Formation of Furan

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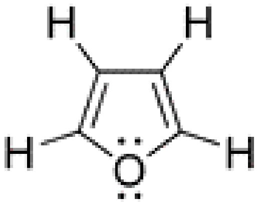
In May 2004, FDA published a survey showing that food undergoing heat treatment can contain Furan

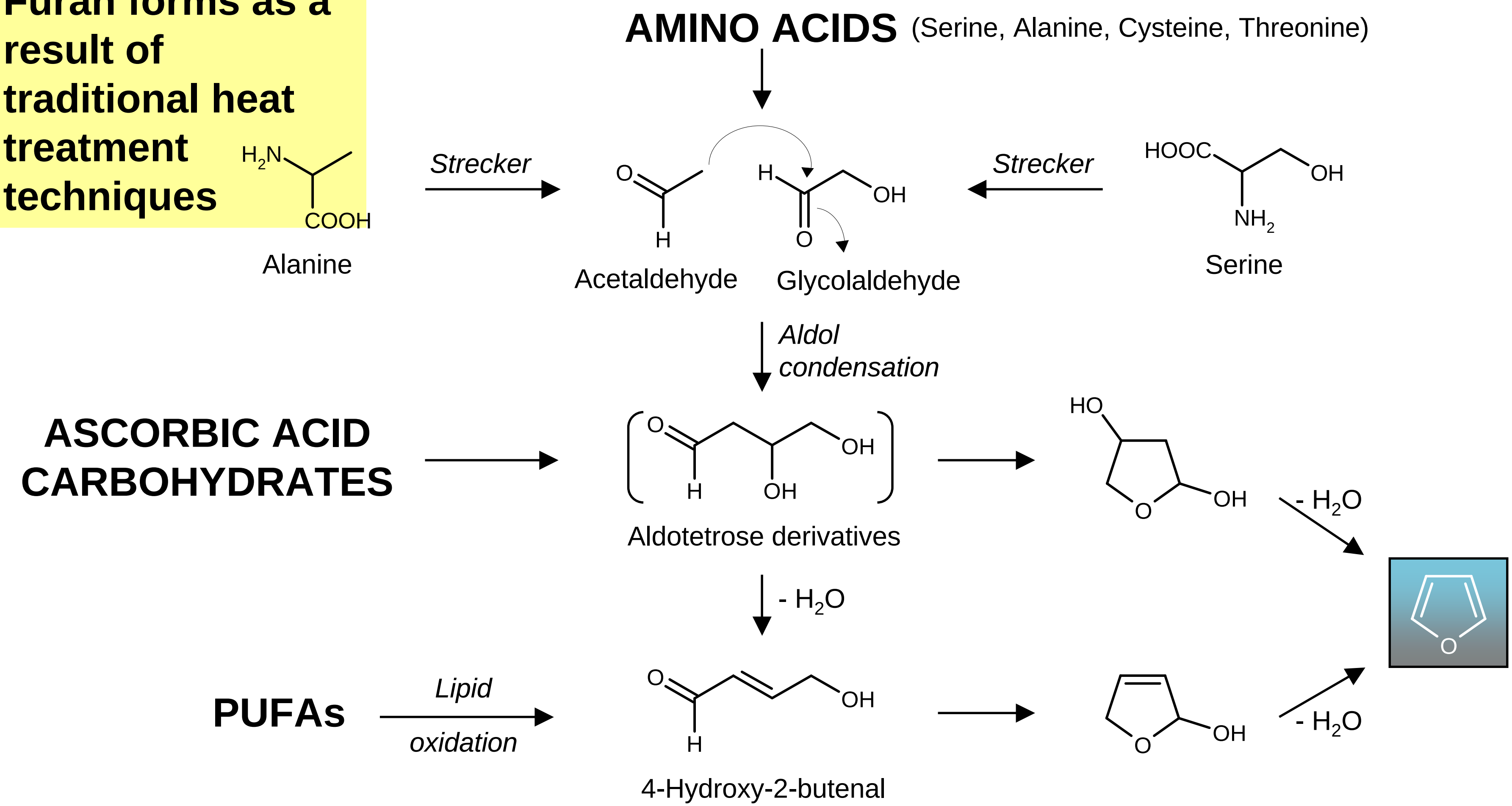
EFSA/IARC/FDA assessment:



- **Furan is carcinogenic to rats and mice**
- **Furan-induced carcinogenicity is probably due to a genotoxic mechanism**
- **International Agency for Research on Cancer (IARC): Possibly carcinogenic to humans (2B)**

- **Up to ~200 μg/kg found in food (canned, jarred)**
  (FDA, June 7, 2004; http://www.cfsan.fda.gov/~dms/furandat.html)
- **A reliable risk assessment would need further data on both toxicity and exposure**
- **FDA has issued a dietary message advising consumers to continue to eat a balanced diet**

Furan forms as a result of traditional heat treatment techniques



(Perez Locas & Yaylayan, *J. Agric. Food Chem.* **2004**, *52*, 6830)

Any consideration of practices to reduce Furan needs to include the impact on

- **Formation of other undesired components (e.g. Acrylamide)**
- **Change of product quality (flavour, texture, colour, nutritional value)**

