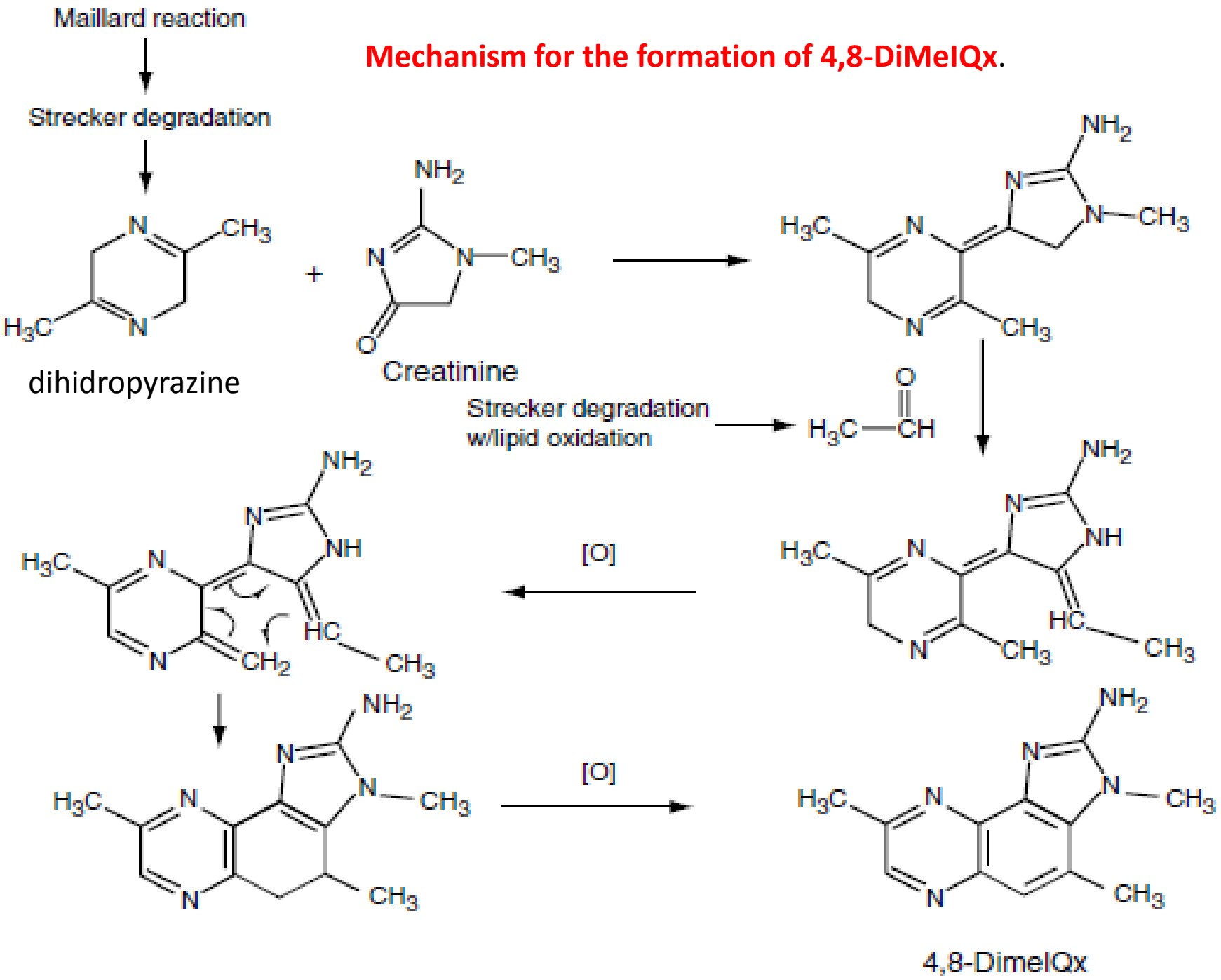
- Strecker degradation between a dicarbonyl compound and amino acid will generate a reactive dihydropyrazine molecule
- Condensation among dihydropyrazine, creatinine, and acetaldehyde* will lead to 4,8-DiMeIQx formation

