

La voie de biosynthèse des phénylpropanoïdes :

Etude des acides chlorogéniques

Défense (pathogènes, herbivores)
Attraction (pollinisateurs)

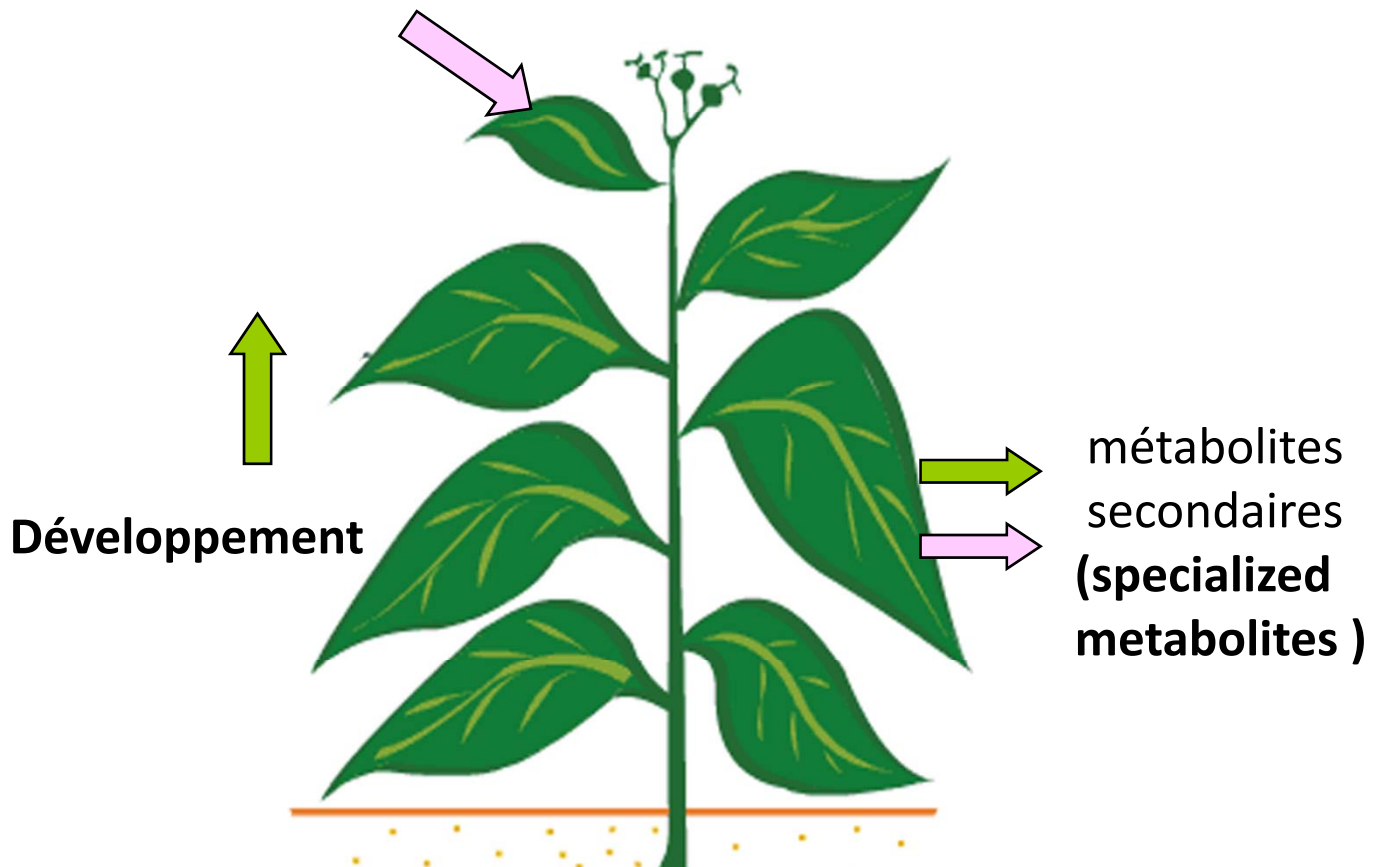
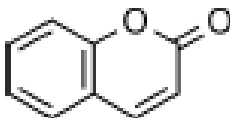
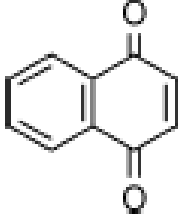
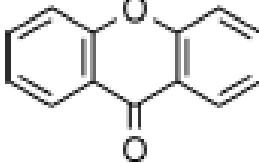
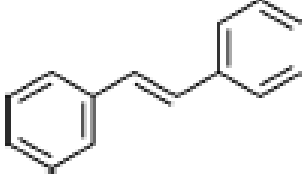
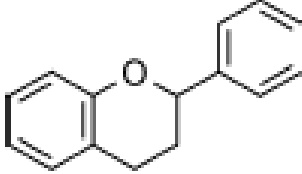


