Enzymes, diffusion and chemical degradation, three factors that impact vitamin C and vitamin B9 when processing fruit and vegetables

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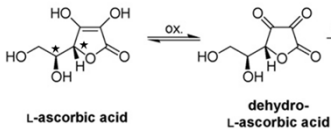
UMR408 Sécurité et Qualité des Produits d'Origine Végétale, Avignon

Biologically Active compounds in Foods
Łódź, 9-10 nov 2017

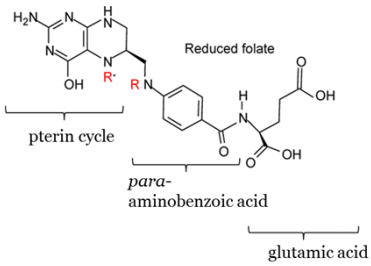
- Introduction
- Chemical degradation
- Leaching
- Enzymic degradation
- The emerging general pattern
- Conclusions and research needs

Two water-soluble vitamins relevant for fruit & vegetables

- Ascorbic acid and dehydroascorbic acid = vitamin C
  - Primarily in plant products – fruits and vegetables
  - Prevention of scurvy – biosynthesis of collagen



- Folates: numerous vitamers
  - Organ meat, green vegetables (40% in France), yeast
  - Prevention of neural tube disorders



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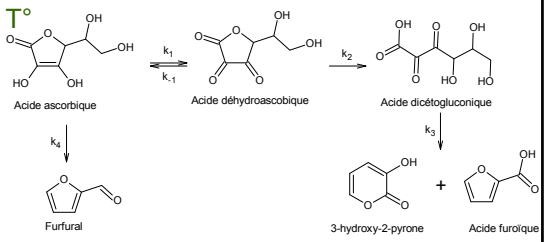
Chemical degradation of vitamin C

- Many articles, mostly on ascorbic acid or total vitamin C, during processing or storage
  - First-order degradation?
  - pH mostly 2-4, T° 30 – 100°C
- Degradation depends on pH, temperature and redox
  - Two mechanisms, oxydoreductive or hydrolytic
  - Hydrolytic: low pH, high T°
  - Different end-products



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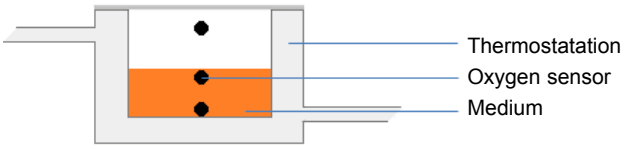
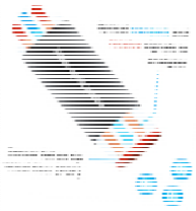
Autooxidation of ascorbic acid requires oxygen… but not only

- Degradation of ascorbic acid at 80°C in non-stirred reactor
- Monitoring of oxygen content in the reactor





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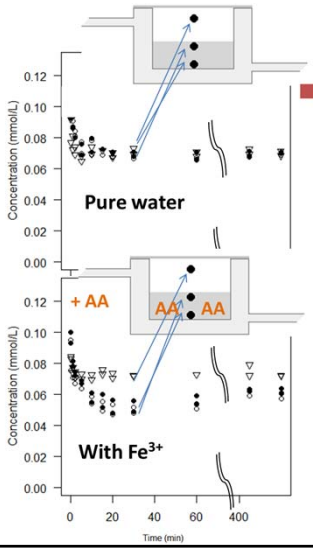
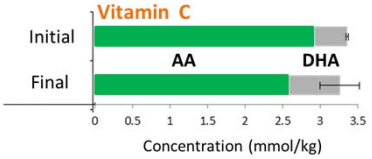
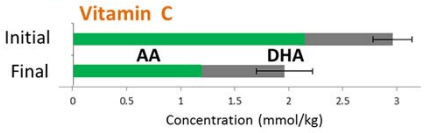
Comparison water with without iron



No AA loss or oxygen use in pure water even after 8h at 80°C.



