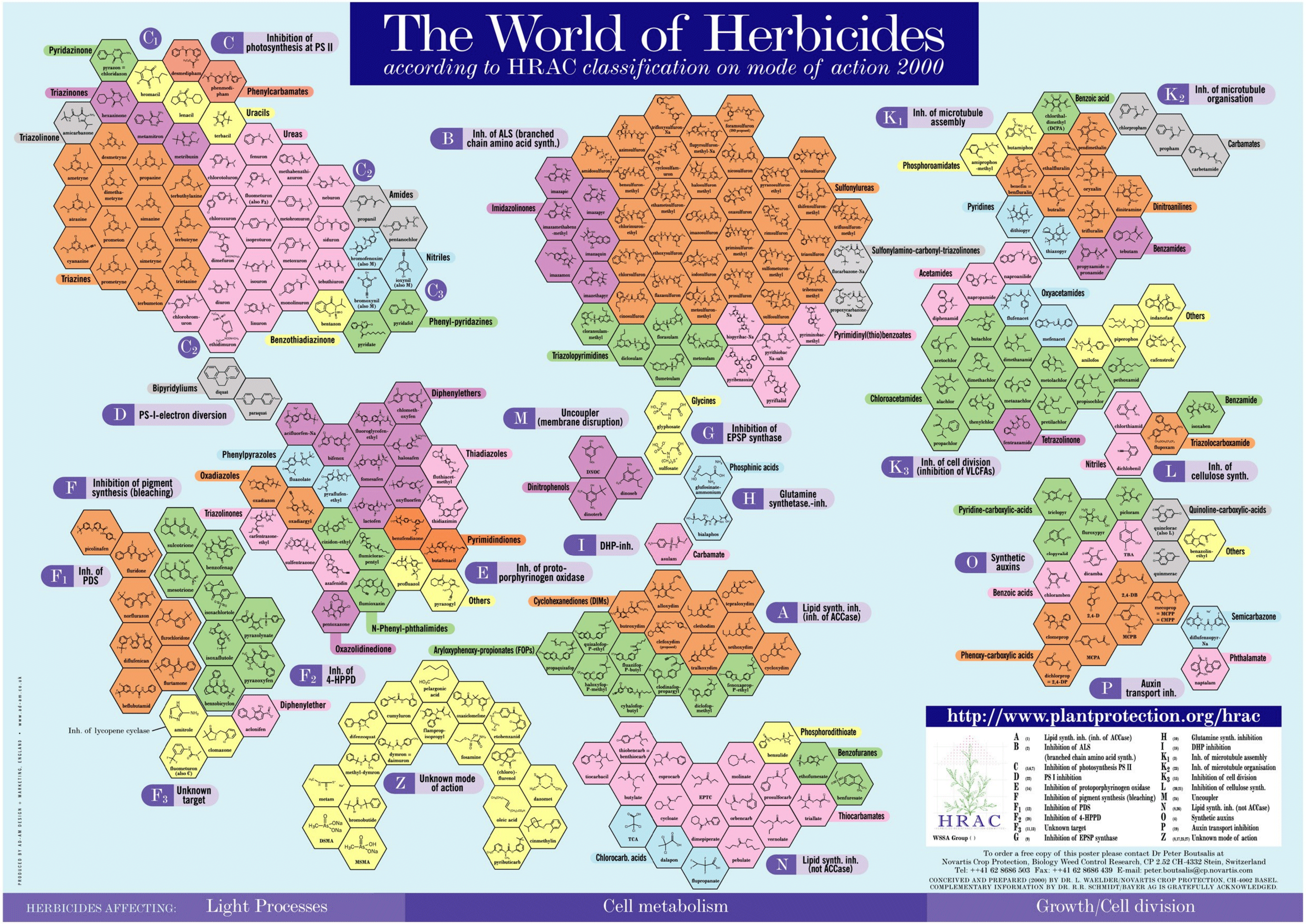
A quoi ça sert ?

Quels risques ?

Comment ça marche ?

Herbicides



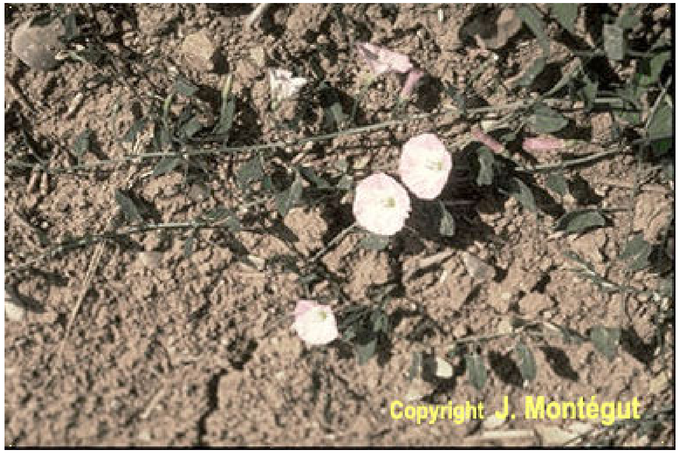
PPP2 – LG – 27.01.11

Herbicides / Malherbologie

« Mauvaises herbes »
= flore adventice

Vulpin des champs
Alopecurus myosuroides

Veronique des champs
Veronica arvensis L.



Liseron des champs
Convolvulus arvensis L.

Folle-avoine d'hiver
Avena sterilis L.ludoviciana

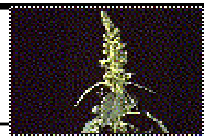
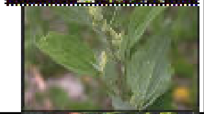
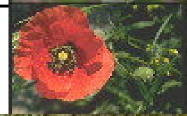
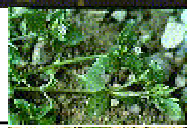
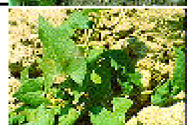
Matricaire inodore
Matricaria perforata

Chiendent rampant
Elytrigia repens (L.)

http://www.inra.fr/Internet/Centres/Dijon/malherbo/phototheque/index.htm

Herbicides / Malherbologie

⇒Création d'un **réseau national de suivi des « mauvaises herbes »**
3000 relevés, 73 départements, 1995-2001
Base de Données ARAF (Atlas de Répartition des Adventices en France)

Amaranthus retroflexus L.	Amarante réfléchie		Maïs, Sorgho
Chenopodium album L.	Chénopode blanc		Maïs, Sorgho, Betterave, Tournesol, Soja
Papaver Rhoeas L.	Coquelicot		Céréales d'hiver, Colza
Galium aparine L.	Gaillet gratteron		Céréales d'hiver, Colza,
Matricaria recutita L.	Matricaire camomille		Céréales d'hiver
Mercurialis annua L.	Mercuriale annuelle		Maïs, Sorgho, Tournesol, Soja
Stellaria media L.	Mouron des oiseaux		Céréales d'hiver, Maïs et Sorgho, Colza
Fallopia convolvulus L.	Renouée des oiseaux Renouée liseron		Céréales d'hiver, Maïs et Sorgho, Tournesol, Soja
Senecio vulgaris L.	Séneçon		Céréales d'hiver, Maïs et Sorgho

http://www.dijon.inra.fr/hyppa/hyppa-f/hyppa_f.htm

***Orobanche ramosa* L.**

plante holoparasite épirhize
⇒ Colza, Chanvre textile, Tabac (Tomates?)