Table 1 Basic structural skeletons of phenolic and polyphenolic compounds.

Skeleton	Classification	Basic structure
C_6-C_1	Phenolic acids	
C_6-C_2	Acetophenones	
C_6-C_2	phenylacetic acid	
C_6-C_3	Hydroxycinnamic acids	
C_6-C_3	Coumarins	
C_6-C_4	Naphthoquinones	
$C_6-C_1-C_6$	Xanthenes	
$C_6-C_2-C_6$	Stilbenes	
$C_6-C_3-C_6$	Flavonoids	

Xie C. *et al* (2011)

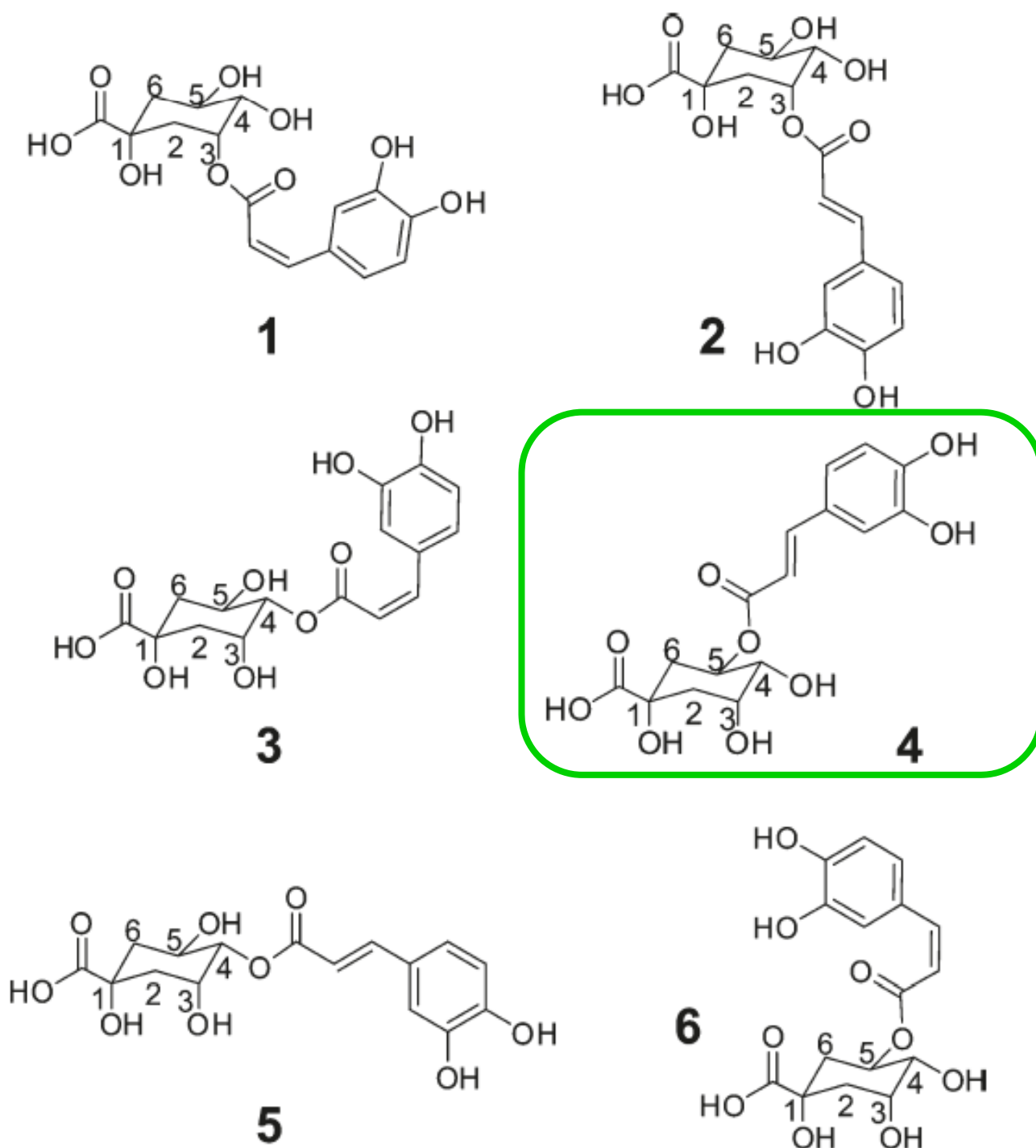
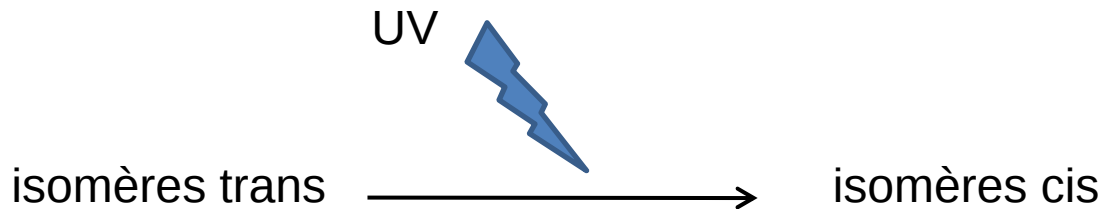