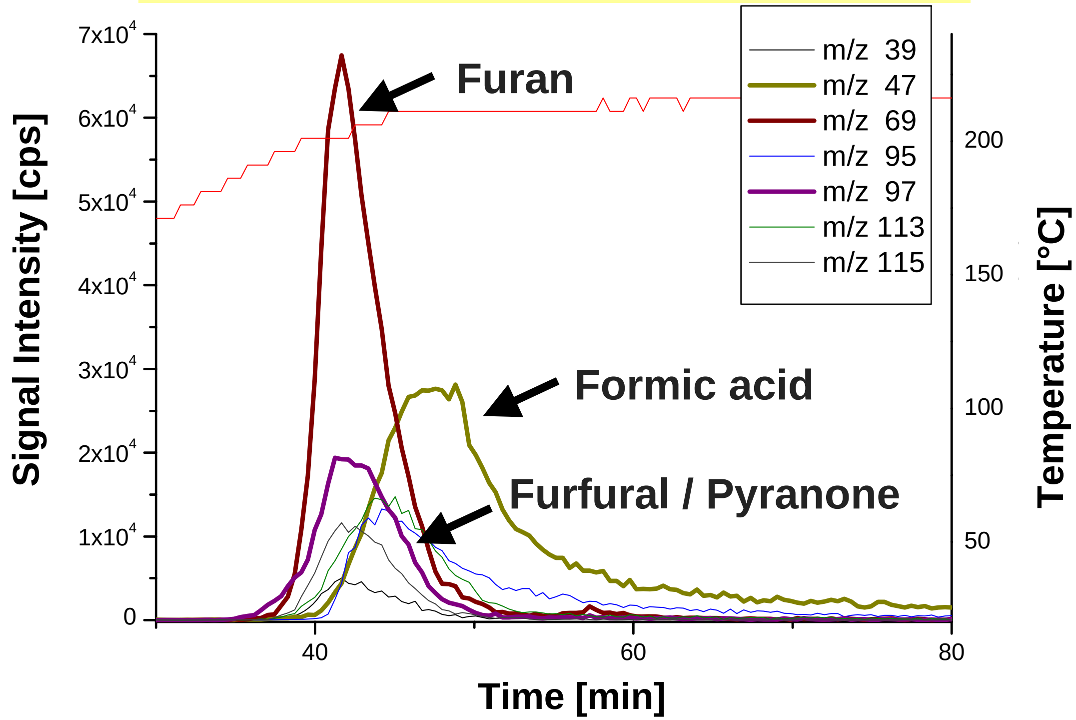
Study furan formation in model systems
- Roasting and sterilisation conditions
- Focus on Ascorbic acid → Furan

Mechanistic insight
- Labelled ascorbic acid
- CAMOLA

Reduce furan formation
- Mitigation study
- Binary mixtures

Thermal decomposition of ascorbic acid

Time-resolved headspace release curves (PTR-MS)

