Inserm

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FACULTE DE MEDECINE HENRI WAREMBOURG

Université de Lille

The glycation and Maillard reactions

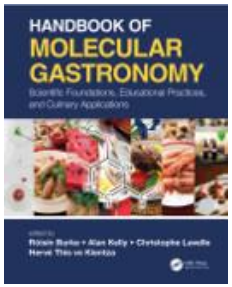
Major non enzymatic browning reactions in food

Frédéric J. Tessier

Launching event for the publication of the Handbook of Molecular Gastronomy
May 12th, 2021

imars

International Maillard Reaction Society



FMaRS

Francophone Maillard Reaction Society

What causes browning in food?

Phenolic compounds + **Enzymes (polyphenol oxidase…)** + O_2 =

Enzymatic browning

Sugars =

Caramelization

Amino acids, Proteins + **Reducing sugars** =

Glycation
Maillard reaction

The never-ending love-hate relationship between Food & *in vivo* Glycation

Maillard 1913

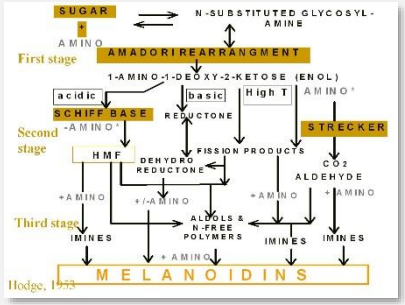
1 volume in 8.
Masson & Cie; p. XI.

This reaction could be implicated in the chemical modification of th nutrients during **food cooking**, and in protein modification **in vivo** catalyzed by hyperglycemia

Hodge 1953

Chemistry of browning reactions in models systems.

JAFC 1(15): 928-43

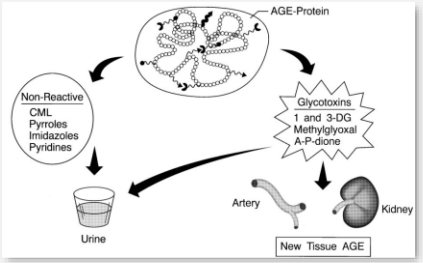


Vlassara et al. 1997

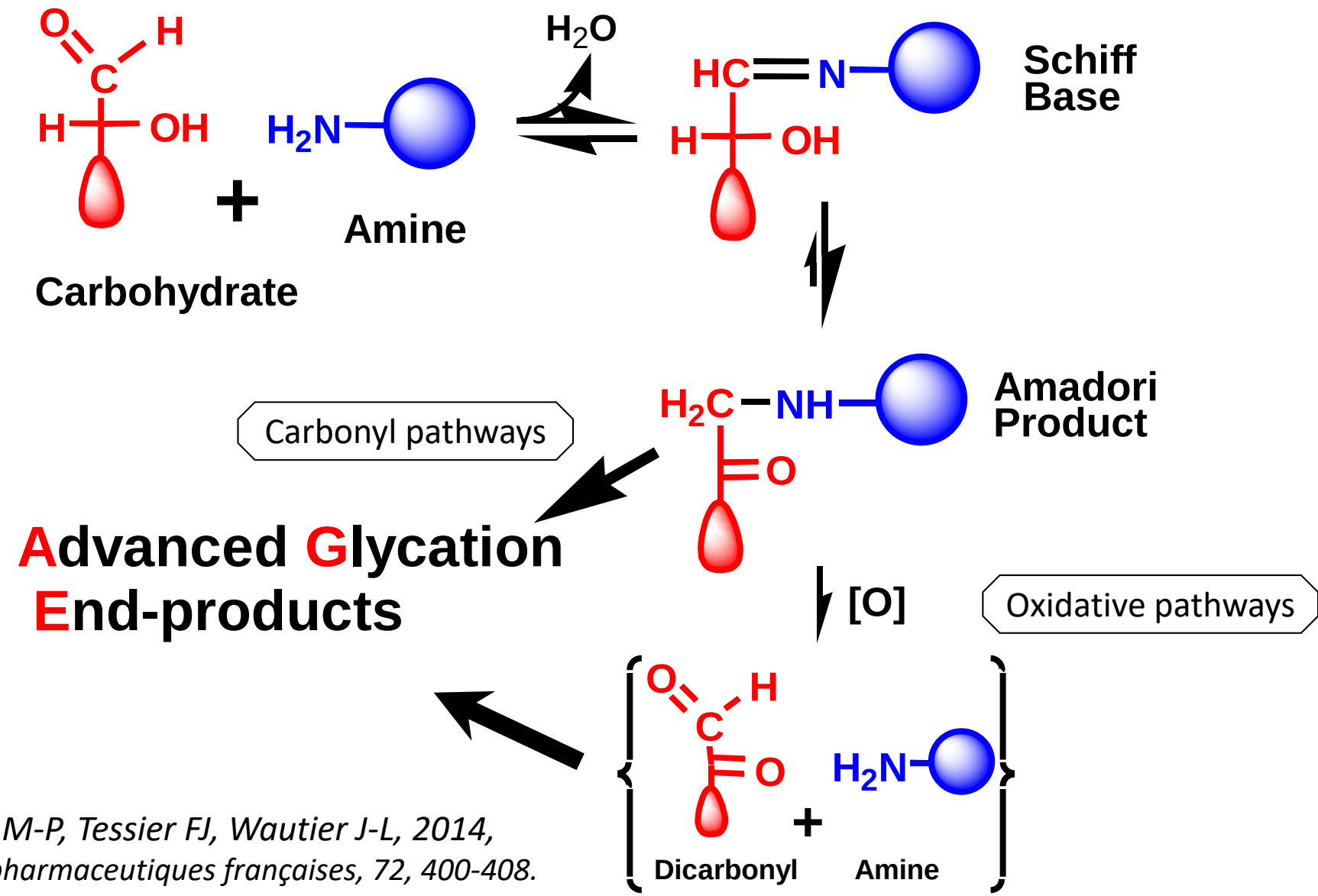
Orally absorbed reactive glycation products (glycotoxins):