But losses occur in presence of Fe^{3+}



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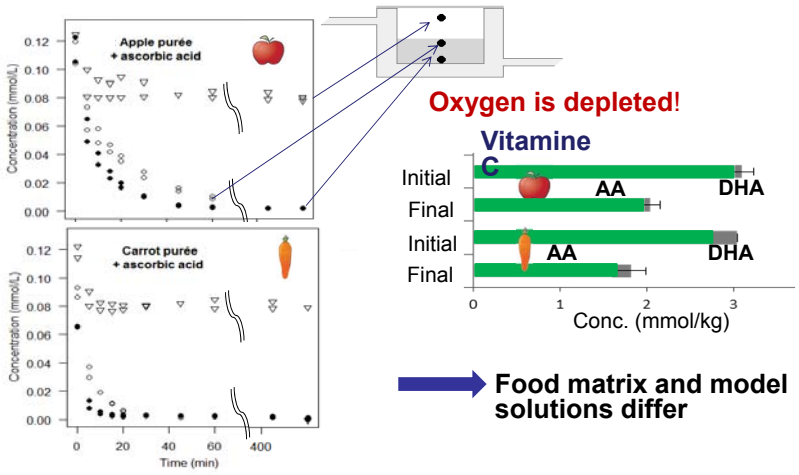
Much faster degradation in fruit & vegetable purees



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What about hydrolytic degradation?

- Degradation of ascorbic acid in strictly anaerobic conditions, pH 3.5
  - 20 to 150°C
  - Up to 5 bar (0.5 MPa)
  - With varying O_2, N_2…
  - 400 mL, stirred
  - Fast sampling rate

Thermoresistometer Mastia ™

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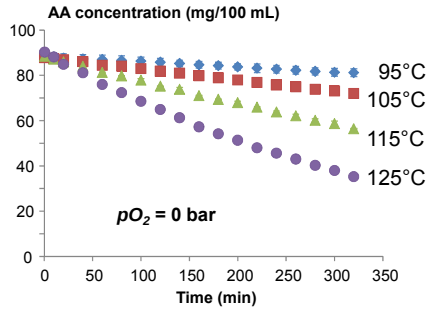
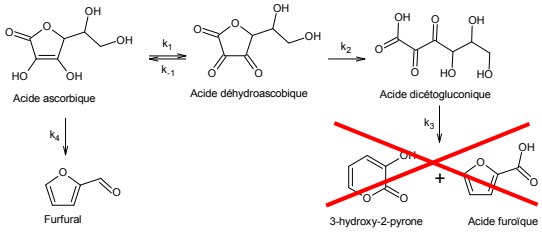
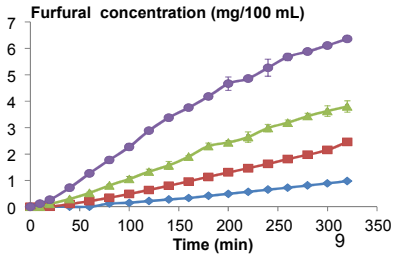
Degradation kinetics



- First order kinetics

$$C_t = C_0 . \exp\left(-3,33.10^6 . \exp\left(-\frac{66430}{RT}\right) . t\right)$$





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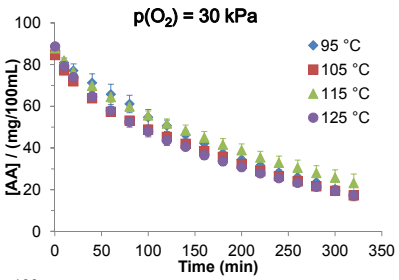
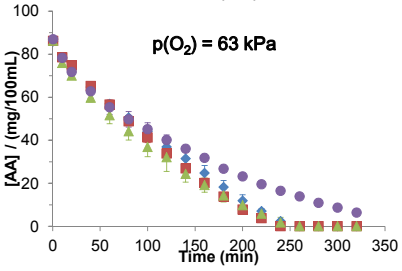
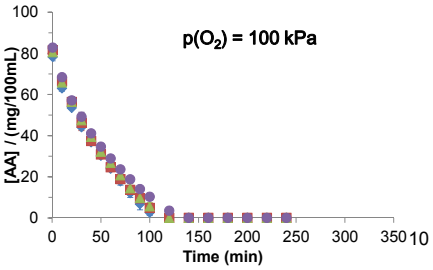
And now with oxygen



Marked acceleration with increased oxygen in the head space

Differences between temperatures disappear!