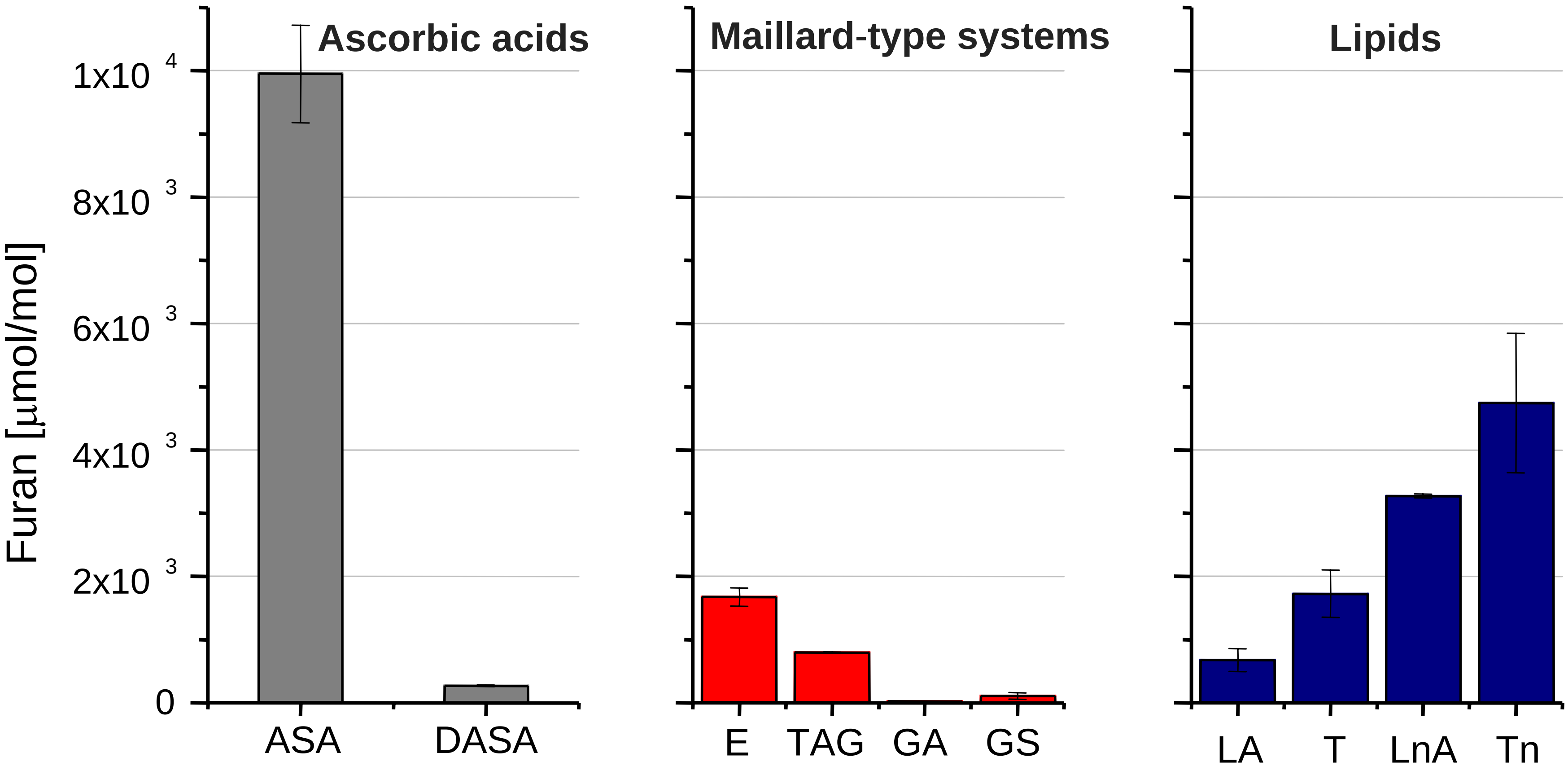


Headspace techniques
- PTR-MS (1)
- SPME GC-MS (2)

Reaction conditions
30 → 220°C (5°C/min) (1)
200°C (10 min) (2)
121°C (25 min) (2)

(Märk et al., *J. Agric. Food Chem.* **2006**, *54*, 2786)

Ascorbic acid is the major furan precursor under roasting conditions



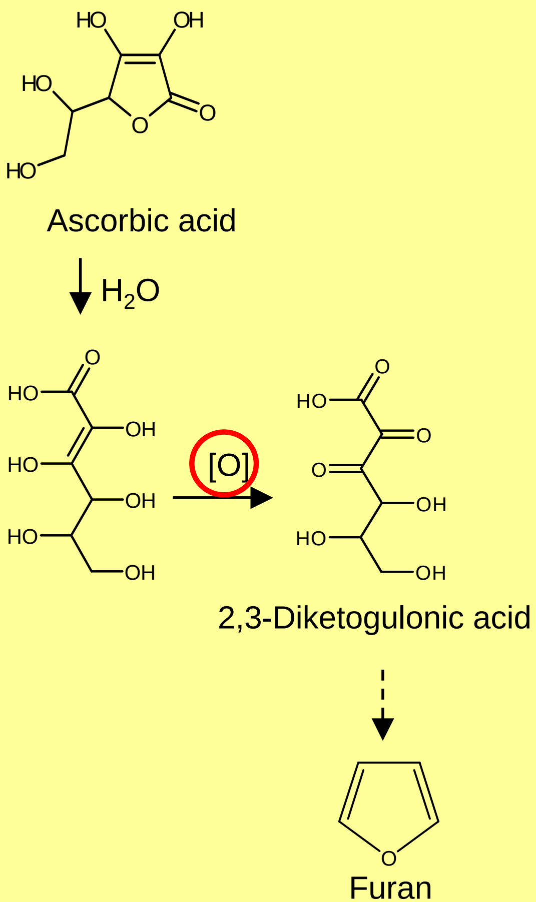
ASA Ascorbic acid
DASA Dehydroascorbic acid

E Erythrose
TAG Threonine+Alanine+Glucose
GA Glycolaldehyde+Alanine
GS Glycolaldehyde+Serine

LA Linoleic acid (C18:2)
T Trilinoleate
LnA Linolenic acid (C18:3)
Tn Trilinolenate