An environmental risk factor in diabetic nephropathy

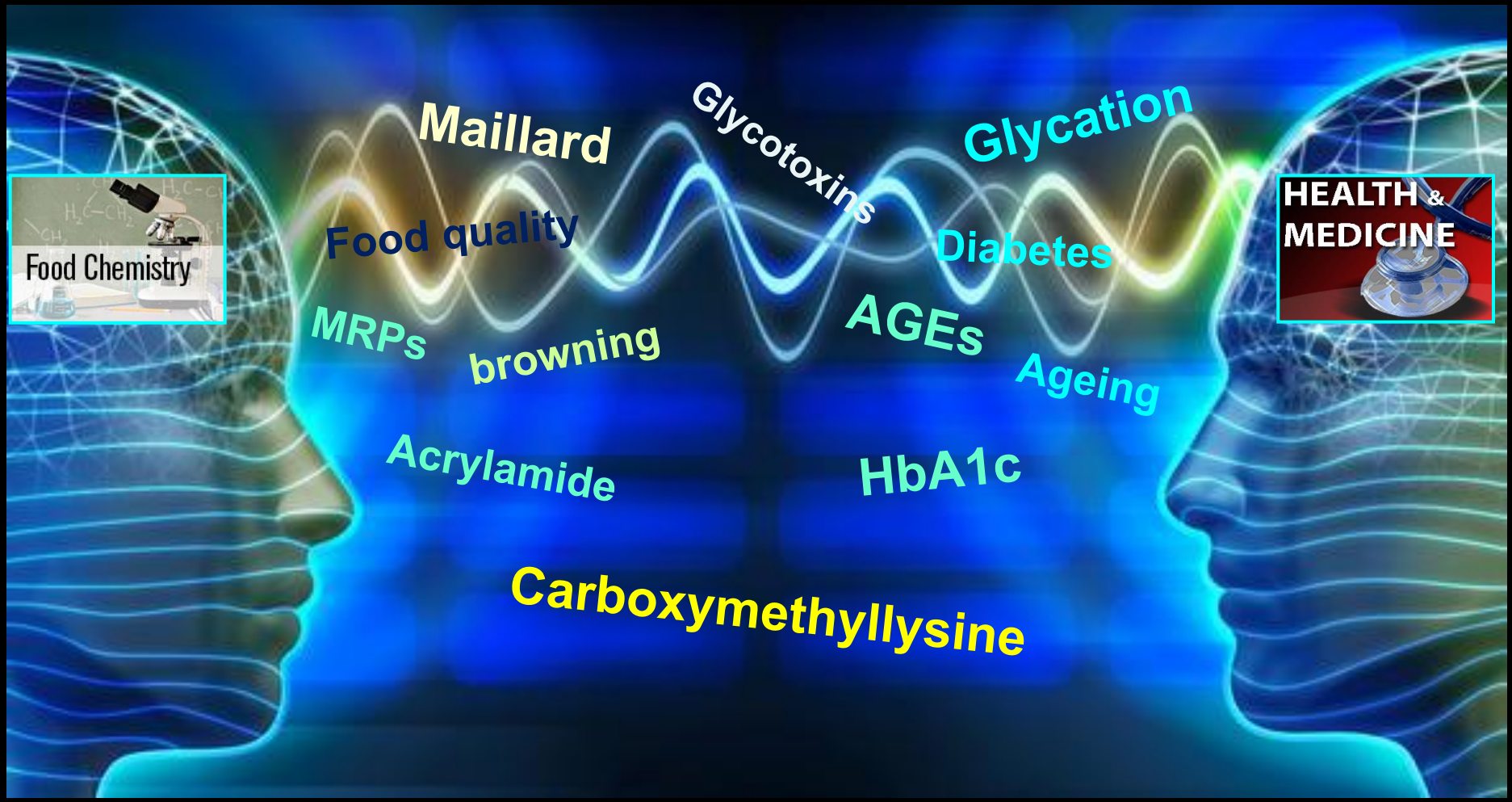
PNAS USA, 94: 6474-9.