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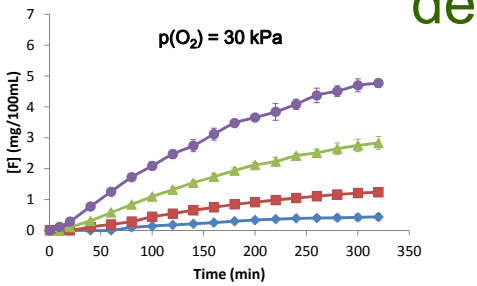
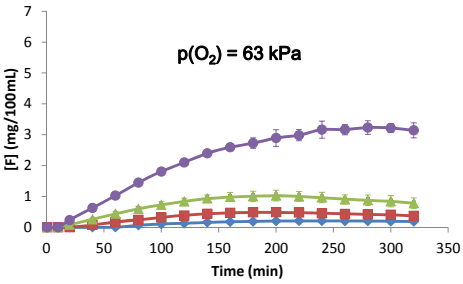
Production of furfural decreases





- No detectable furfural at the highest P(O2)
- The higher the temperature, the more furfural (the more hydrolytic degradation?)

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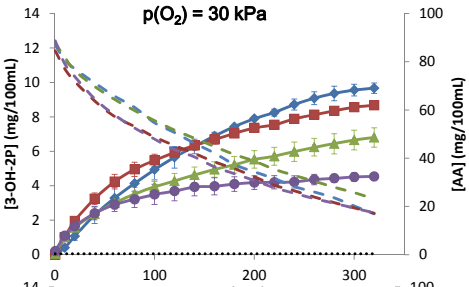
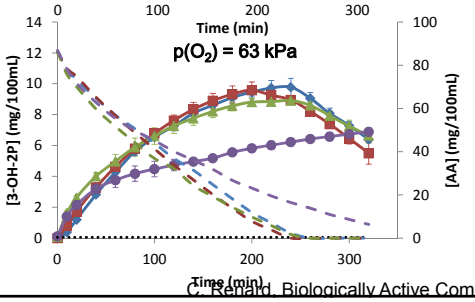
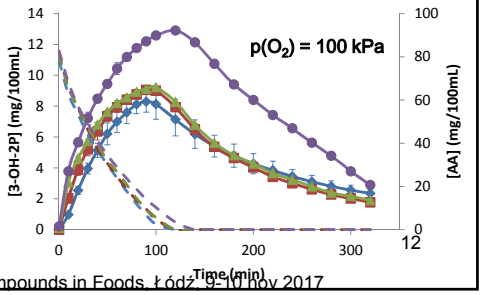
While that of 3OH2P and furoic acid increases







Kinetics vary with T° and *p(O2)*
NOT stable end-products

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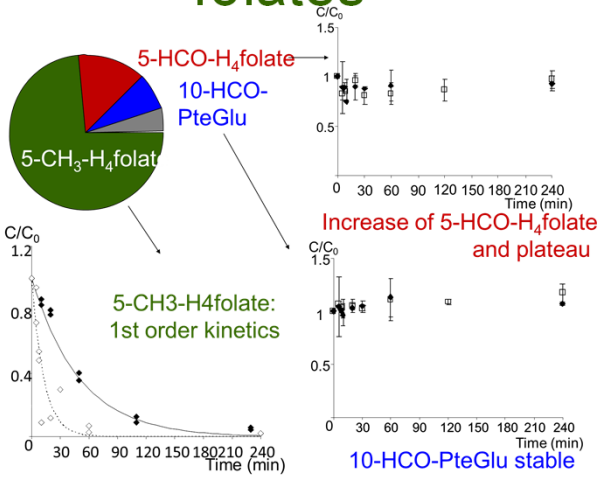
Losses of folates

- Degradation studies: vegetables – model solutions
  - Model solutions:
    - First order kinetics
    - High impact of oxygen
    - Stabilisation with ascorbic acid or β-mercaptoethanol
    - Higher stability at acidic pH
  - Vegetables
    - Treatments: blanching, steaming, microwaves
    - Losses: from 10 % to 75 %
    - Leaf vegetables > roots vegetables
- Mechanisms:
  - Oxidation – irradiation – catabolism : break between pteridin ring and p-ABA