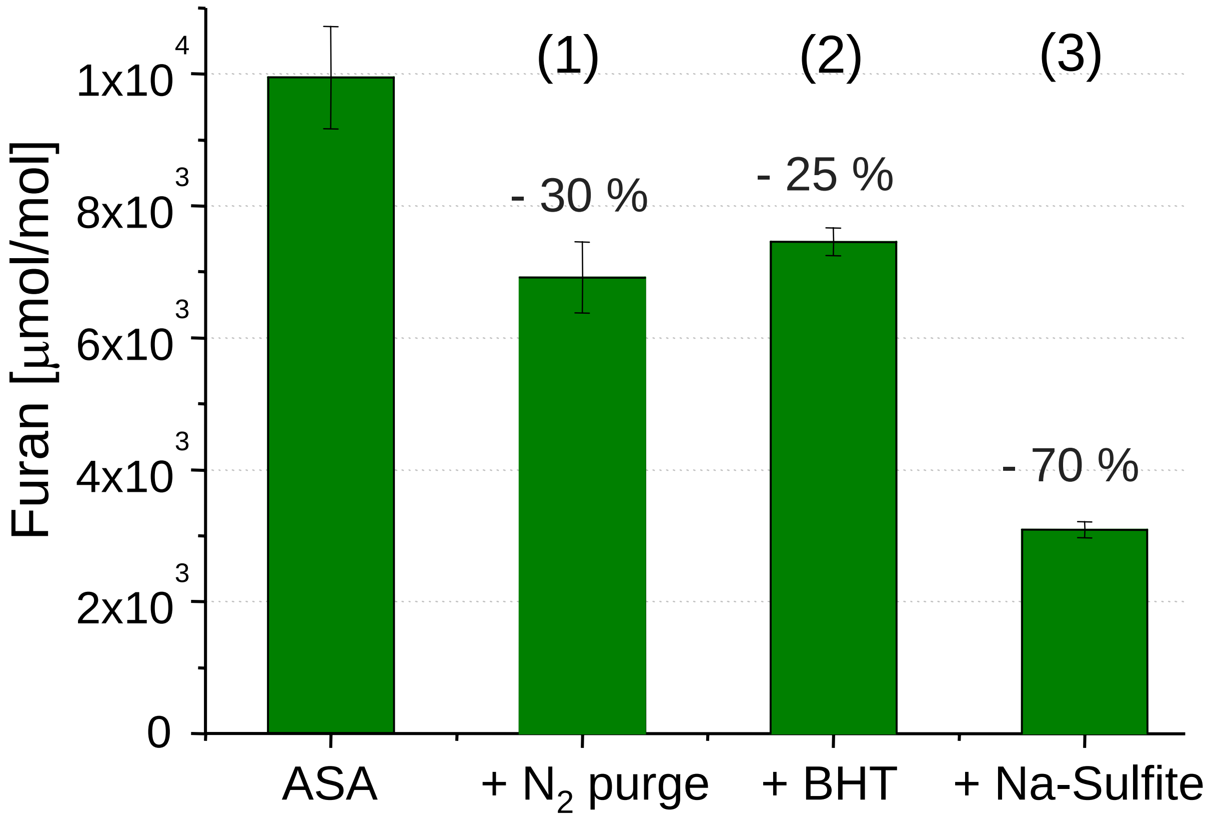
(Märk et al., *J. Agric. Food Chem.* **2006**, *54*, 2786)

Ascorbic acid → Furan (roasting conditions)



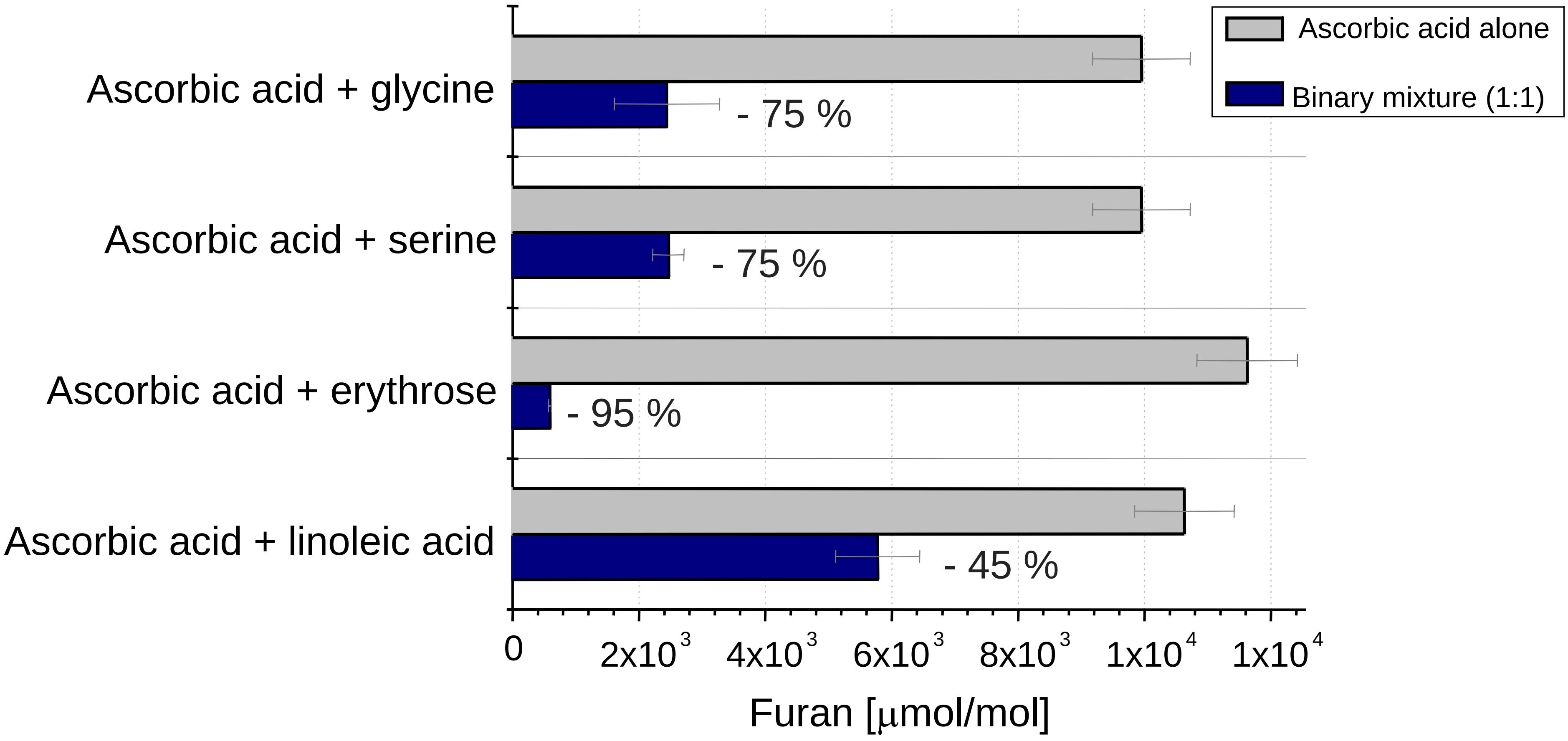
(Perez Locas & Yaylayan, *J. Agric. Food Chem.* **2004**, *52*, 6830)