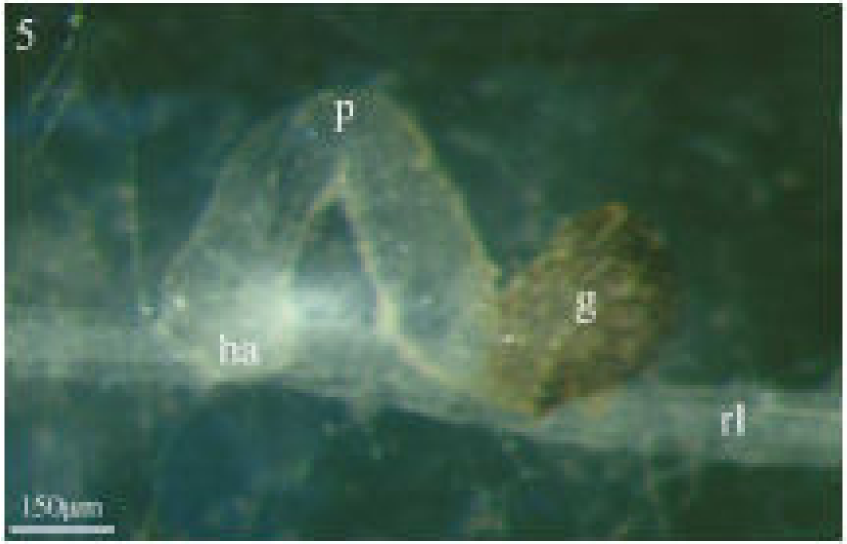
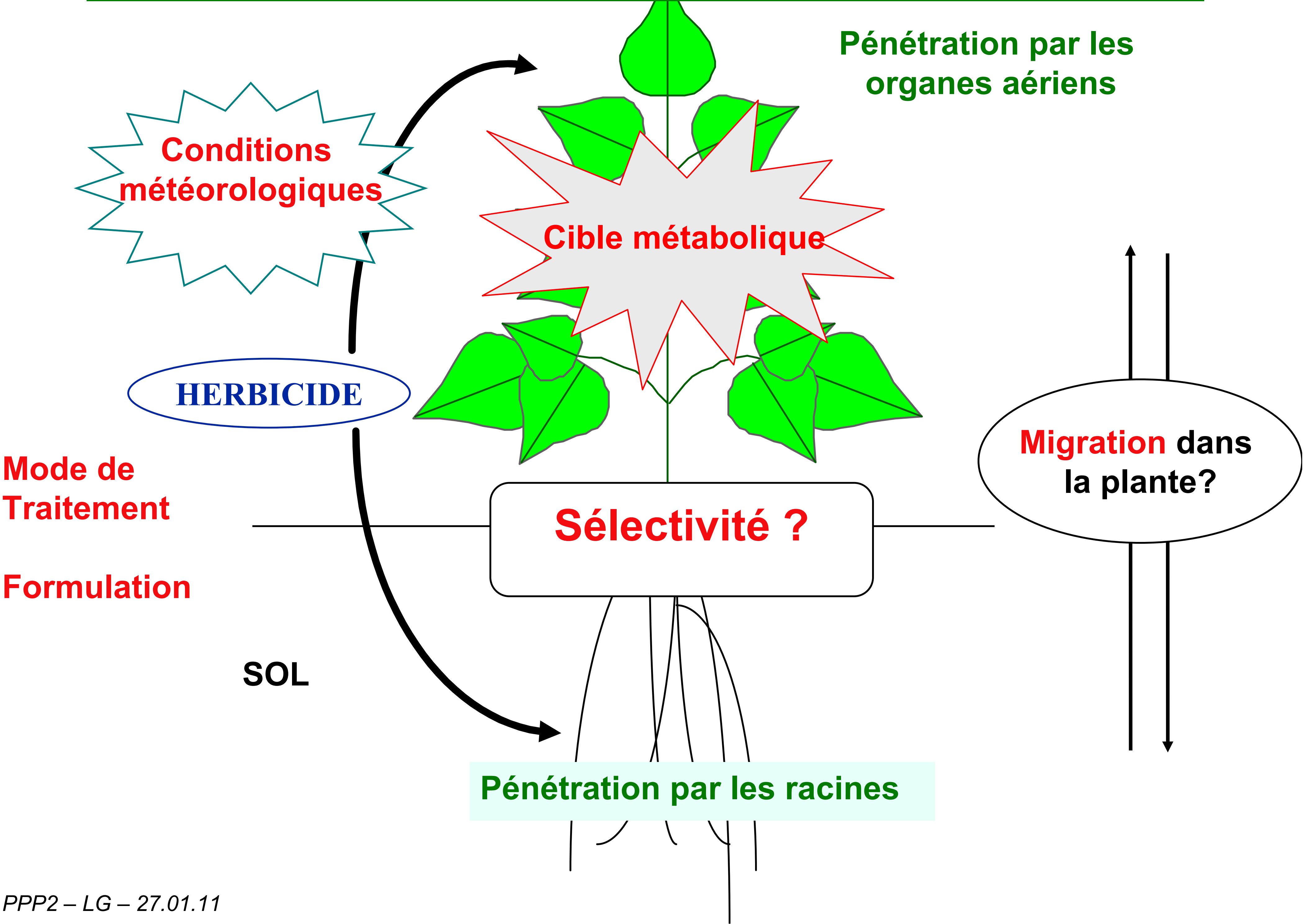


Fig. 5. Co-culture in vitro de colza/*Orobanche ramosa*. Le procaulôme (p) sortant de la graine (g) s'est allongé et son extrémité s'est dirigée vers le système racinaire latéral du colza (rl), au niveau duquel est appliqué l'haustorium (ha). Grossissement : ×67.

Fig. 6. Dans les mêmes conditions de culture, stade plus avancé de l'orobanche : le jeune tubercule (t) s'est développé sur la racine latérale (rl) du colza. (g) Graine de l'orobanche. Grossissement : ×83.

Gibot-Leclerc et al., 2003

Herbicides


Pénétration par les organes aériens
Conditions météorologiques
Cible métabolique
HERBICIDE
Mode de Traitement
Formulation
Sélectivité ?
Migration dans la plante?
SOL
Pénétration par les racines

Herbicides / Phytotoxicité

http://www.psu.missouri.edu/agronx/weeds/herbinjsymptoms/muhrbinj.html

Inhibition d 'une cible métabolique

Les différentes composantes de l'activité d'un herbicide

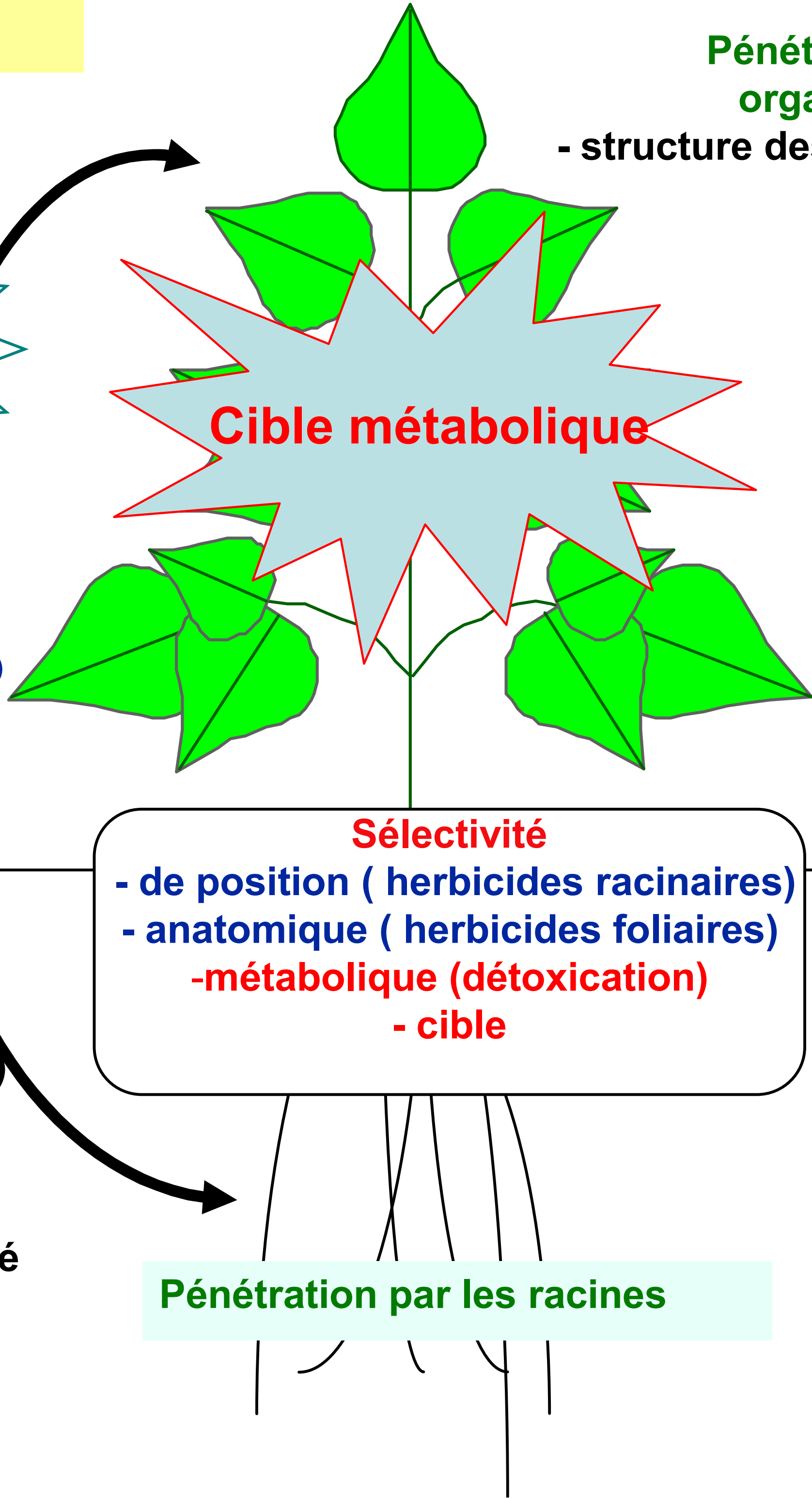
Conditions météorologiques
- température
- vent
- pluie