Chemical degradation of folates

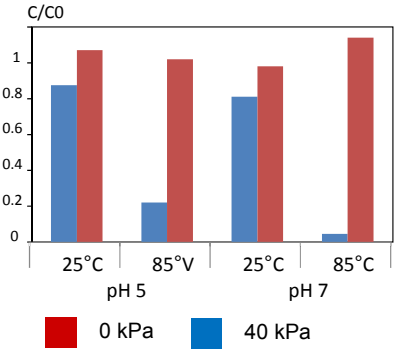
Losses of folates in spinach purée at 45°C and 65°C



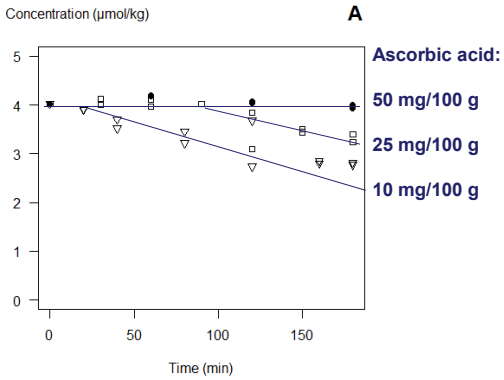
- 5-methyltetrahydrofolate is the main vitamer and one of the most susceptible to degradation

In absence of oxygen or with vit. C, folates can be stable

Loss of 5-Me-CH_3 folate with different pH and oxygen



Loss of added 5-Me-CH_3 folate in apple



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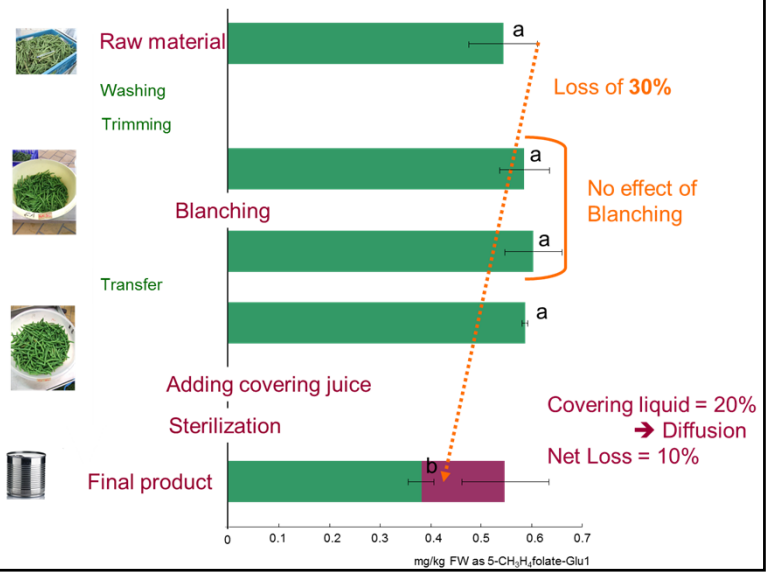
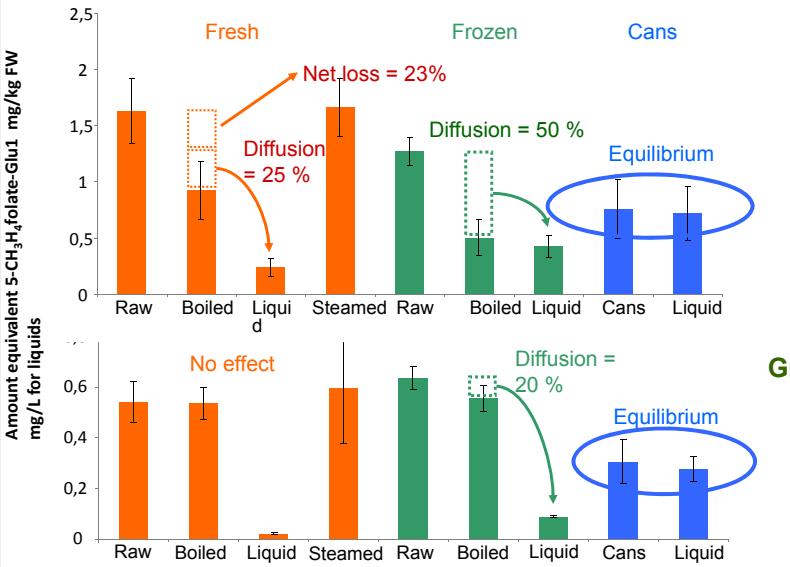
Is chemical degradation actually the main mechanism?