Furan mitigation: (1) + N_2 purge (instead of air)
(2) + BHT
(3) + Na-Sulfite



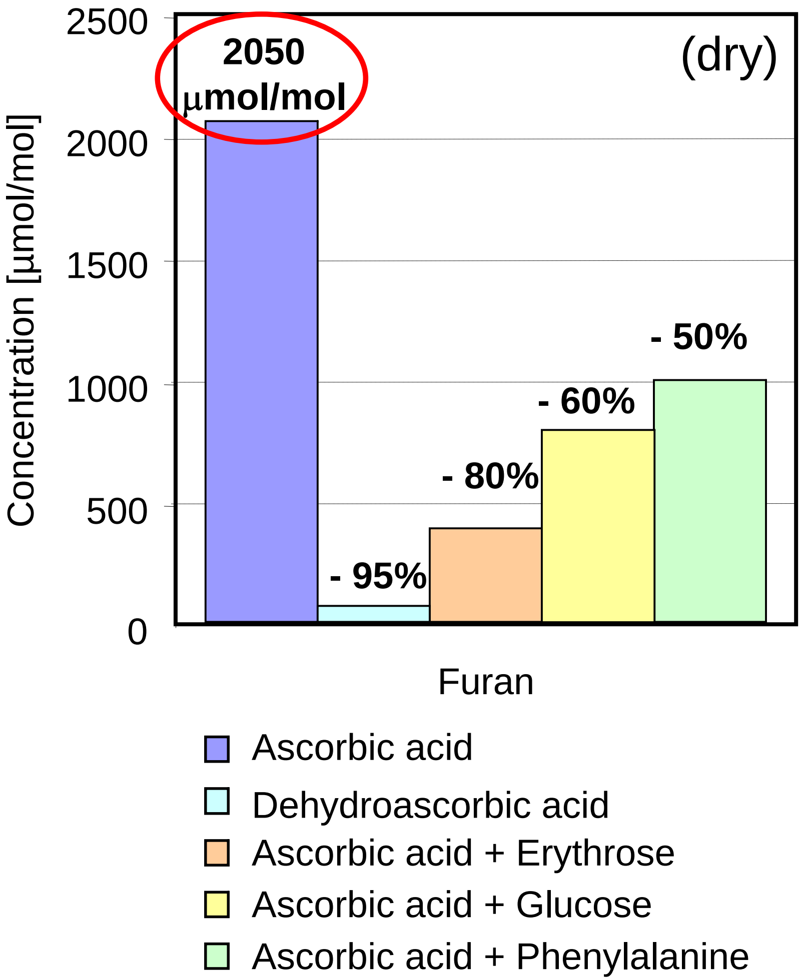
(Märk et al., *J. Agric. Food Chem.* **2006**, *54*, 2786)

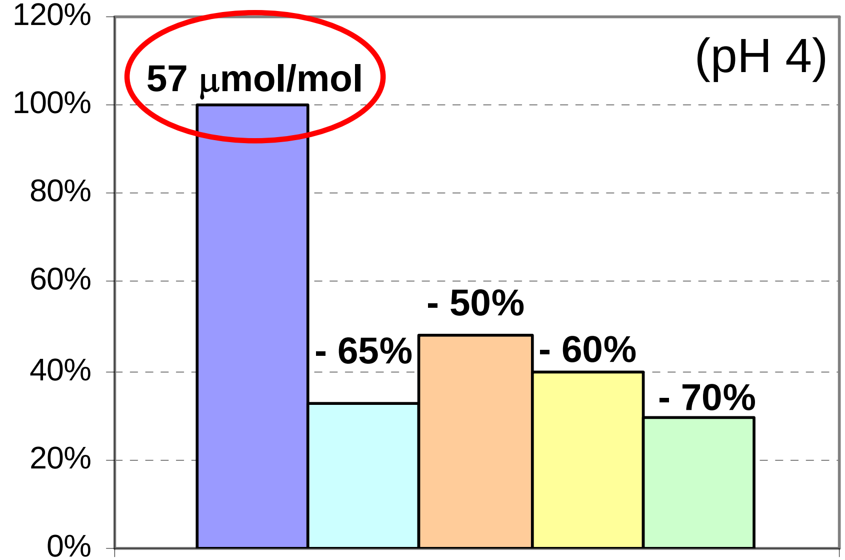
Precursor mixtures (roasting conditions)