*Acetaldehyde :

-Strecker degradation product of amino acids such as alanine and cysteine

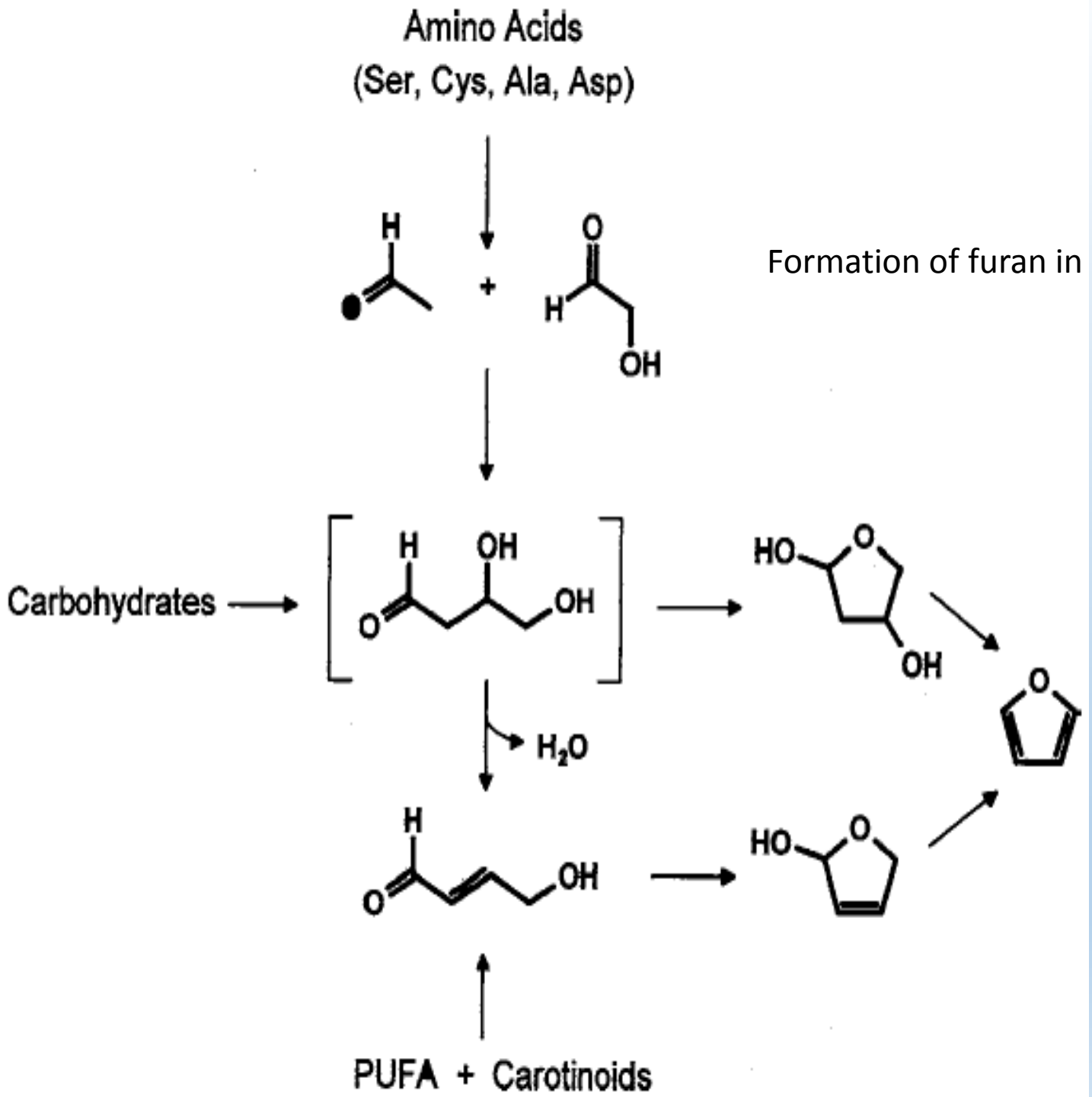
- important product of lipid oxidation → the presence of triacylglycerols facilitates the formation of heterocyclic aromatic amines.