Figure 1. Molecular structures of *trans*-5-caffeoylquinic acid and its transformation products: 1, *cis*-3-caffeoylquinic acid; 2, *trans*-3-caffeoylquinic acid; 3, *cis*-4-caffeoylquinic acid; 4, *trans*-5-caffeoylquinic acid; 5, *trans*-4-caffeoylquinic acid; 6, *cis*-5-caffeoylquinic acid.

Xie C. *et al* (2011)



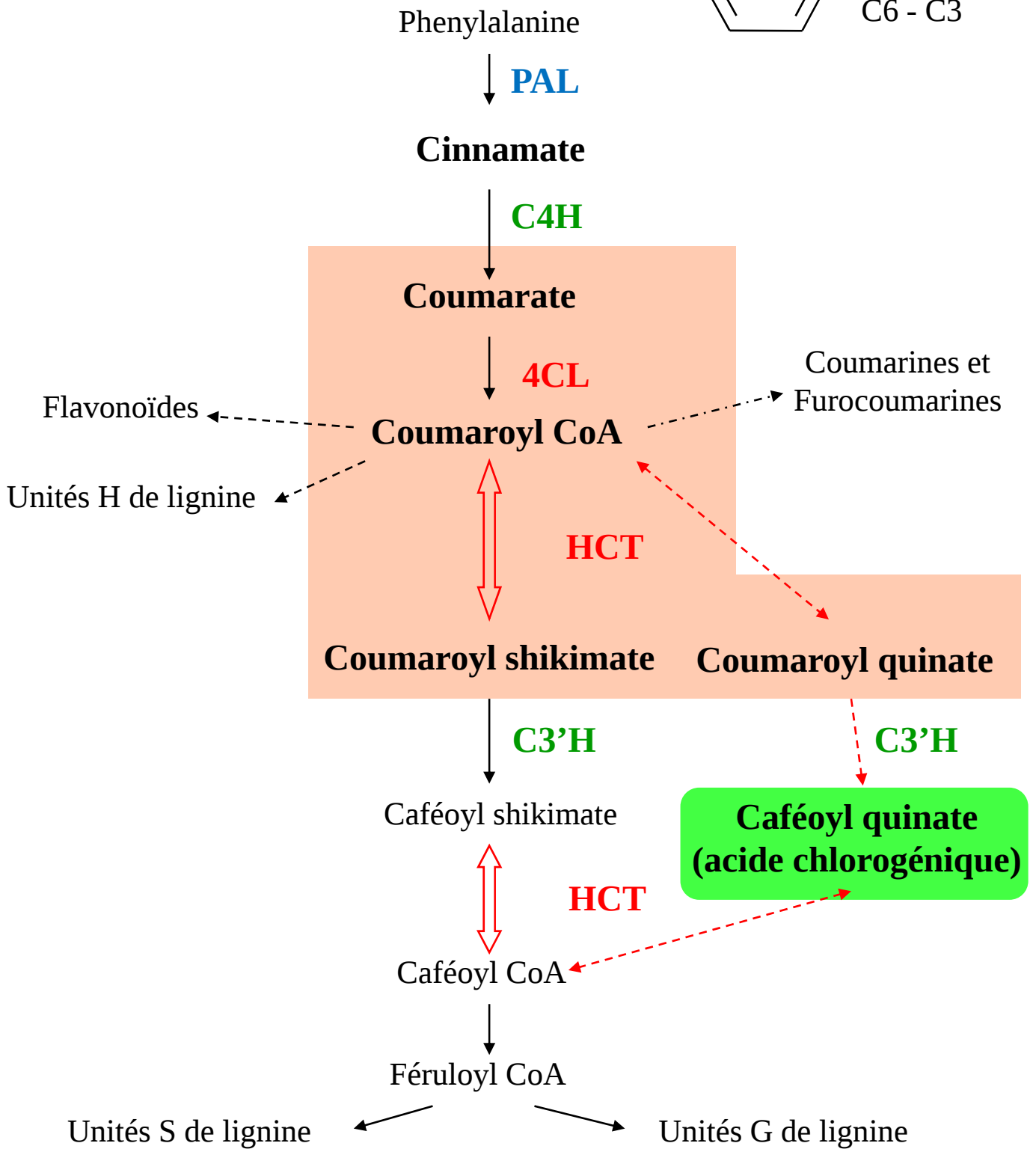
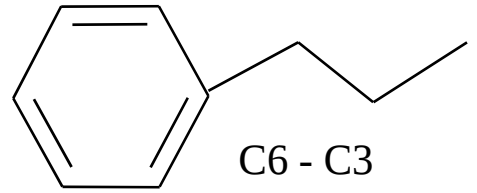
trans-5-Caffeoylquinic acid



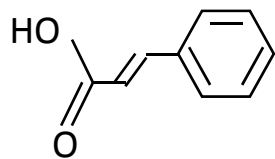
isomérisation
pH et température – dépendante
(ex : 60% conversion en 2h à 37°C
tampon phosphate 0,1M pH 9)

trans-3-Caffeoylquinic Acid
trans-4-Caffeoylquinic Acid.

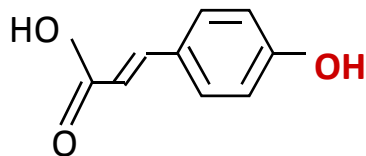
trans-5-Caffeoylquinic acid : stable dans acetonitrile
pur ou methanol : 24 h à 37 C,
1 semaine à 20 C
1 mois à 4 C.