Folates during canning of green beans



With different cooking methods



Spinach

Green beans

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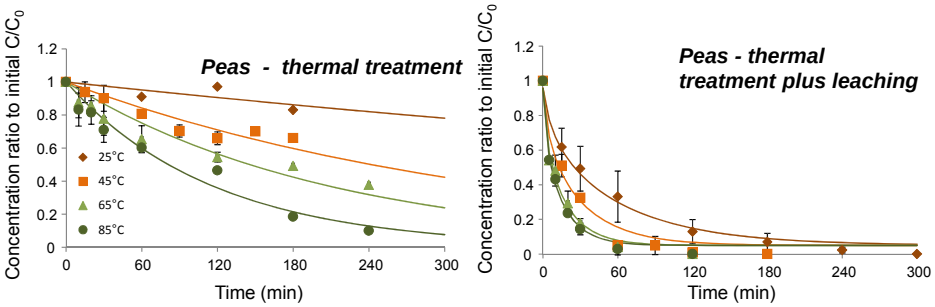
With a systematic experiment

- Comparison of losses for ascorbic acid in peas in closed bags or in mesh bags



- Losses are much faster in open mesh bags: marked rôle of leaching specially for shorter times and lower temperatures

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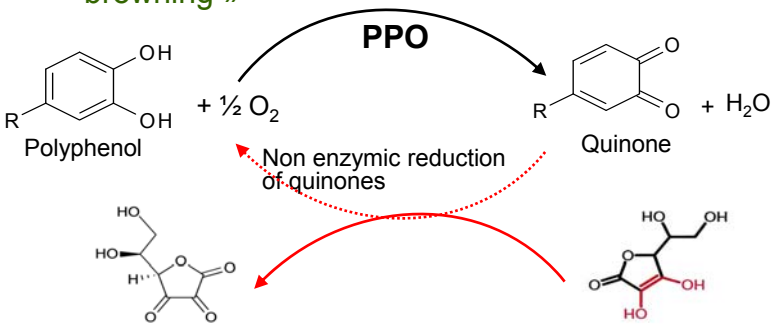
Mechanisms for enzyme-driven degradation

- Usually not a direct oxydation of vitamin C:
  - Scavenger molecule for other oxidation reactions
  - Notably for quinones from polyphenols (« enzymic browning »



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Enzymic degradation of folates

- Deglutamation
  - Loss of the glutamate chain (deglutamation)
    - By a γ-glutamyl hydrolase (GGH, EC 3.4.19.9)
    - During crushing or after high pressure processing
  - Leads to improved bioavailability

Food Chem 117 (2009) 568, JAFC 58 (2010) 4230

- Oxidative cleavage of the pterin – *p*ABA bond
  - Loss of the activity

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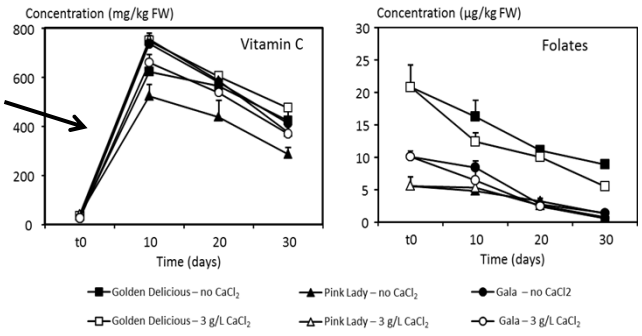
Losses during storage of HPP-treated products

- Apple slices in apple juice, treated by high pressure processing

AA added during processing



- Limited losses during processing, but degradation during storage

Is there a general pattern?