## Mechanism for the formation of 4,8-DiMeIQx.



# Furan

- Possibly carcinogen (EFSA)
- Furan is formed from amino acids which yield acetaldehyde and glycolaldehyde on thermal degradation
- Aldol condensation, cyclization and elimination of water are the reaction steps.
- Other precursors of furan are carbohydrates, polyunsaturated fatty acids and carotenoids
- Furan can also be formed from the thermolysis of ascorbic acid.

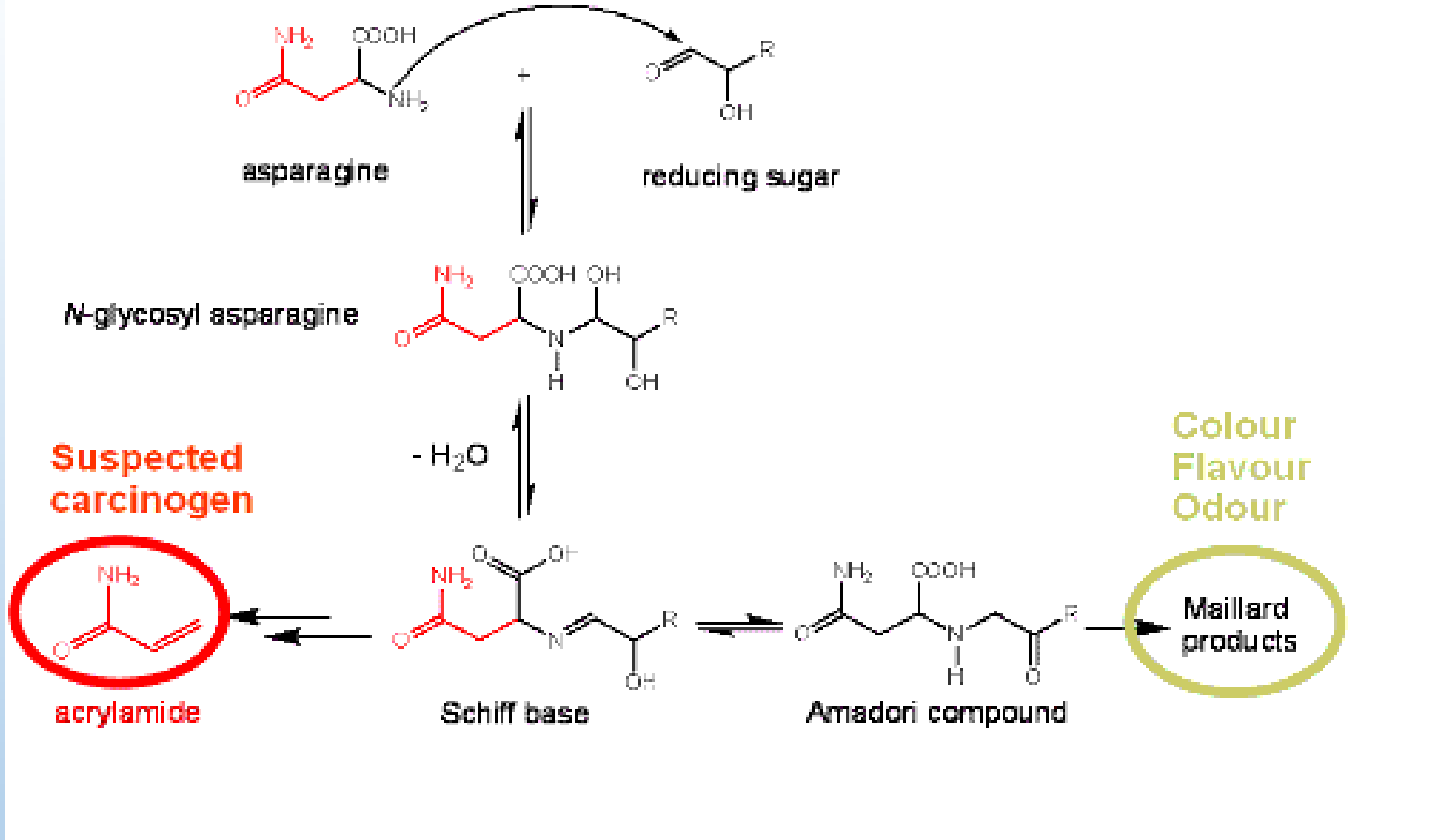



Formation of furan in heating food

Furan

# Acrylamide

- Acrylamide is preferentially formed by the reaction of the amino acid asparagine with reductive carbohydrates (or their degradation products).
- Carcinogenic on chronic exposure in animal tests
- Concentration of acrylamide in water ≤ 0.1 µg/l (EU)
- To avoid:
  - enzymatic hydrolysis of asparagine with asparaginase
  - lowering the pH value
  - reducing the heating temperature.




Acrylamide formation