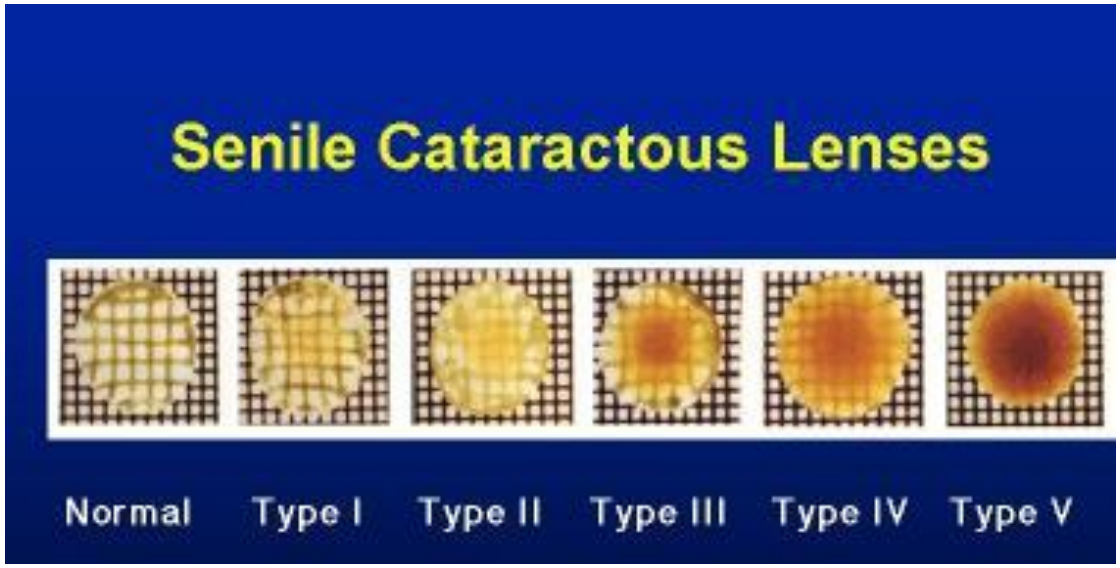


Chemical pathways of the glycation

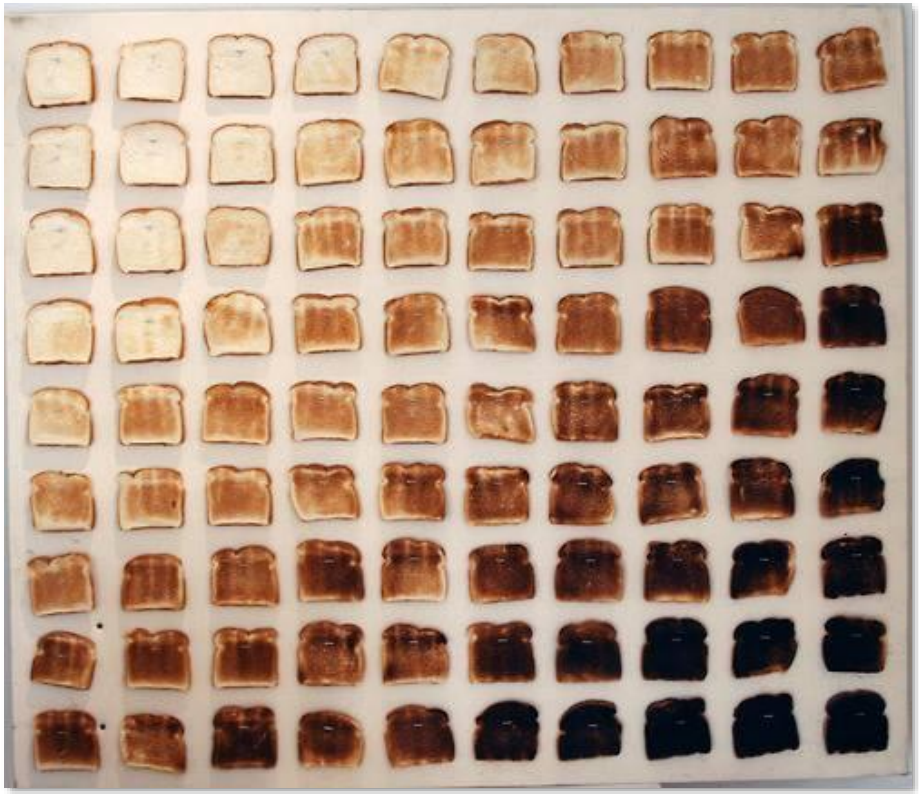


Wautier M-P, Tessier FJ, Wautier J-L, 2014,
Annales pharmaceutiques françaises, 72, 400-408.


Food Chemistry
Maillard
Food quality
MRPs
browning
Acrylamide
Glycotoxins
Glycation
Diabetes
AGEs
Ageing
HbA1c
Carboxymethyllysine
HEALTH & MEDICINE



Brown Color Palettes used in ophthalmology and in food



Glycation in food

(Maillard reaction)




Tessier & Niquet 2007, Journal de la Société de Biologie, 201, 199-207

Quotes:

“MRP contents have increased vastly in the last 50 years in the western diet”

Vlassara H., Adv.Nephrol. Necker Hosp. (1996) 25, 303-307

Quotes:

"How does the body deal with this enormous load of nonphysiological amino acids?"

Henle T., Kidney International (2003), 84, p S145-S147

Choose Glycotoxin-Free Foods

Overall, foods in the fat and meat groups contain 30-fold and 12-fold higher AGE content, respectively, than foods in the carb. group

Carboxymethyl-lysine (CML)