- In terms of speed:
  - Enzymes > leaching > chemical degradation
- Three points of attention during processing for preservation of vitamin B9 and C:
  - Enzyme activity : no grinding, fast blanching
  - Leaching is faster than chemical degradation
    - Water presence
  - Oxygen is a major co-factor:
    - Anaerobiosis ?
    - Decrease/eliminate oxygen?

Conclusions

- Leaching is a major mechanism when the fruit & vegetables are in contact with water
  - We need to better understand and model this mechanism (diffusion constants, rôle of cellular structure in fruit & veg)
- Oxygen can be the limiting factor in vitamin C & B9 degradation
  - Oxygen availability?
  - Need to monitor ascorbic acid and dehydroascorbic acid
- No all folate vitamers are equally susceptible to degradation in foods
  - In-depth chemistry is needed to understand their losses
  - Very limited data on polyglutamation

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- Thanks to
  - Prof. Michael Rychlik
  - Dr. Nicolas Delchier
  - Hanna Bricks
  - Dr. Anna-Lena Herbig
  - Dr. Nizar Al-Fata
  - Stéphane Georgé
- Thank you for your attention!

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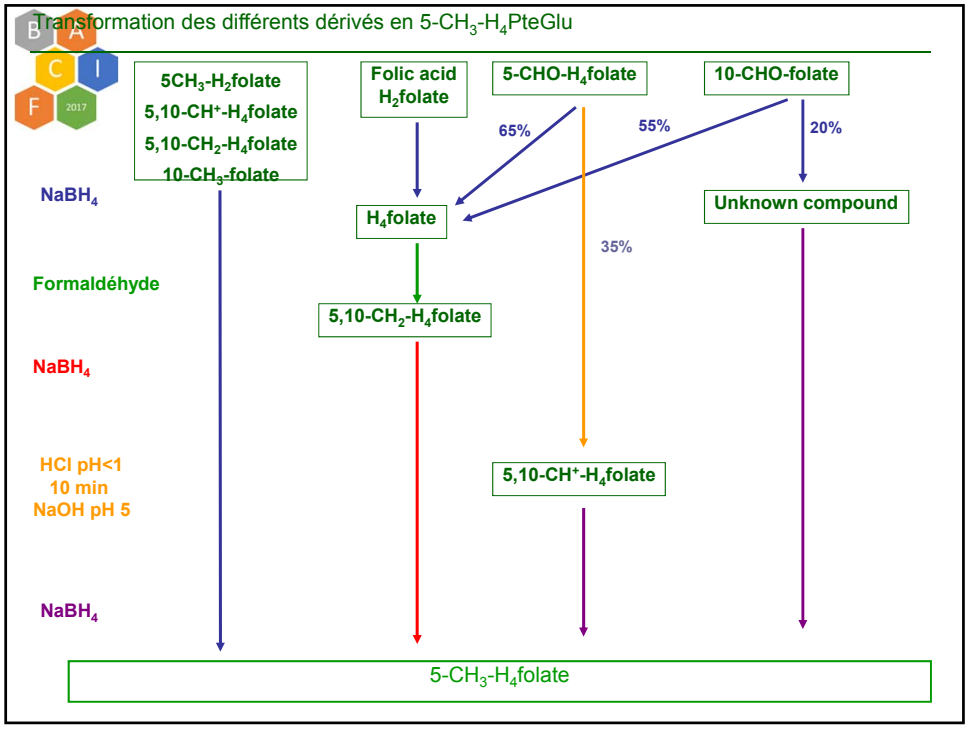
Transformation des différents dérivés en 5-CH3-H4PteGlu
5CH3-H2folate
5,10-CH+-H4folate
5,10-CH2-H4folate
10-CH3-folate
Folic acid
H2folate
5-CHO-H4folate
10-CHO-folate
65%
55%
20%
35%
NaBH4
H4folate
Unknown compound
Formaldéhyde
5,10-CH2-H4folate
NaBH4
HCl pH<1
10 min
NaOH pH 5
5,10-CH+-H4folate
NaBH4
5-CH3-H4folate