HERBICIDE

Mode de Traitement (pulvérisation/ taille des gouttes)
Formulation (adjuvants)

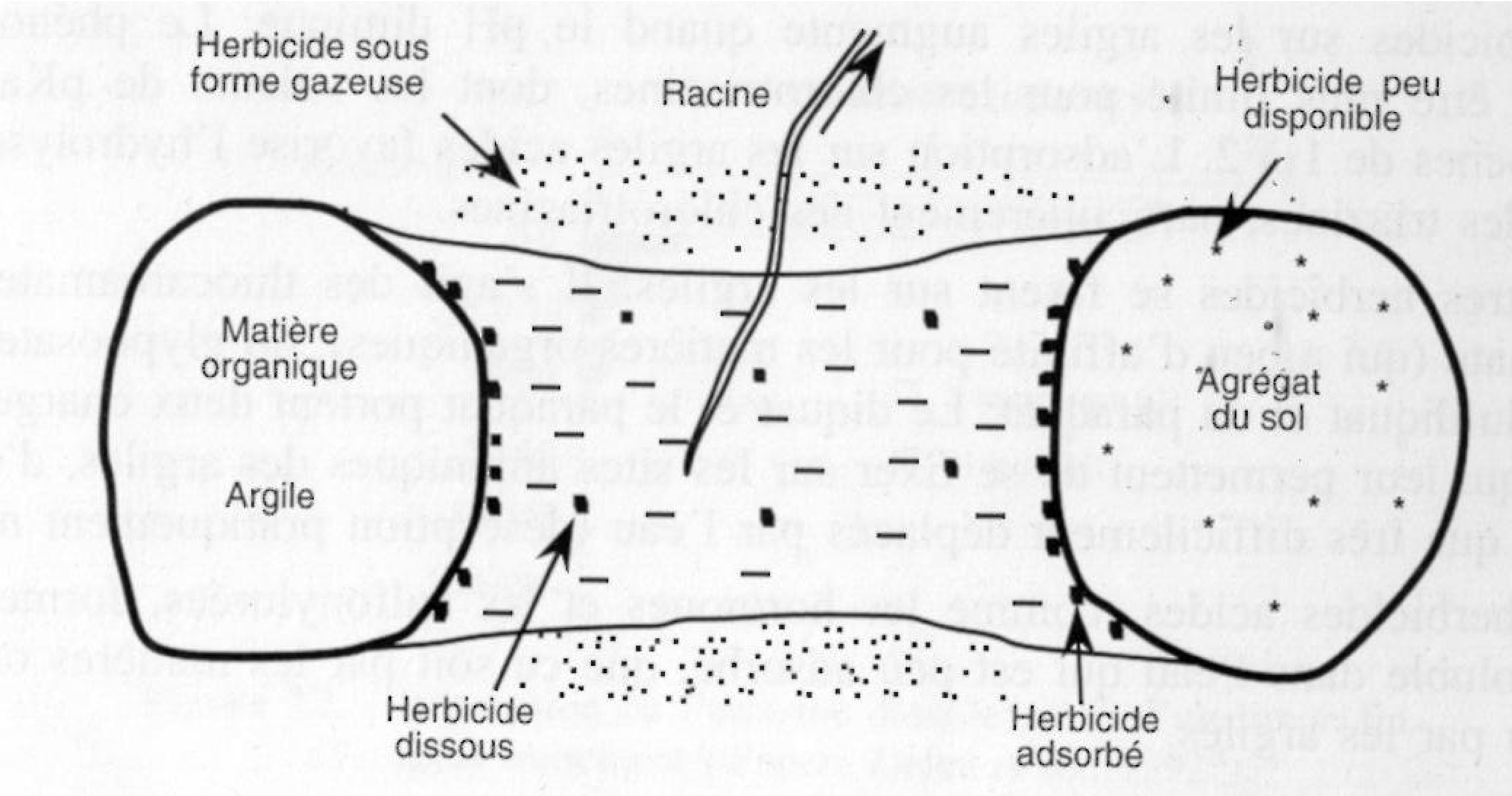
SOL
=> **texture** (sol sableux, ou riche en argile et en matière organique)
-**adsorption, dégradation** microbiologique ou chimique
=>**Persistance**
- **humidité** (effet sur la disponibilité des herbicides et sur la morphologie des plantes)

Pénétration par les organes aériens
- structure des cires épicuticulaires

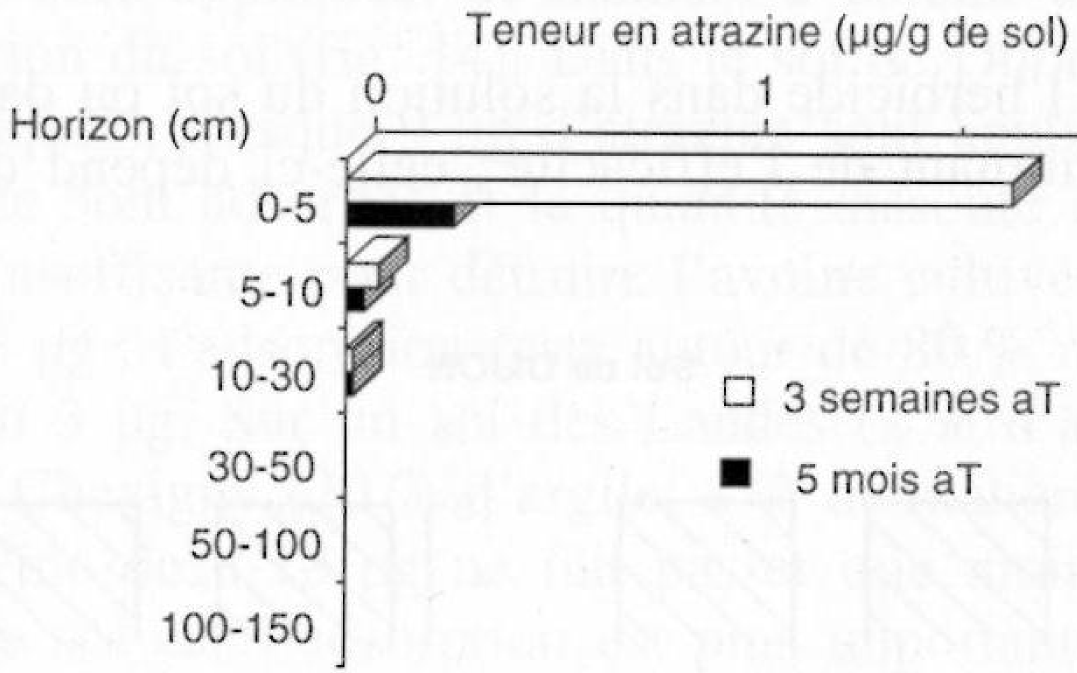


Migration dans la plante?
Systémique/
de contact

Les différentes formes d'un herbicide dans le sol / Notion de **biodisponibilité**