- In butter

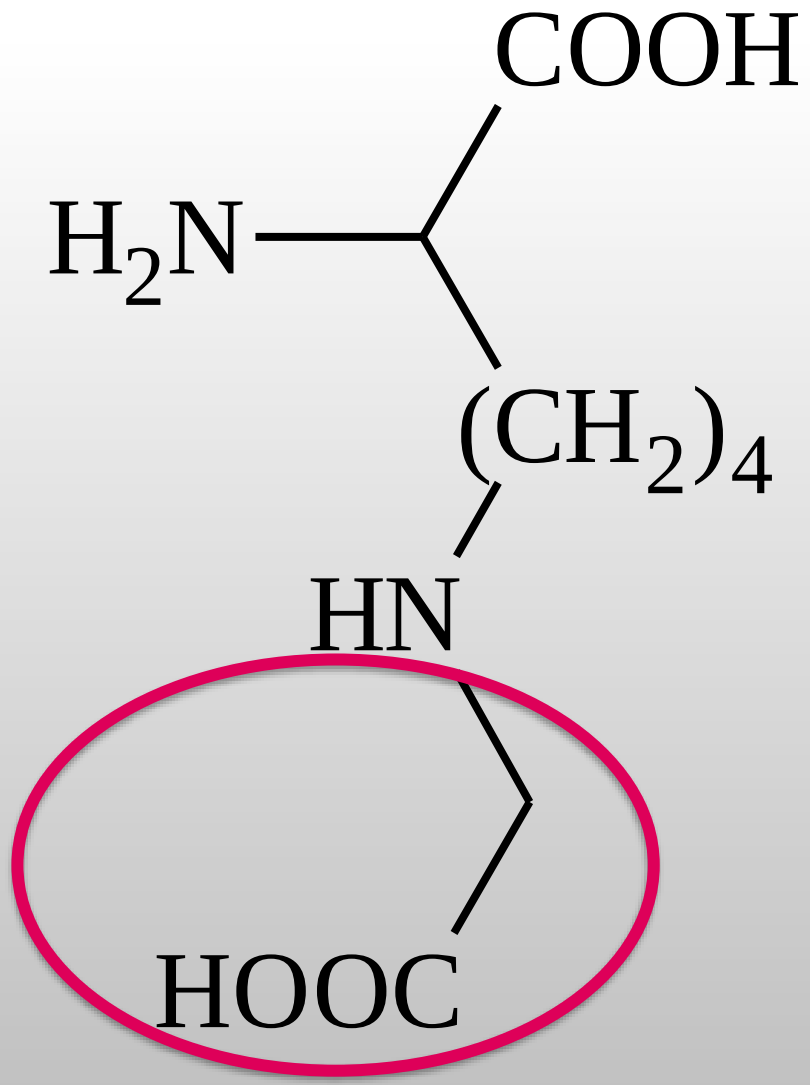
Acrylamide

- How to limit its formation?

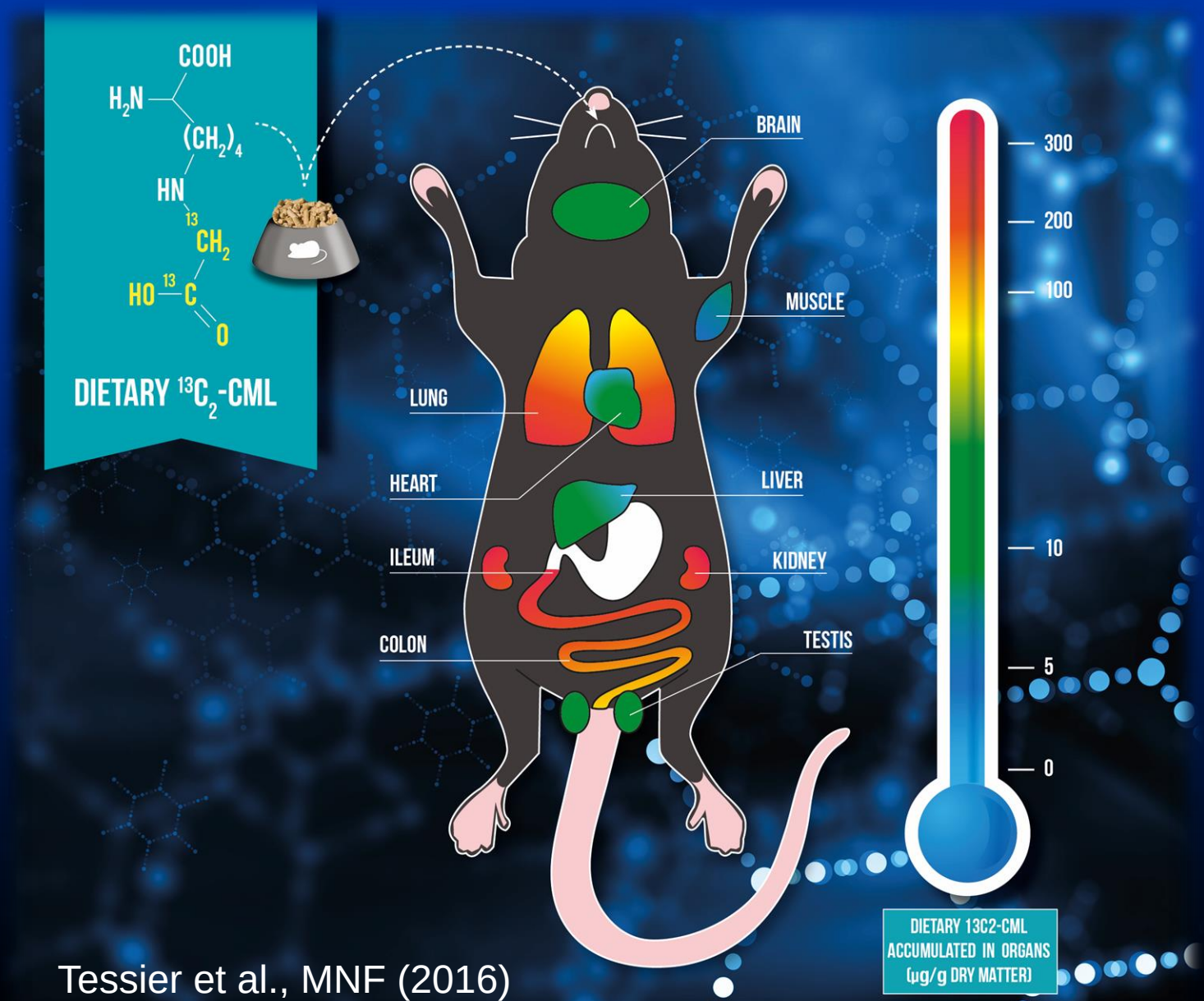
Mélanoidins

- Health effects?