La voie des phénylpropanoïdes

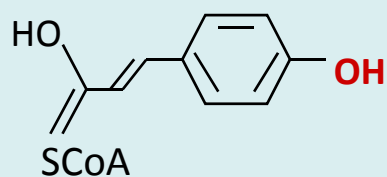


trans-cinnamic acid



p-coumaric acid

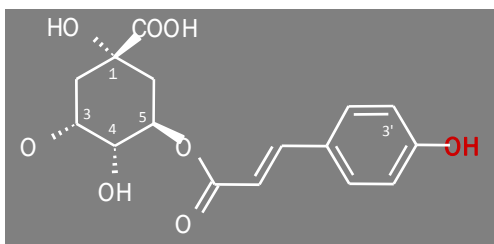
4CL



p-coumaroyl CoA

quinic acid

HCT



p-coumaroylquinic acid

shikimic acid

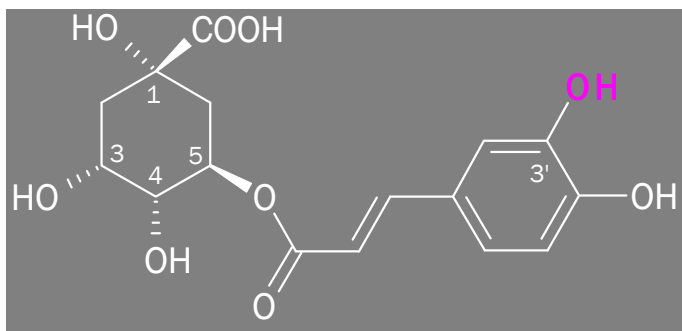
HCT



p-coumaroylshikimic acid

C3'H

+ NADPH + O₂



trans-5-O-caffeoyl-D-quinic acid



Caffeoylshikimic acid

acide *trans*-5-O-caféoyl-D-quinique
(5-CQA, acide chlorogénique)

phénol soluble majeur chez les :

- Solanacées (**tomate**, **aubergine**, tabac, pomme de terre)
- Rosacées (**pomme**) *
- Ericacées (**canneberge**, myrtille)
- Rutacées (**café**)

* conférence M. Guyot / stage Amélie au Québec...

...572 000 résultats dans Google
1870 articles référencés dans PubMed
(mot-clé : chlorogenic acid)
de 1947 à oct 2011 (182 en 2011)

Mono-hydroxycinnamoyl esters :

acides caféique, *p*-coumarique, et ferulique
conjugués à :

-acide quinique ou shikimique

-acide tartarique (raisin) Singleton V. et al (1986)
Castillo-Munoz N. et al (2009)

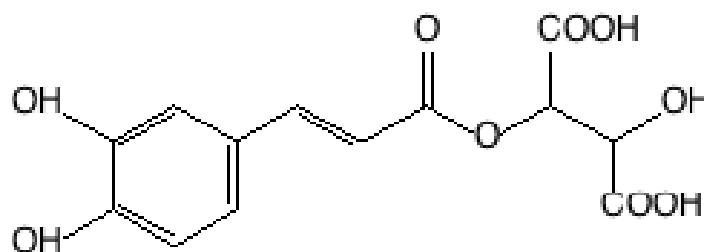
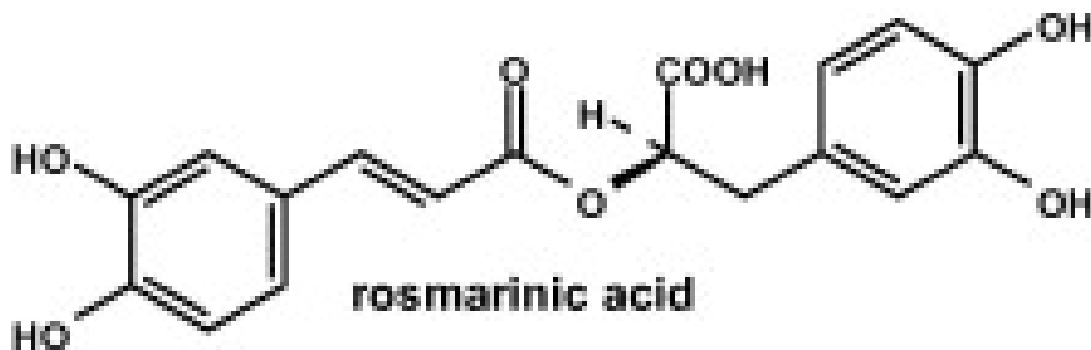