↳Répartition de l'herbicide dans le sol : localisation superficielle (0-5 cm)

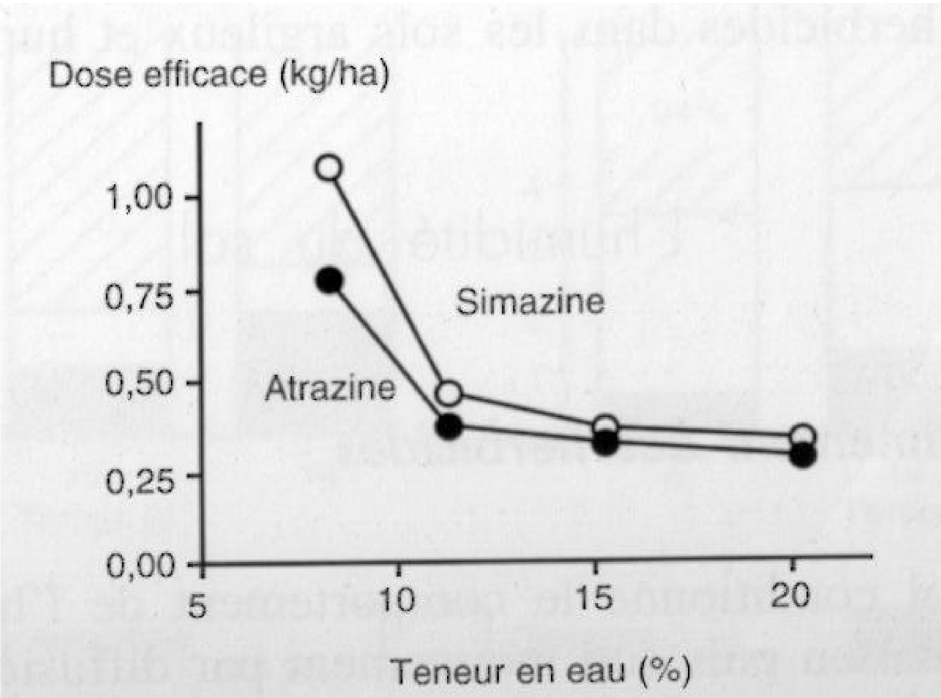


– Répartition de l'atrazine dans le profil d'un limon fin. aT : après traitement (d'après Deleu *et al.*, 1992[a]).

Relations Sol /Herbicides racinaires

-Importance de la **texture du sol** : efficacité herbicide réduite dans sols riches en argile et en matières organiques

- Importance du **taux d'humidité**



Efficacité herbicide meilleure en sol humide

Effet sur la morphologie des plantes

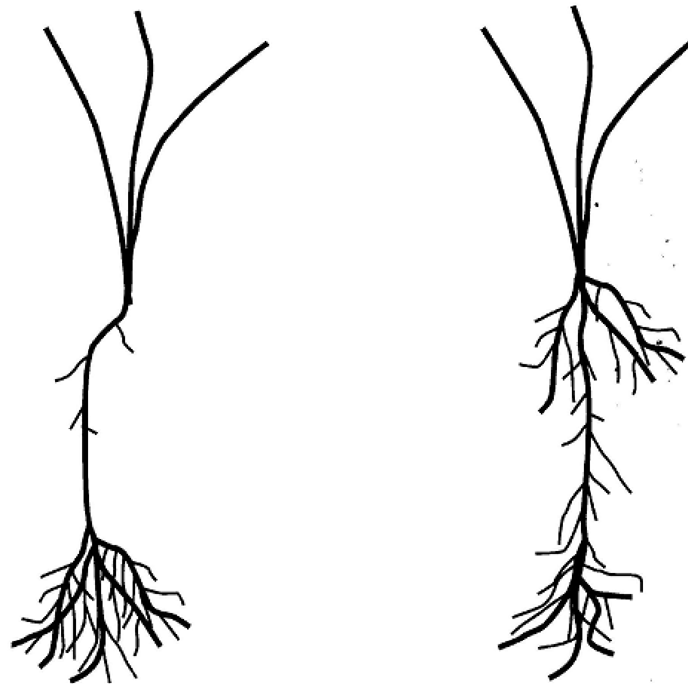
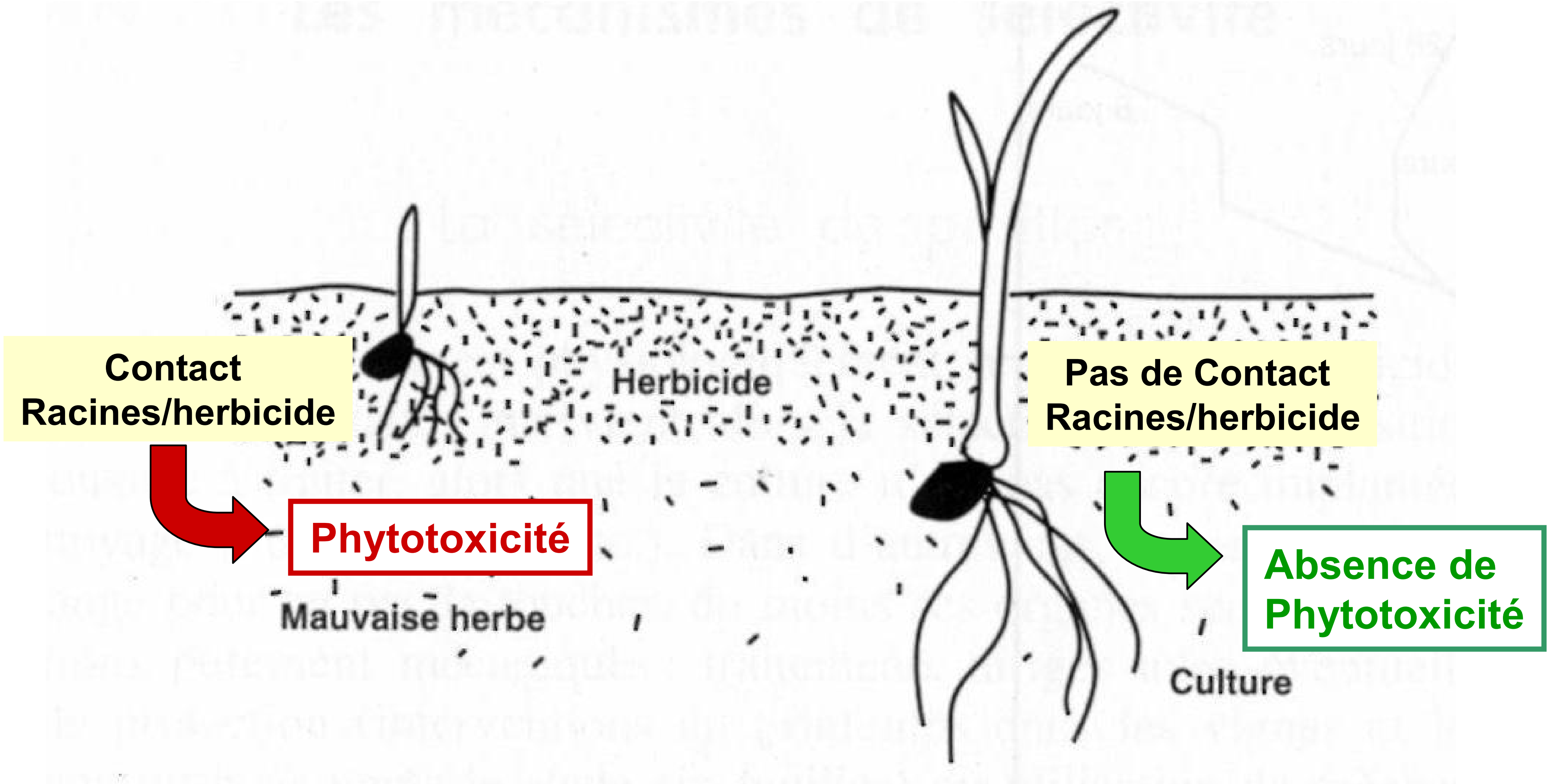