Carboxymethyl-lysine

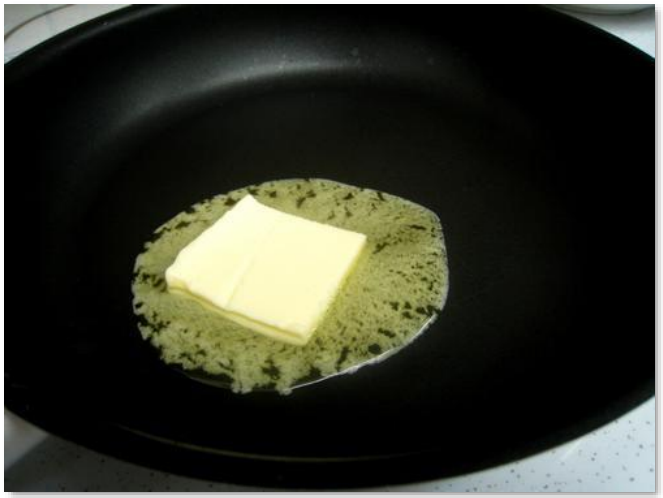


Accumulation of dietary CML in organs

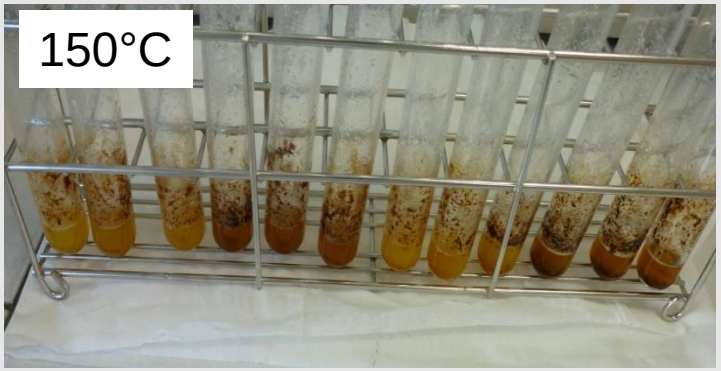


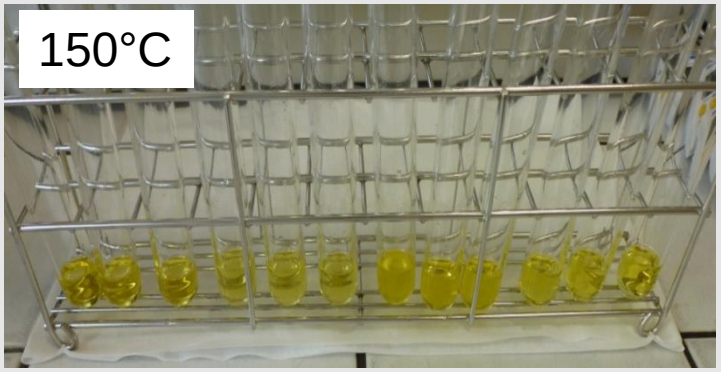
Tessier et al., MNF (2016)

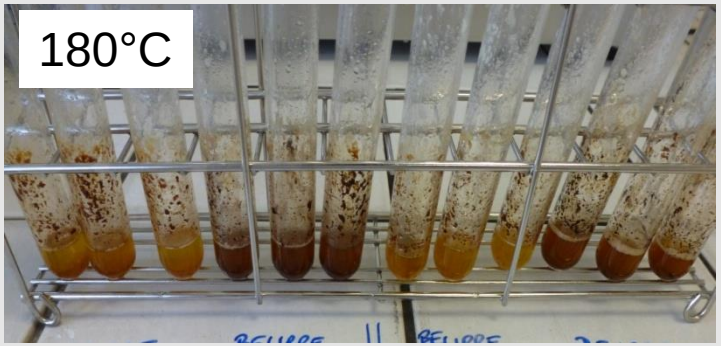
Why does butter turn brown during cooking?

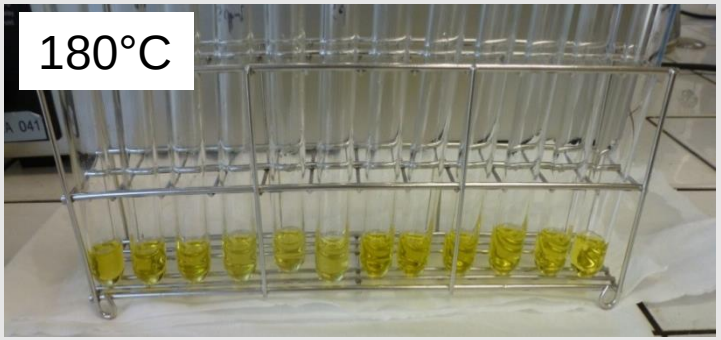


Niquet-Léridon et al. 2015, Food Chemistry, 177, 361-368.