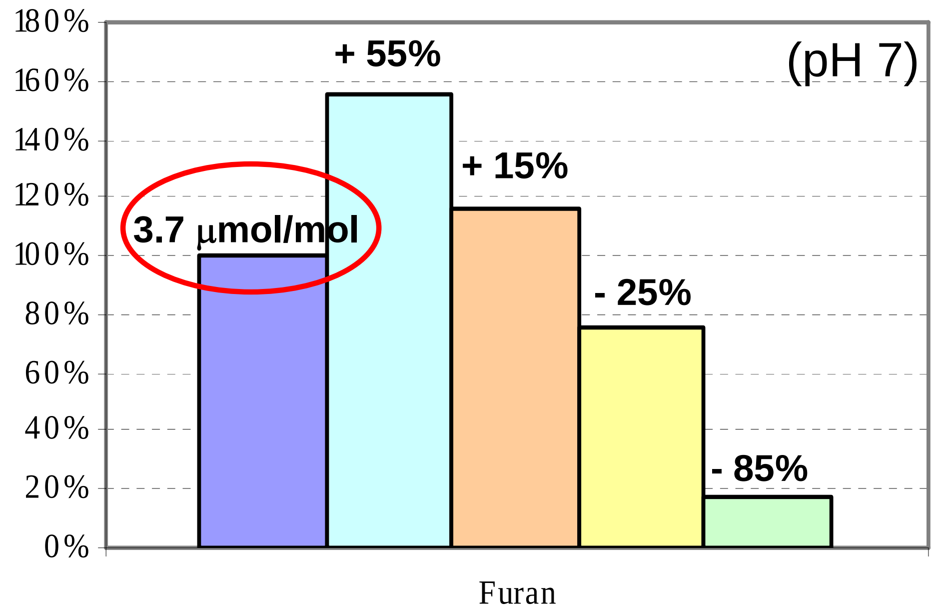


→ Drastic reduction of furan in the presence of food constituents, even if they are potential precursors of furan (competing reactions)

Ascorbic acid → Furan





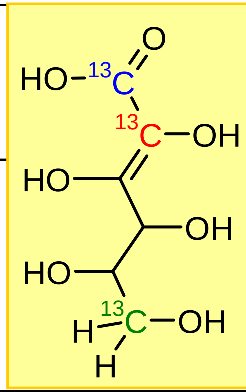


Analysis by SPME-GC-MS

Using d_4-furan as internal standard

(Goldmann et al., *Analyst* **2005**, *130*, 878)

Labelling studies: Ascorbic acid → Furan



	Model system	M (68)	M+1 (69)	M+2 (70)	M+3 (71)	M+4 (72)
L-[1-^{13}C]-ASA	Dry	**100 %**	0 %	0 %	0 %	0 %
L-[2-^{13}C]-ASA	aq. pH 4	**100 %**	0 %	0 %	0 %	0 %
L-[6-^{13}C]-ASA	aq. pH 7	0 %	**100 %**	0 %	0 %	0 %
L-ASA + D-[U-$^{13}C_6$]-Glc (1:1)	Dry	**73 %**	0 %	0 %	0 %	**27 %**
L-ASA + D-[U-$^{13}C_6$]-Glc (1:1)	aq. pH 7	**84 %**	0 %	0 %	0 %	**16 %**
L-ASA + D-[U-$^{13}C_6$]-Glc (1:1)	aq. pH 4	**99 %**	0 %	0 %	0 %	1 %