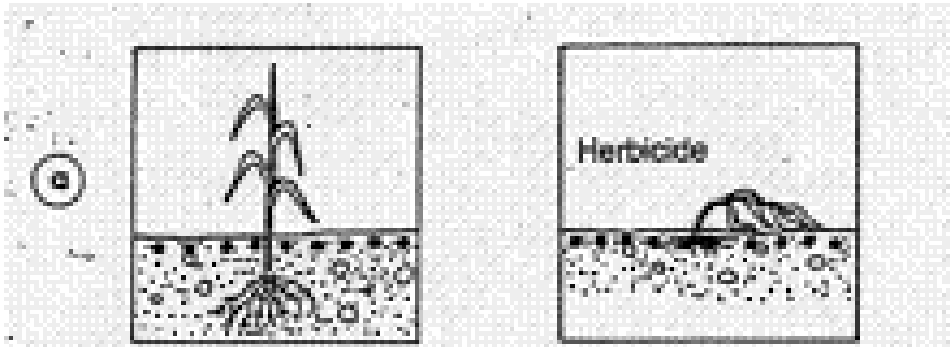
Figure 16. – Morphologie du système racinaire du vulpin en fonction de la teneur en sol. A, 50 % de la CRC ; B, 4 jours après le retour à 100 % de la CRC (d'après Blair, 1

-Sélectivité de position (herbicides racinaires) : **due au positionnement relatif des racines de la plante de culture et de la plante adventice dans le sol, qui seront en contact ou non avec l'herbicide**



-Paramètres qui affectent l'action d'un herbicide racinaire

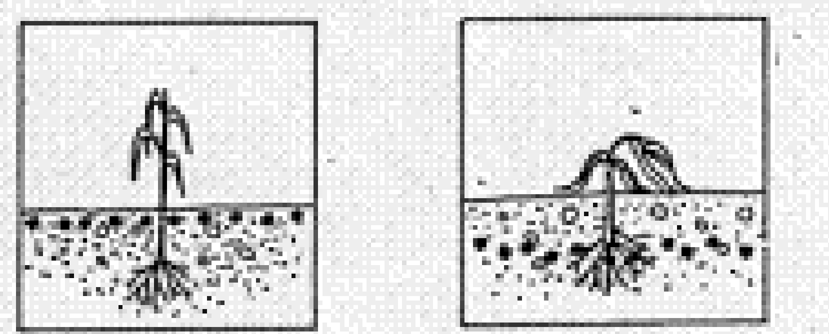
↳ **qualité du sol**



Sol normal

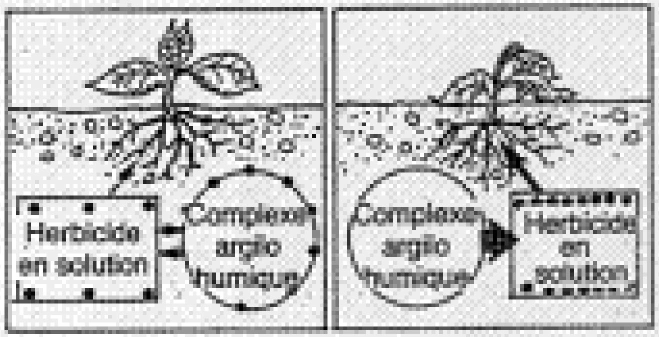
Sol asphyxié : l'enracinement de la culture est superficiel

↳ **pluviométrie**



Pluviométrie normale

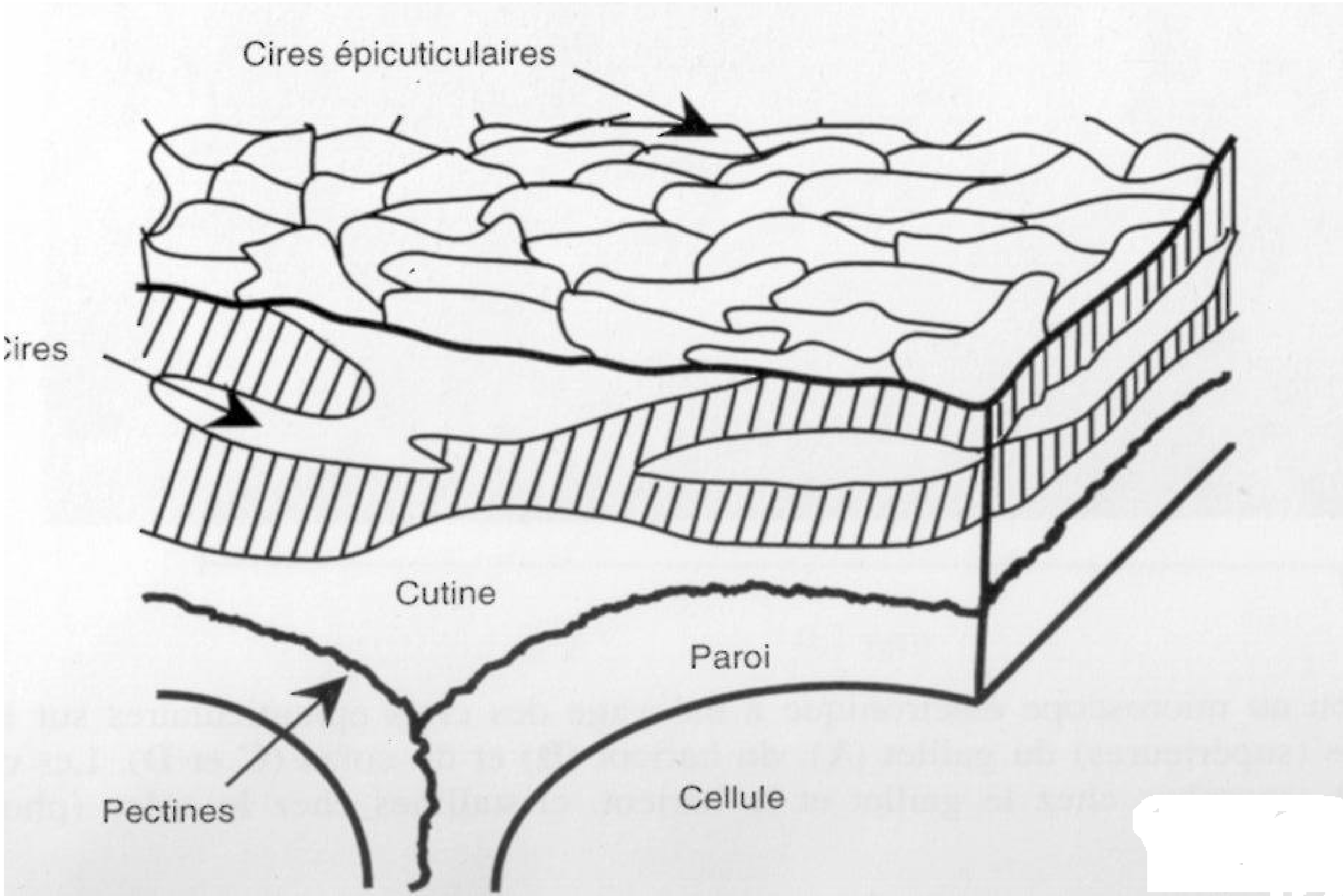
Migration de l'herbicide par excès d'eau