Figure 2. Gallic Acid

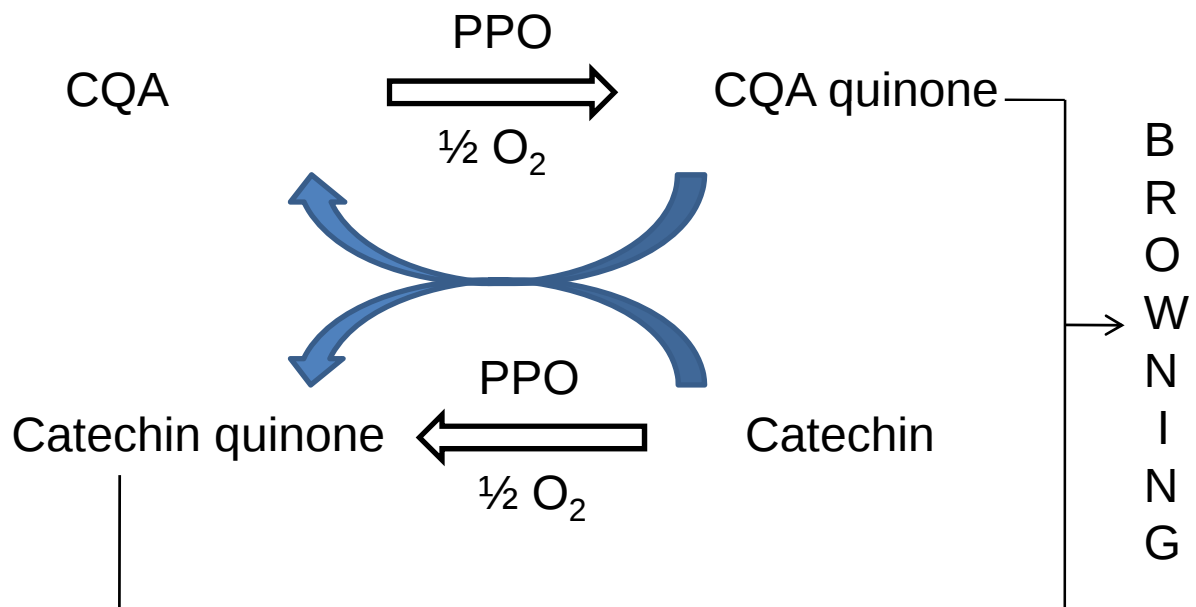
-acide dihydroxyphenyllactique (romarin)

Petersen M. et al (2009)



Coupure, blessure
⇓
Brunissement de fruits et légumes

Amaki K *et al* (2010) : role of chlorogenic acid quinone and interaction of chlorogenic acid quinone and catechins in the enzymatic browning of apple



Dégradation *trans*-5-CQA...

enzymatique (estérases de bactéries et champignons)

Purification and characterization of a chlorogenic acid hydrolase from *Aspergillus niger* catalysing the hydrolysis of chlorogenic acid

Asther M. *et al* (2005)

INRA/Univ Marseille

CQA-hydrolase : dimère / 170 kDa

Coffee pulp from the production co-operative Beneficio de cafe (Mexico)

apple marc from the company Valde-Vire (France) and the Unité INRA de Recherches Cidricole de Rennes

Table 2

Release of caffeic acid from apple marc and autoclaved coffee pulp by enzymatic treatment