**Table 9.11.** Maximum concentrations and variation ranges of acrylamide in selected foods

| Food | Concentration (µg/kg) | |
|---|---|---|
| Gingerbread | 7800 | (80–7800) |
| Potato chips | 3700 | (100–3700) |
| Crispbread | 2800 | (25–2800) |
| Roasted nuts | 2000 | (10–2000) |
| Ground coffee | 500 | |
| Roasted meat | 50 | |
| Bread | 40 | |

Acrylamide presents at various thermally treated food

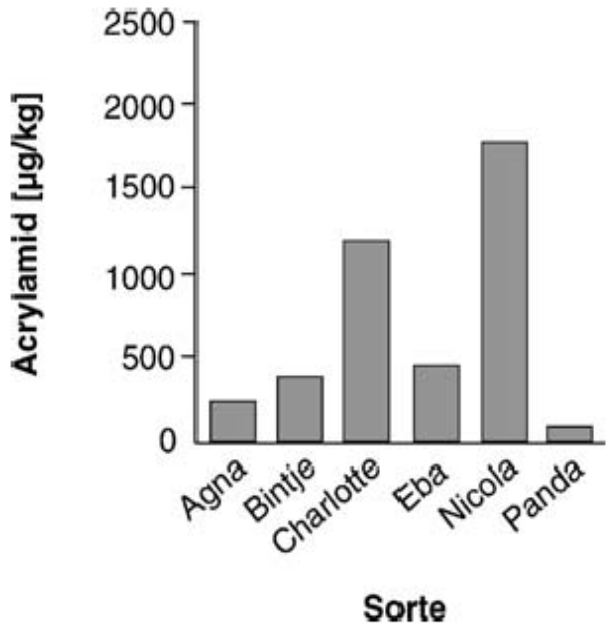
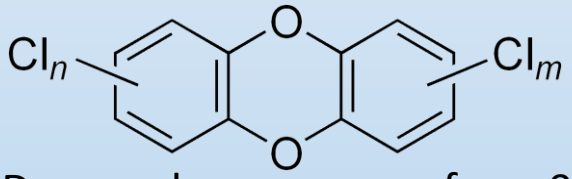



**Fig. 9.5.** Formation of acrylamide during the frying of potato strips from different varieties of potatoes (according to *Amrein* et al., 2003)

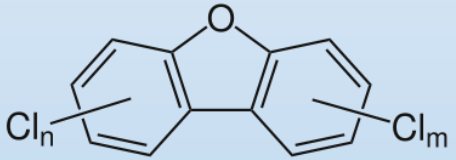
Different Acrylamide level of potato strips made from different varieties of potato

# Polychlorinated Dibenzodioxins (PCDD) and Dibenzofurans (PCDF)

- Informally called “dioxins”
- They are formed in many thermal processes (600 ◦C > T ≥ 200 ◦C) in the presence of chlorine or other halogens in inorganic or organic form