Fonctionnement normal

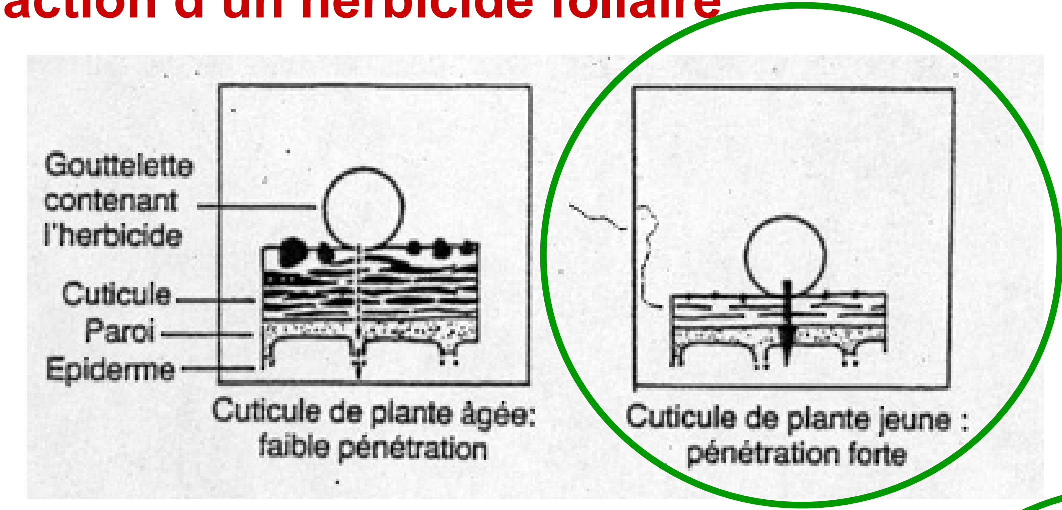
Relargage de l'herbicide par le complexe argilo-humique dû à un excès d'eau

-Sélectivité anatomique (herbicides foliaires) : existence à la surface des feuilles d'une structure hydrophobe plus ou moins épaisse : la cuticule

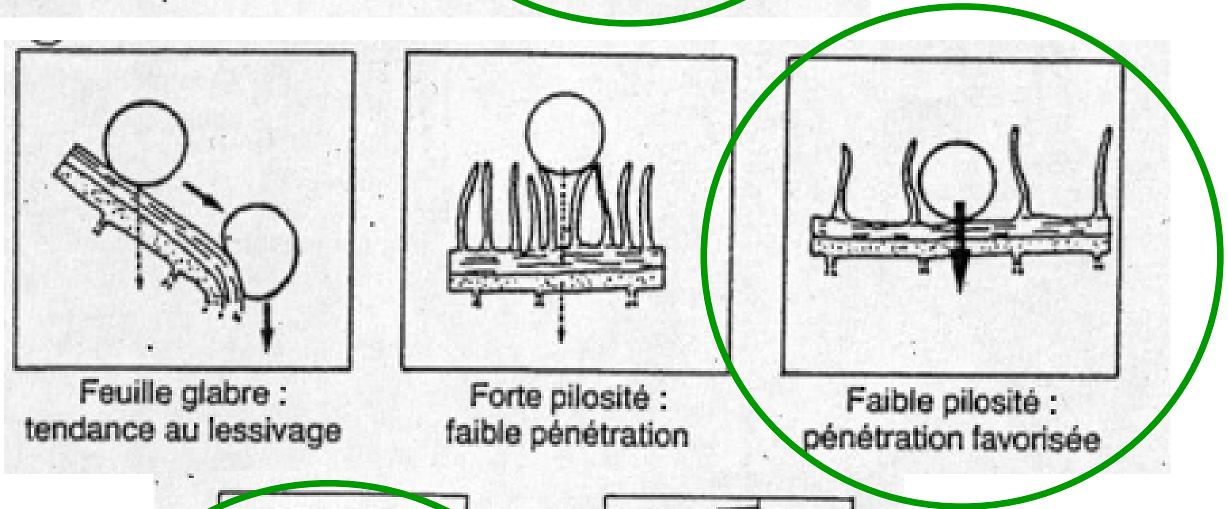


-Paramètres qui affectent l'action d'un herbicide foliaire

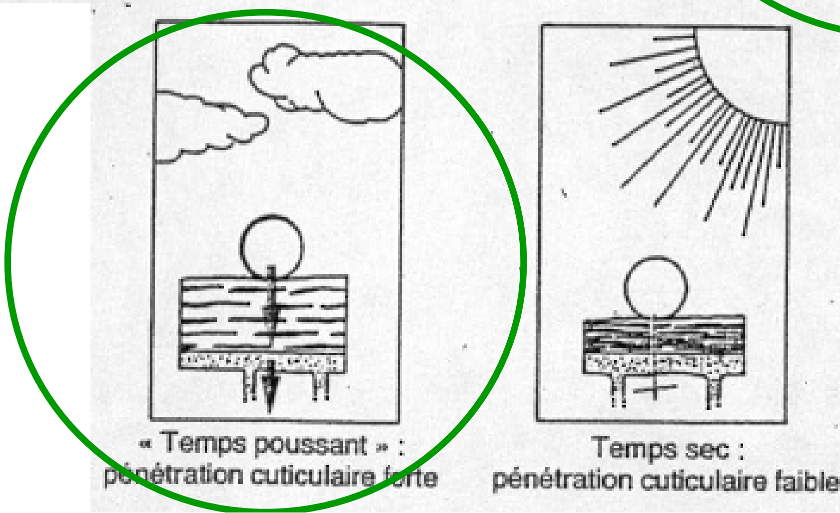
↳importance de **l'âge de la plante**



↳importance de la **pilosité de la feuille**



↳importance des **conditions météo**



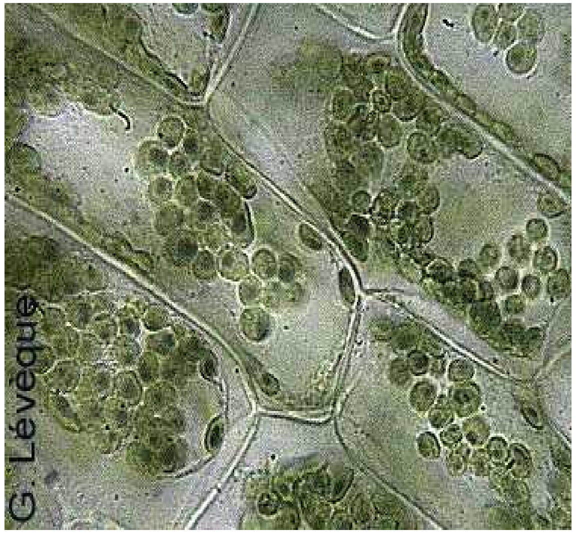
Herbicide Resistance Action Committee
Classification of herbicides