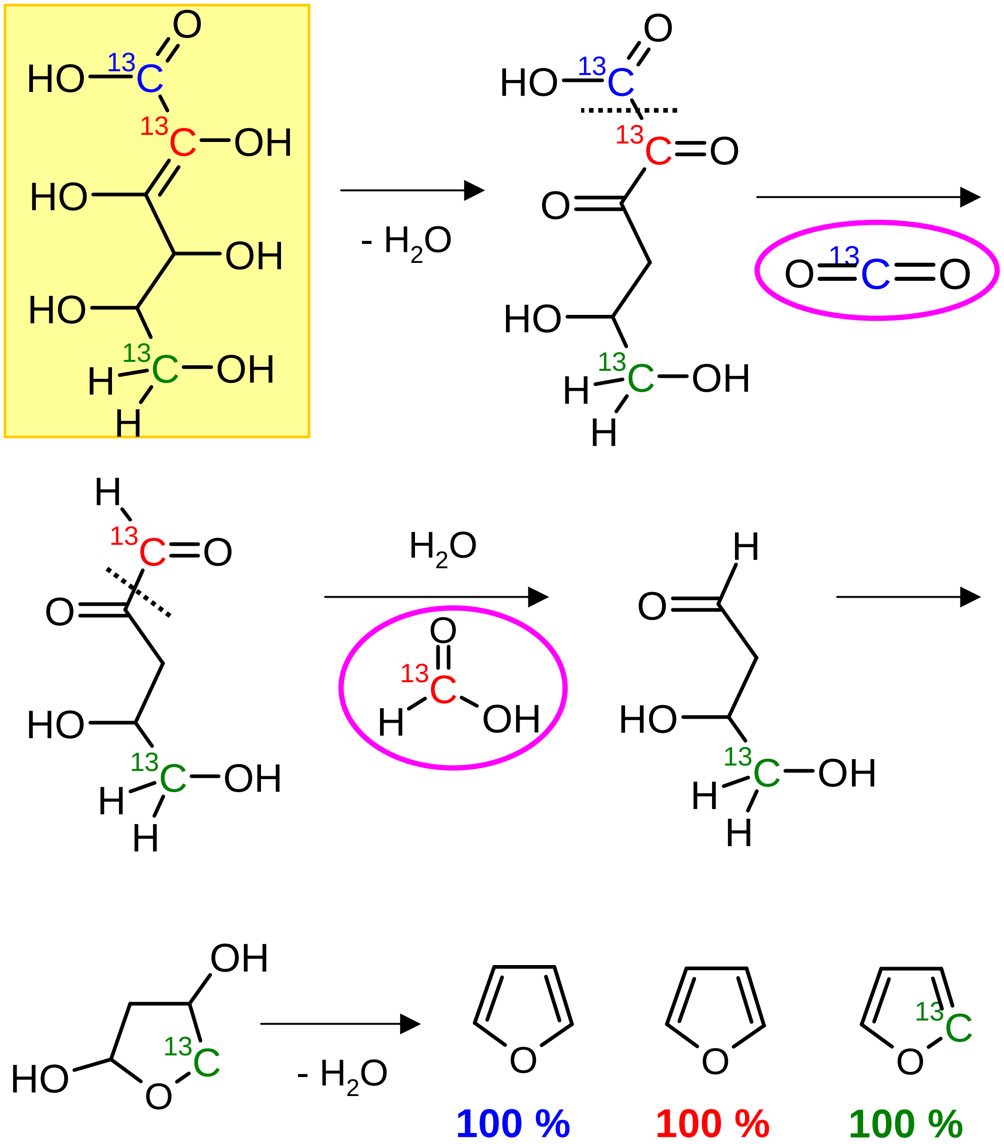
→ C-1 and C-2 not incorporated into Furan (composed of C-3 to C-6)
→ No recombination of ascorbic acid fragments

→ Glucose contributes to the total Furan amount (dry, aq. pH 7)

Formation mechanism: Ascorbic acid → Furan

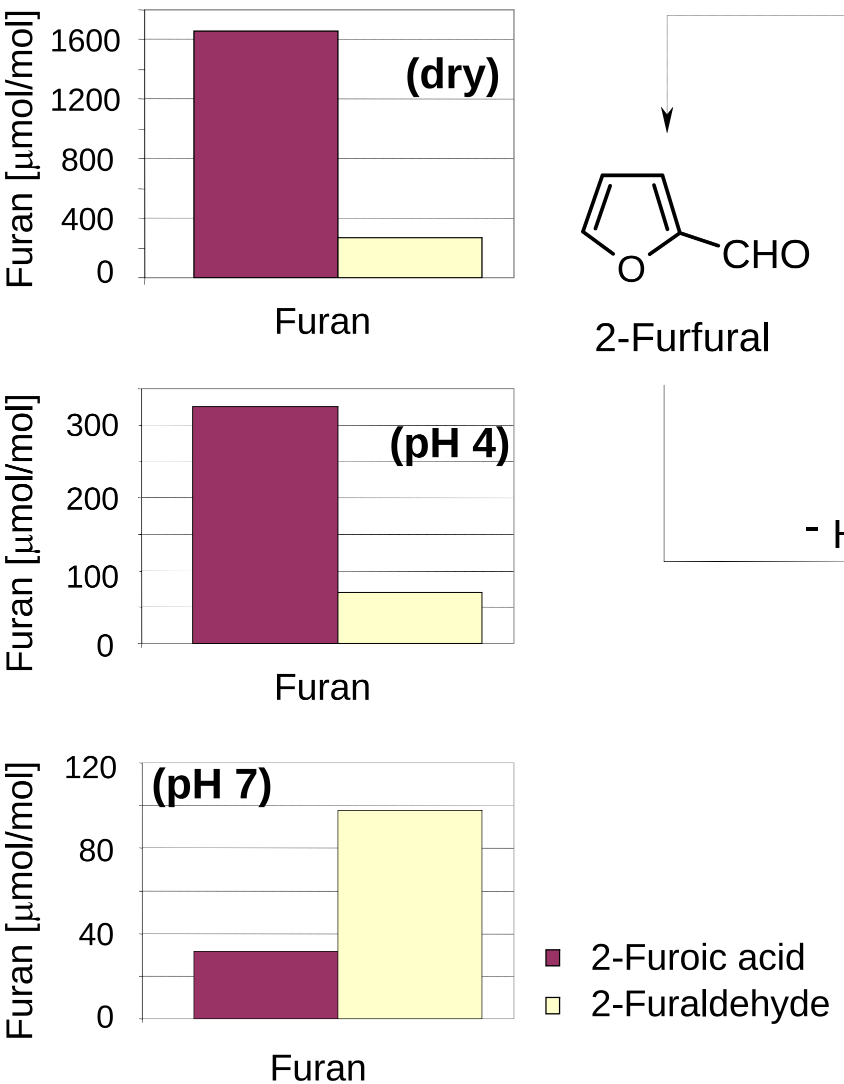
Model system	Ratio CO_2 / $^{13}CO_2$
L-[1-^{13}C]-Ascorbic acid	1 : 1.79
L-[2-^{13}C]-Ascorbic acid	1 : 0.25
L-[6-^{13}C]-Ascorbic acid	1 : 0.16