Niquet-Léridon et al. 2015, Food Chemistry, 177, 361-368.

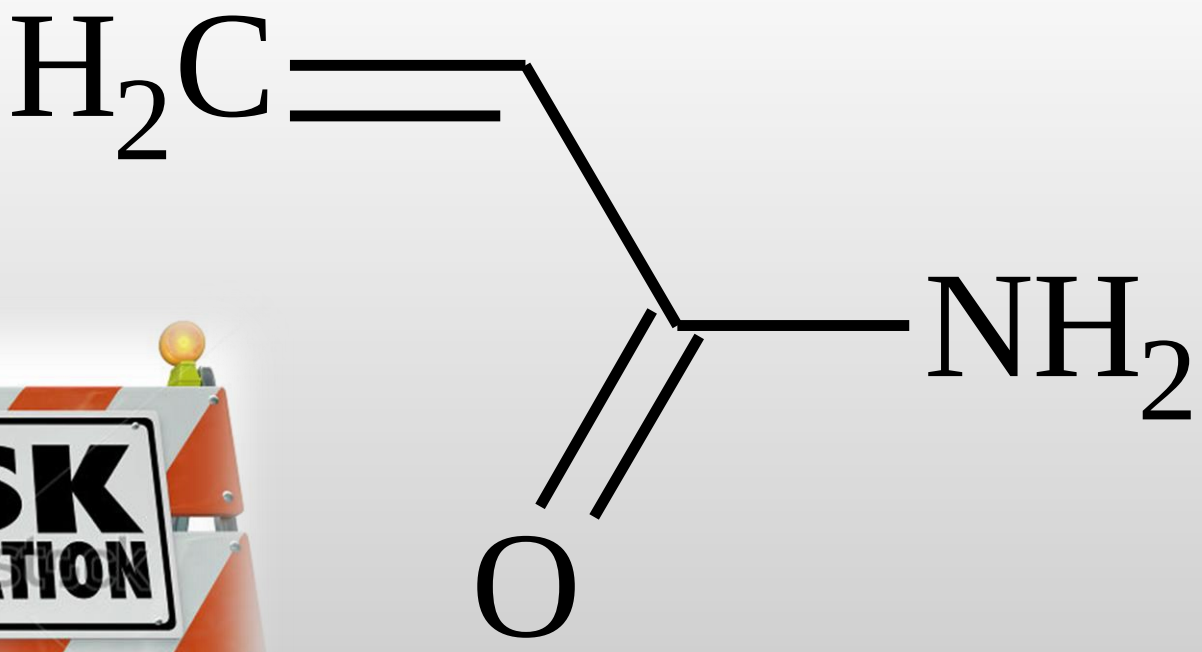
Amino acids, Proteins + **Reducing sugars** =

1.2%

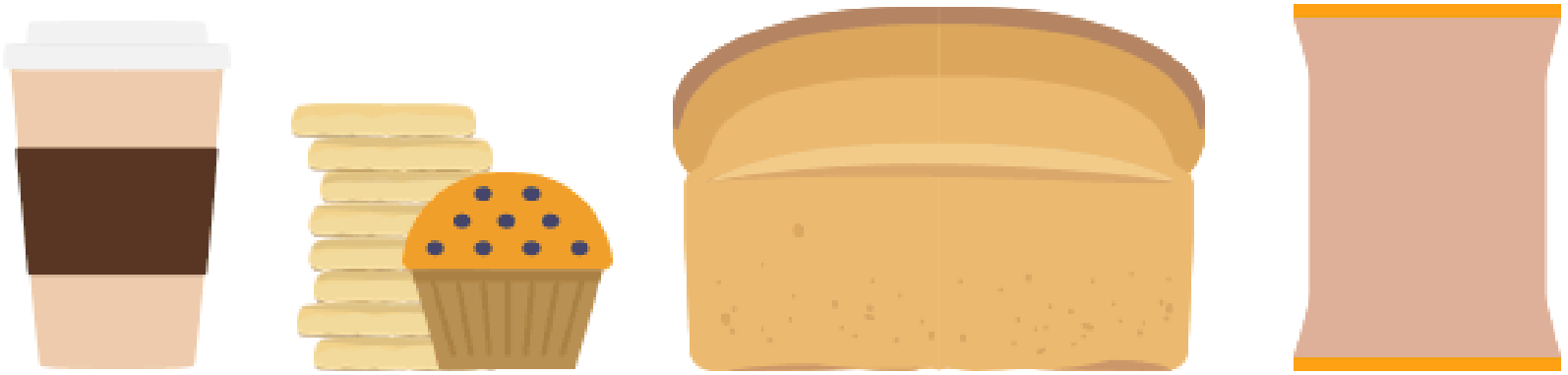
Dietary CML

Niquet-Léridon et al. 2015, Food Chemistry, 177, 361-368.

Acrylamide



What foods can acrylamide be found in?