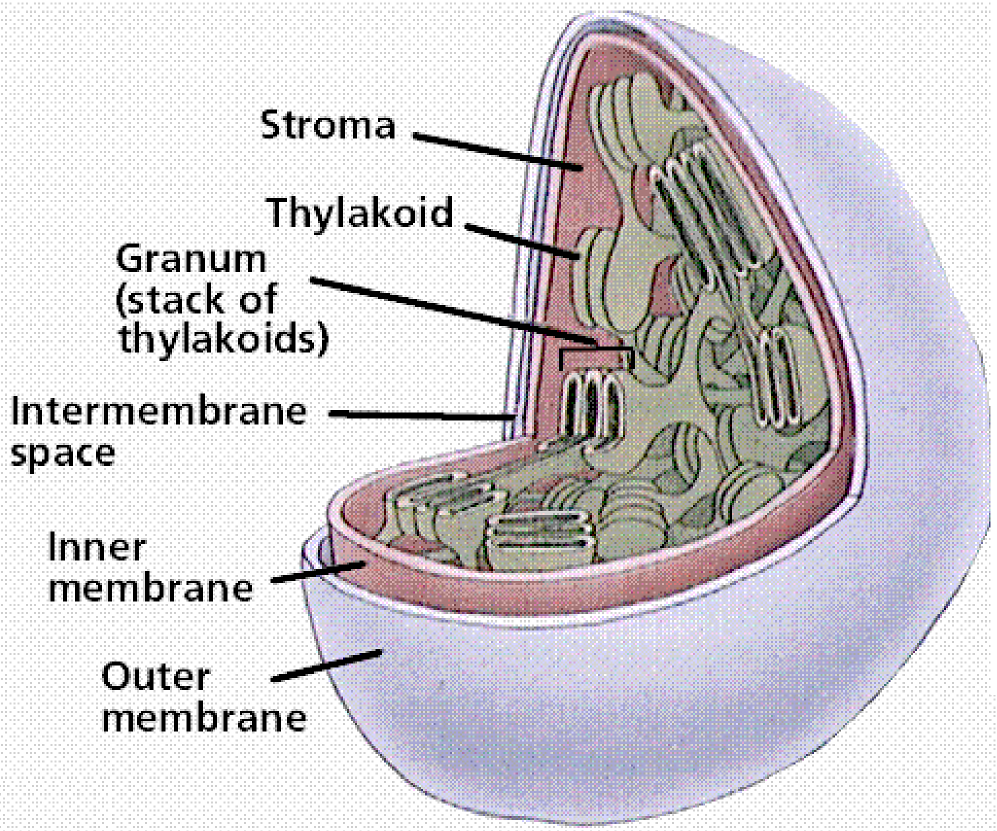
(Cf Autre système de classification **WSSA** "Weed Science Society of America »)

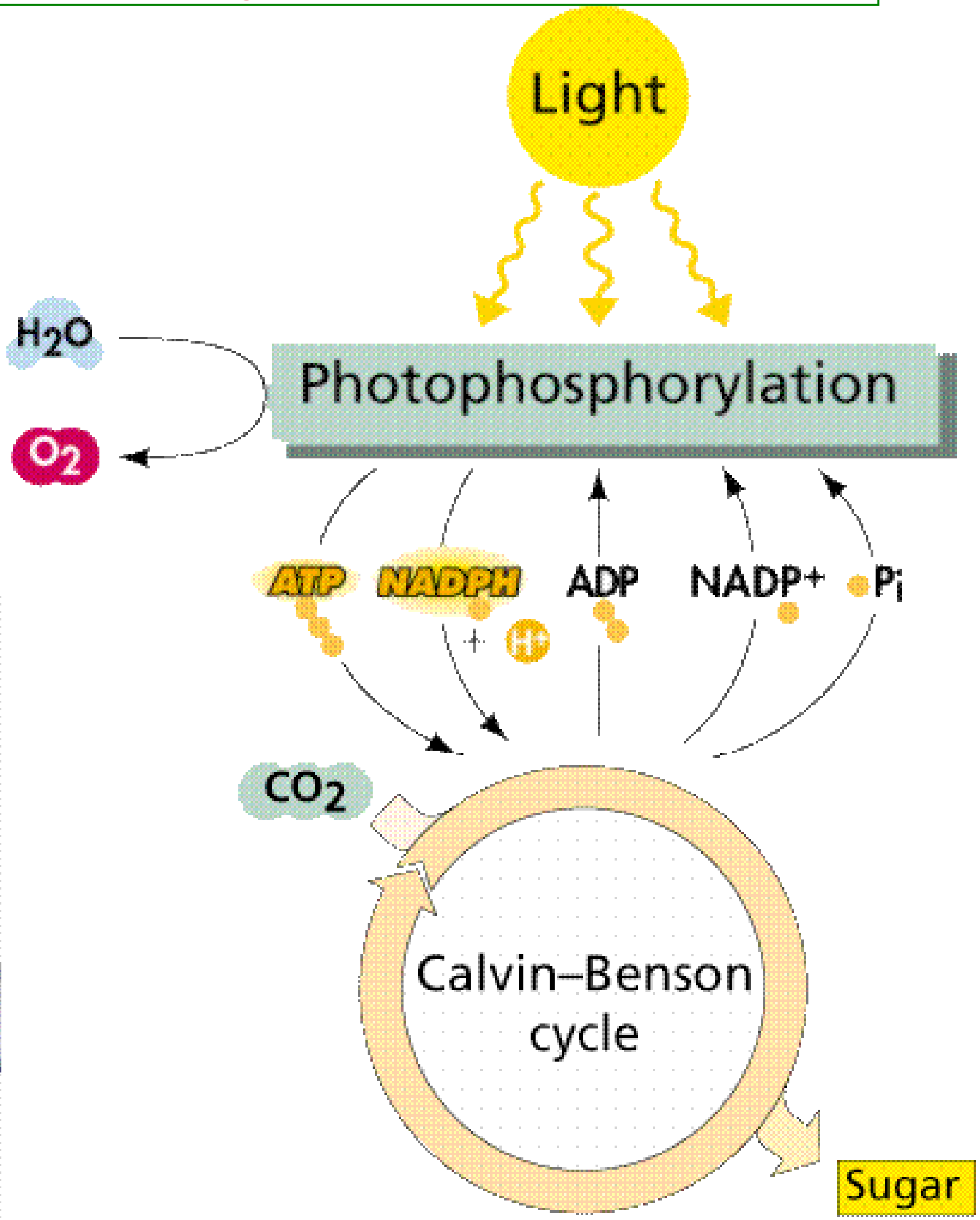
http://www.plantprotection.org/HRAC/ **http://www.wssa.net/**

A (1) / Inhibition **ACCase**	**H (10)** / Inhibition **Glutamine Synthase**
B (2) / Inhibition **ALS** (AHAS)	**I (18)** / inhibition of **Dihydroptéorate (DHP) synthase**
C1 (5), C2 (7), C3 (6) / inhibition **PSII (prot. D1)**	**K1 (3), K2 (23),K3 (15)** / inhibition **divisions cellulaires** (microtubules, VLCFA)
D (22) / capture électrons **PSI**	**L (20, 21,26)** / inhibition synthèse **paroi cellulaire** (cellulose)
E (14) / inhibition **Protox**	**M (24)** / agents découplants (disruption membranaire)
F1 (12) / inhibition **Phytoène désaturase** (PDS)	**N (8, 26)** / inhibition synthèse lipides (sauf ACCase)
F2 (27) / inhibition **HPPD**	**O (4)** / herbicides auxiniques **P (19)** / inhibition transport auxine
G (9) / inhibition **EPSP Synthase**	**R,S,Z (17, 25 à 27)** / mode d'action inconnu