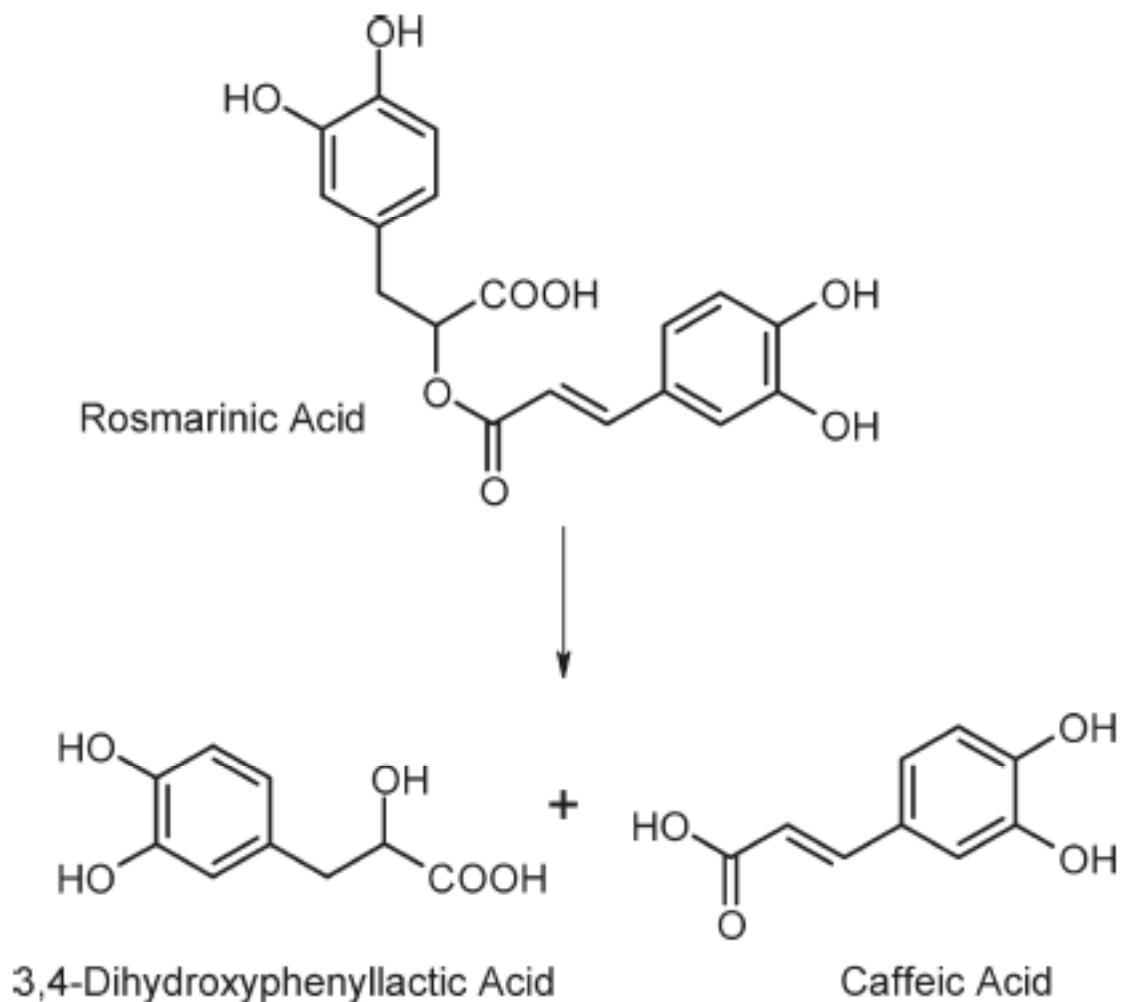
Substrate	Treatment	Chlorogenic acid ($\mu\text{mol g}^{-1}$)	Caffeic acid ($\mu\text{mol g}^{-1}$)
Apple marc	Control	2.2	1.0
	Enzyme	0.3	2.8
Autoclaved coffee pulp	Control	12.0	0.8
	Enzyme	0	21.0

Data are means of triplicate analysis and are expressed as μmoles of compound per gram of starting material dry matter.

...et d'autres esters d'HCA

Hydrolysis of Rosmarinic Acid from Rosemary Extract with Esterases and *Lactobacillus johnsonii* in Vitro and in a Gastrointestinal Model

Bel-Rhlid R. et al (2009)
Nestle Research Centre, Lausanne



Extraction et dosage d'acide
trans-5-O-caféoyl-D-quinique (*trans*-5-CQA)
dans plusieurs variétés d' aubergine
(*Solanum melongena*)

Ghostbuster



Black Magic



displayit-info.com

swallowtailgardenseeds.com

Orient Express



Classic



black beauty



Zebra



greeneearthgrowers.net

PU 10/2011

Bilan extraction d'acides chlorogéniques dans les aubergines

Techniques	Echantillon (quantité)	Appareillage	Solvant	°C	Durée	Rendement
Sonication						
Stirring						
Rotary shaker						
Reflux						
Shaker						
PLE						

Extraction d'acides chlorogéniques dans différentes plantes

	Echantillon (nature, quantité, état...)	Technique	Solvant	Rendement
Aubergine				
Tomate				
Café				
Cidre				
Jus de canneberge				