Coffee

Cakes and biscuits

Bread and toast

Crisps and chips

Source: food standards agency

Acrylamide

Mottram et al.
NATURE, Vol. 419
3 0ct. 2002

Food chemistry

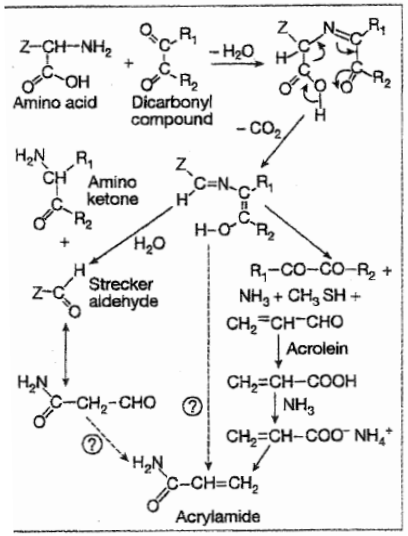
Acrylamide is formed in the Maillard reaction

Reports of the presence of acrylamide in a range of fried and oven-cooked foods[1,2] have caused worldwide concern because this compound has been classified as probably carcinogenic in humans[3]. Here we show how acrylamide can be generated from food components during heat treatment as a result of the Maillard reaction between amino acids and reducing sugars. We find that asparagine, a major amino acid in potatoes and cereals, is a crucial participant in the production of acrylamide by this pathway.

Products of the Maillard reaction are responsible for much of the flavour and colour generated during baking and roasting. An important associated reaction is the Strecker degradation of amino acids by these intermediates (Fig. 1), in which the amino acid is decarboxylated and deaminated to form an aldehyde.

We investigated whether this reaction could provide a possible route to acrylamide. The amino acid asparagine should be a particularly suitable reactant as it already has an amide group attached to a chain of two carbon atoms. We therefore performed a series of Maillard reactions between glucose and asparagine, as well as with other amino acids that do not have the correct carbon backbone for acrylamide (Fig. 1).

Significant quantities of acrylamide (221 mg per mol of amino acid) were found when an equimolar mixture of asparagine and glucose was reacted at 185 °C in phosphate buffer in a sealed glass tube. The temperature dependence of acrylamide formation from asparagine indicates that this is favoured above 100 °C and that very high temperatures are not necessary (Fig. 2). In similar reactions with glucose and glycine, cysteine or methionine at



gure 1 Proposed pathways for the formation of acrylamide after recker degradation of the amino acids asparagine and methionine in the presence of dicarbonyl products from the Maillard action. In asparagine, the side chain Z is $-CH_2CONH_2$; in ethionine, it is $-CH_2CH_2SCH_3$.

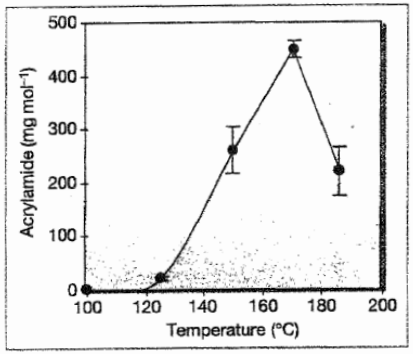
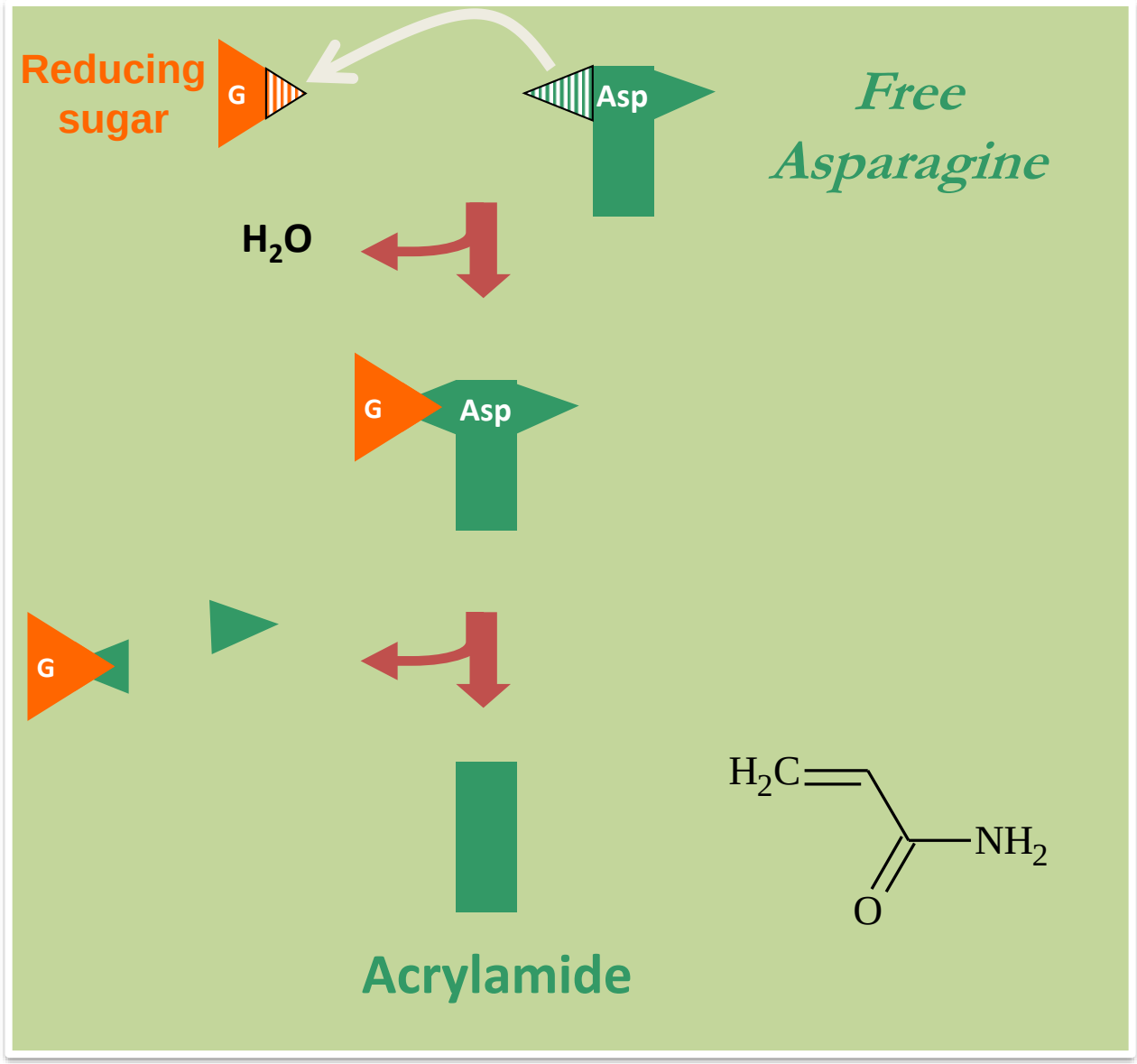