PCDDs, *n* and *m* can range from 0 to 4




PCDFs, 2 ≤ n+m ≤ 8

- Side product of paint, pesticide, paper bleaching, steel industries, fuel combustions
- Non-volatile, lipophilic
- Exposure : animal based food (egg, meat, milk)

**Table 9.17.** Risk assessment of dibenzo-p-dioxins and dibenzofurans

| Congener | TEF[a] |
|---|---|
| *Dibenzo-p-dioxins* | |
| 2,3,7,8-TCDD | 1 |
| 1,2,3,7,8-PnCDD | 1 |
| 1,2,3,4,7,8-HxCDD | 0.1 |
| 1,2,3,6,7,8-HxCDD | 0.1 |
| 1,2,3,7,8,9-HxCDD | 0.1 |
| 1,2,3,4,6,7,8-HpCDD | 0.01 |
| OCDD | 0.0001 |
| *Dibenzofurans* | |
| 2,3,7,8-TCDF | 0.1 |
| 1,2,3,7,8-PnCDF | 0.05 |
| 2,3,4,7,8-PnCDF | 0.5 |
| 1,2,3,4,7,8-HxCDF | 0.1 |
| 1,2,3,6,7,8-HxCDF | 0.1 |
| 1,2,3,7,8,9-HxCDF | 0.1 |
| 2,3,4,6,7,8-HxCDF | 0.1 |
| 1,2,3,4,6,7,8-HpCDF | 0.01 |
| 1,2,3,4,7,8,9-HpCDF | 0.01 |
| OCDF | 0.0001 |

[a] Toxicity equivalent factors (2,3,7,8-TCDD = 1).

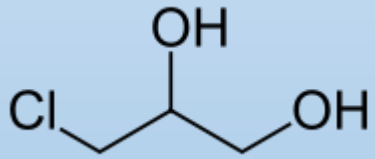
→ The most toxic one

# TOXIC COMPONENTS FORMED DURING PROCESSING

# 3-MCPD (3-monochloropropane-1,2-diol )

- 3-Monochloropropane-1,2-diol (3-MCPD) is a food processing contaminant classified as a possible human carcinogen for which the SCF established a tolerable daily intake (TDI) of 2 µg/kg b.w (EFSA)
- Formed by heat as a reaction product of triacylglycerols, phospholipids or glycerol and hydrochloric acid in fat-based or fat-containing foods.
- 3-MCPD can also be formed from NaCl + food  fats + thermal process (e.g. Grilling)
- Depending on the type of food it may occur as a free substance, in the form of an ester with fatty acids or in both forms

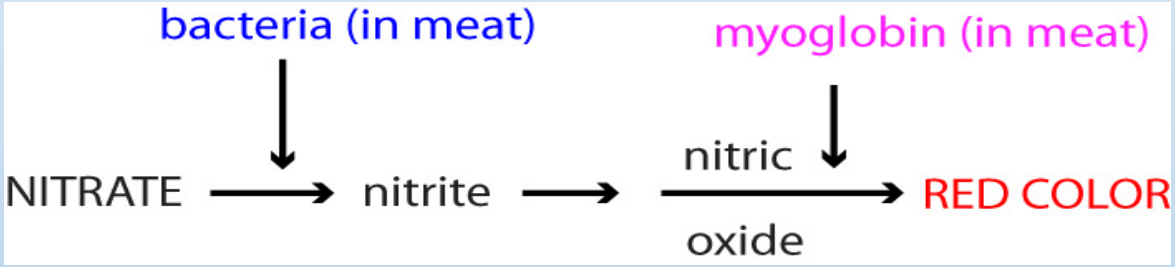

1-Oleyl-2-Stearyl-3-chlorpropandiol (3-MCPD-Ester)