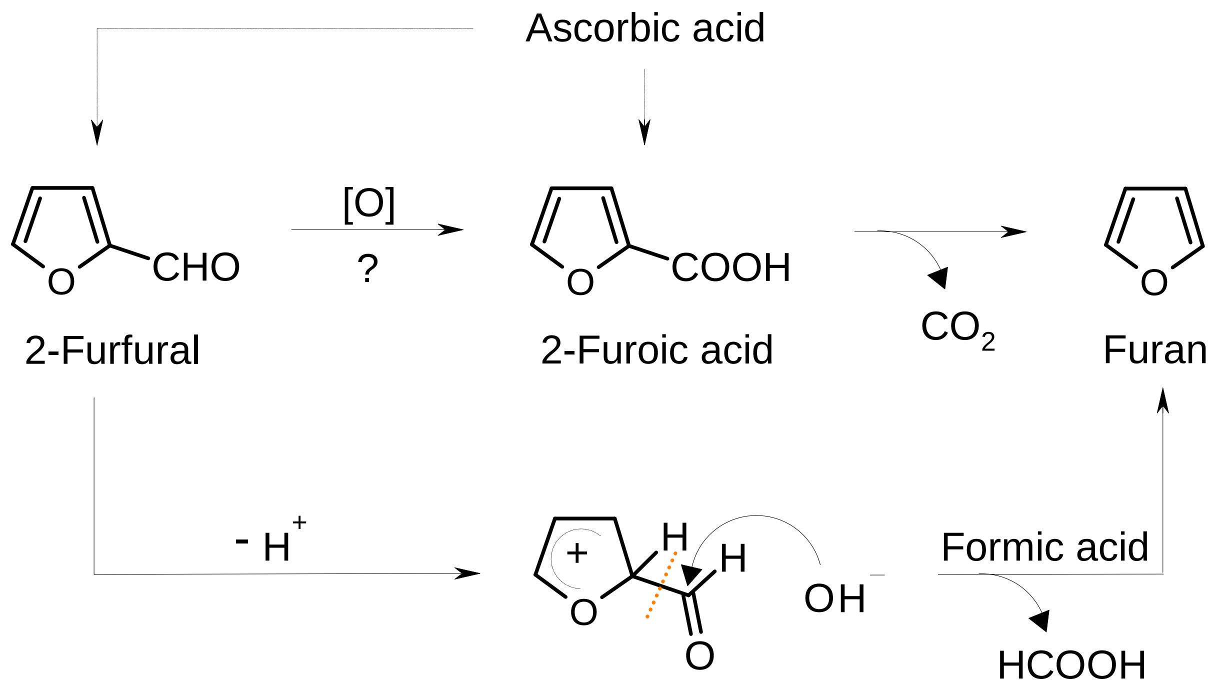
	HCOOH (M) (m/z = 46)	HCOOH (M+1) (m/z = 47)
L-[1-^{13}C]-ASA	80 %	20 %
L-[2-^{13}C]-ASA	68 %	32 %
L-[6-^{13}C]-ASA	84 %	16 %



Furan formation in three steps:
1. Decarboxylation
2. Dicarbonyl cleavage
3. Cyclization/dehydration

Various pathways exist in the degradation of ascorbic acid





Summary

- Ascorbic acid and PUFAs are the major sources of furan in dry systems $\rightarrow$ hydrophilic and lipophilic precursors
- Furan formation is much reduced in the presence of food constituents $\rightarrow$ competing pathways
- Significant reduction of furan amounts observed in aq. Vit. C systems (pH 4 > pH 7) $\rightarrow$ competing pathways
- Furan formation from Vit. C occurs in three steps:
  – Decarboxylation (- CO_2) = C1
  – Loss of formic acid (- HCOOH) = C2
  – Cyclization & dehydration to furan = C3-6

Outlook

- Better understanding of formation pathways
  - dry, aqueous, pH, heating conditions (t/T), kinetics
  - various precursor systems, their relative impact
  - labelling studies, CAMOLA
- Further investigation / mitigation in food systems
  - more realistic food models
  - validation in real food
- Revisit handling of micronutrients in food processing, e.g. vitamins (C, E), PUFAs, amino acids, etc.
- Health risks to humans

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