Figure 2 Temperature-dependent formation of acrylamide (mg per mol of amino acid) from asparagine (0.1 mmol) and glucose (0.1 mmol) in 0.5 M phosphate buffer (100 μl, pH 5.5) heated in a sealed glass tube for 20 min. Error bars represent standard deviations ($n=3$). Acrylamide produced in the reaction was extracted with ethyl acetate and analysed by gas chromatography with mass spectrometry after derivatization to 2,3-dibromopropanamide[7], using 2-methylacrylamide as the internal standard. Selected ion monitoring was used to detect the analytes, with m/z 150 and 152 for acrylamide and m/z 120 and 122 for methylacrylamide. The presence of acrylamide in selected samples was confirmed in full mass spectra.

Formation of acrylamide

(major pathway)

(Minor pathways : from acrolein, acrylic acid wheat gluten…)



REDUCE ACRYLAMIDE

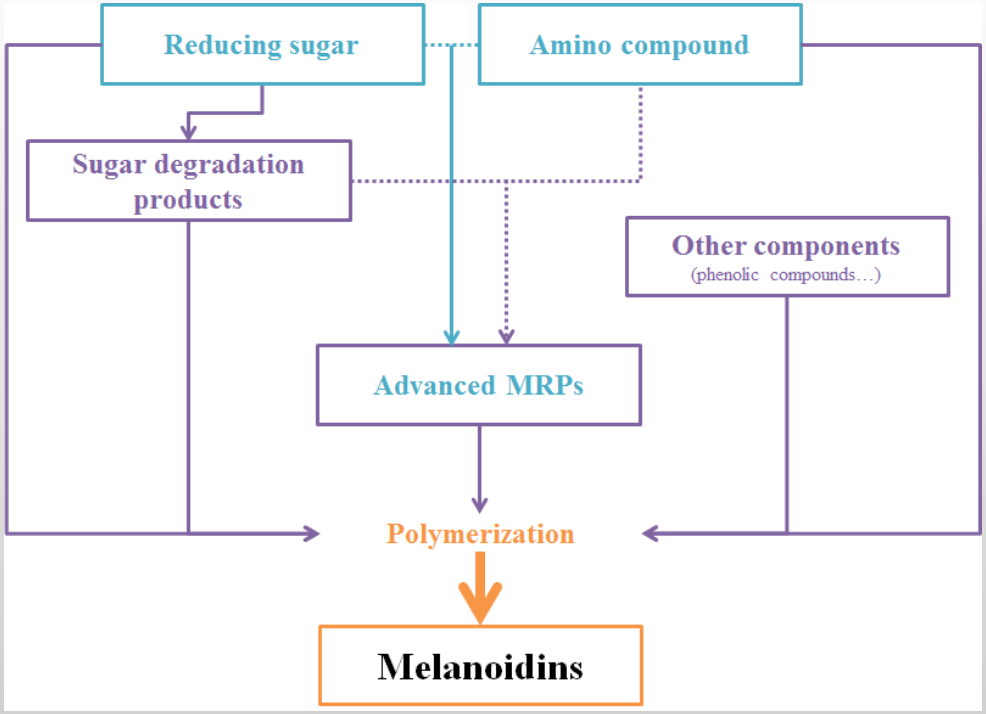
GO FOR GOLD

Aim for a golden colour, rather than dark brown, when frying, baking, roasting or toasting.

Food Standards Agency
food.gov.uk

Melanoidins

Melanoidins are high molecular weight, nitrogen-containing, brown pseudo-polymers generated during the last stage of the Maillard reaction



- **Health promoting effects**
  - Antioxidant, antimicrobial…
  - Potential correlation to dietary fibers
- **No chemical structure is fully identified**
  - Variable according to foodstuff composition and heating conditions

Anton et al. 2012, Food & Function, 3, 941-949
Helou et al. 2014, Amino Acids, 46, 267-277
Helou et al. 2017, Food & Function, 8, 2722-2730

CONCLUSIVE REMARK

New studies are required to relate dietary glycation to long-term health effects

EXOAGEING

2020 - 2024

Effects of early-life and chronic exposure to dietary AGEs on chronic low grade inflammation and age-associated disorders

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Projet financé par l'ANR – Project funded by the ANR

Cook Better, Age Better ©

Thank you for your attention