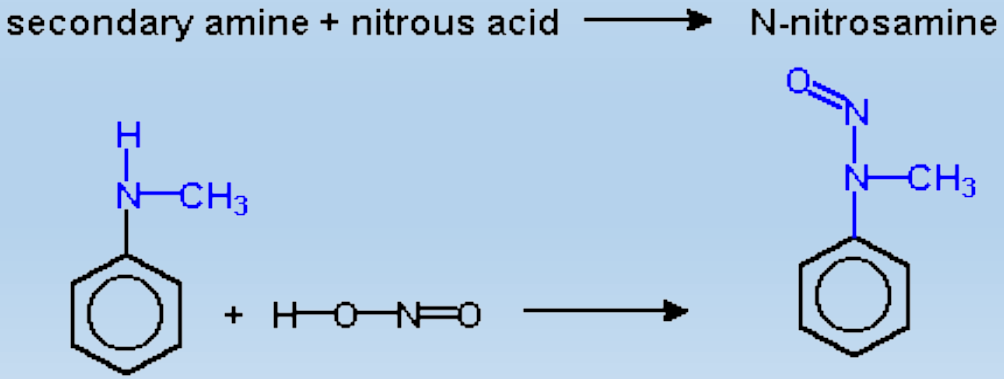

3-MCPD

# Nitrate, nitrite, nitrosamine

- Nitrite (NO2) or nitrate (NO3) is used in meat/meat products as preservative (inhibiting *C. botulinum* growth and fat oxidation) and to obtain pink-red colour and specific flavor

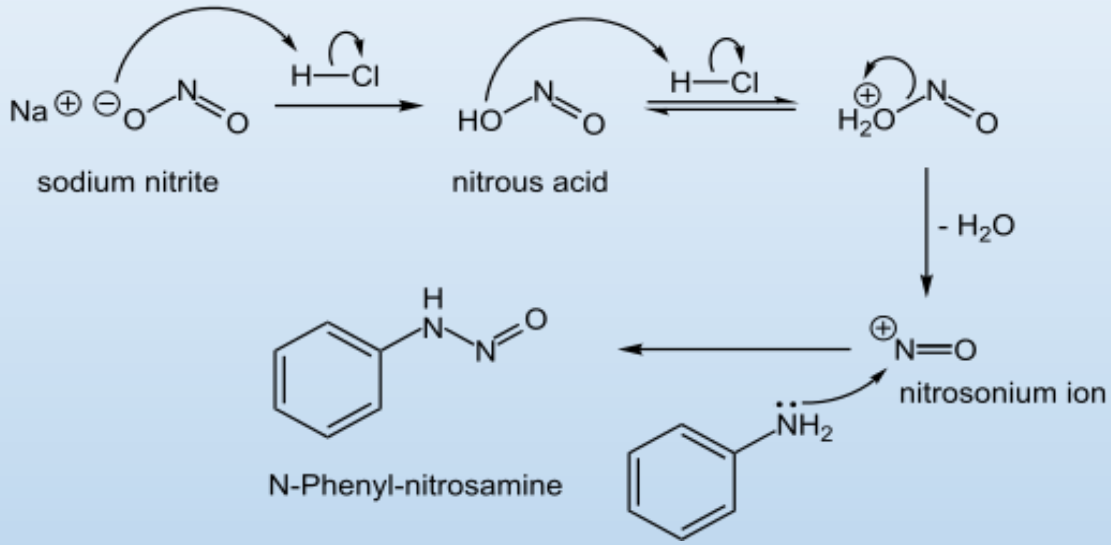



- Nitrite reacts with secondary amines to form nitrosamines which are carcinogenic



# Nitrate, nitrite, nitrosamine

- Other reaction




- To avoid nitrosamine formation:
  - Use ascorbic acid (500 ppm) together with nitrites (100-200 ppm)→ reduce the use of nitrites up tp 90%
  - Adjusting the dose of nitrites used in curing so that it inhibits C. botulinum growth but insufficient to be converted into nitrosamines

# Referensi:

Hand out Kimia Komponen Pangan, Fateta IPB