Herbicides / Photosynthèse

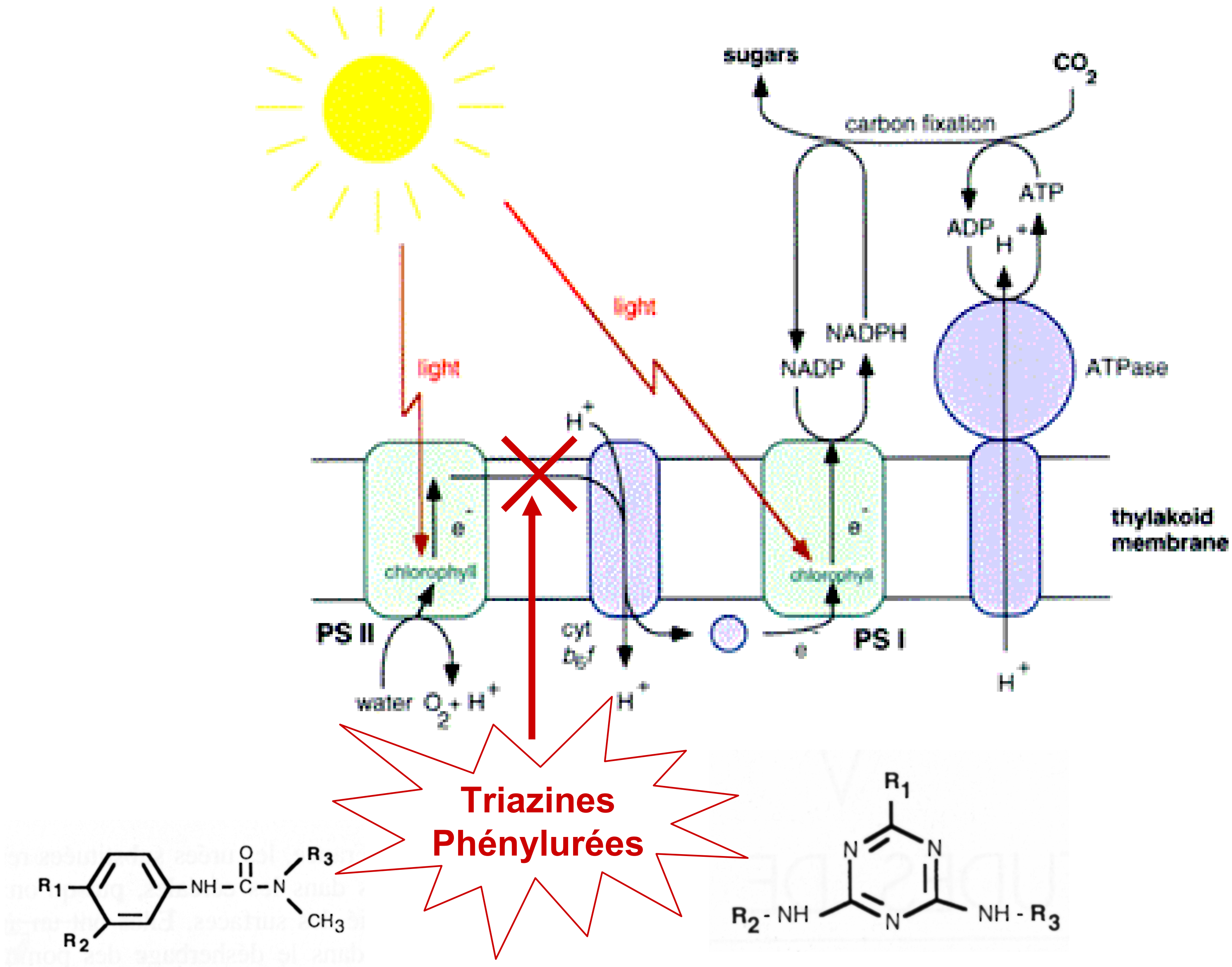


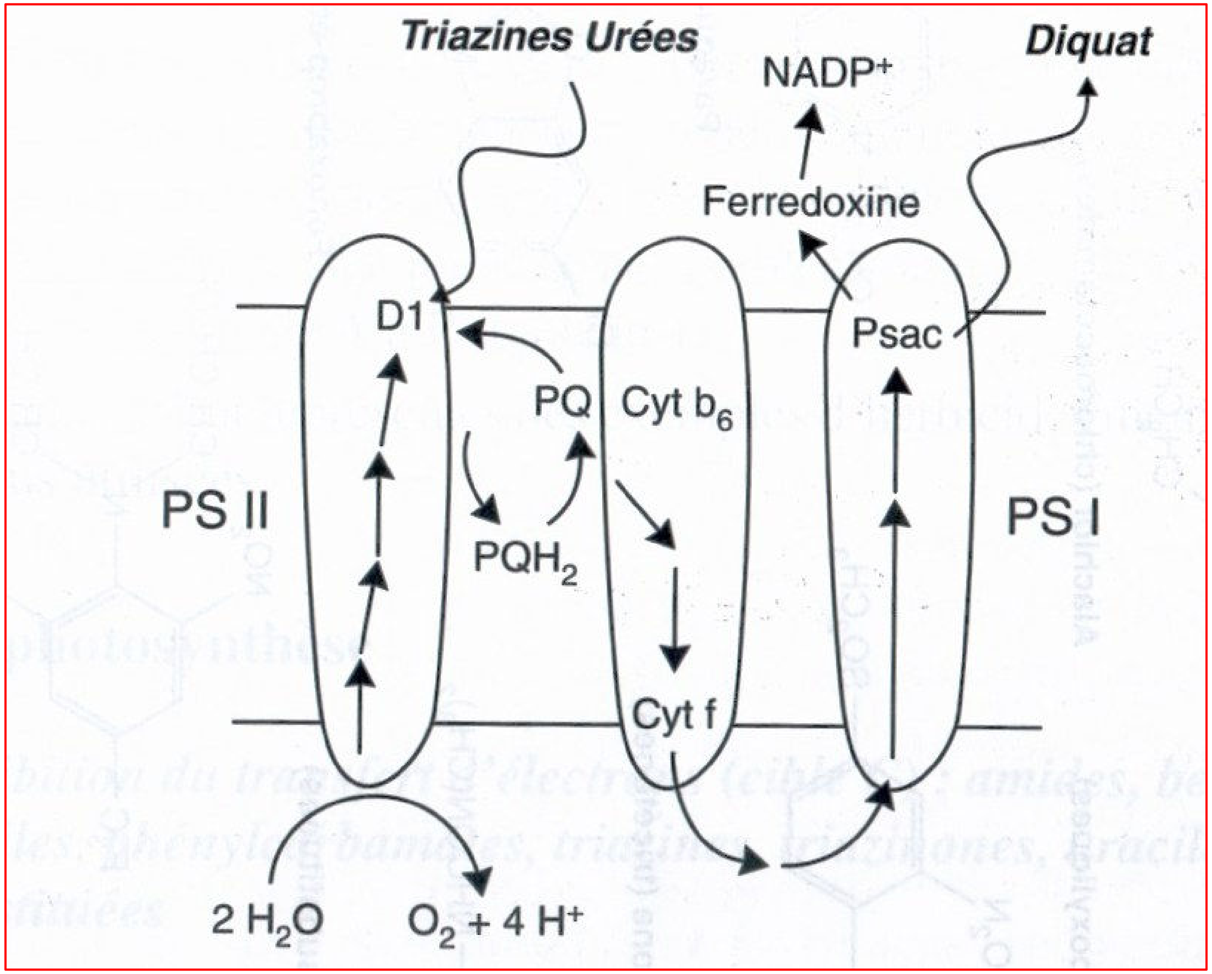




Herbicides / Photosynthèse

n/photointro.html



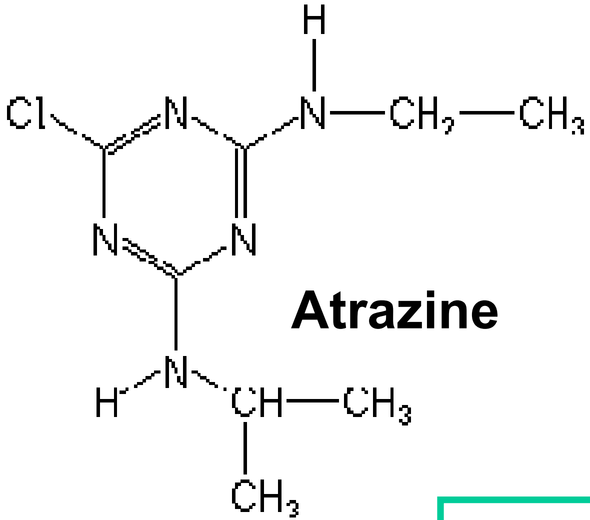


C. Regnault-Roger (2005)

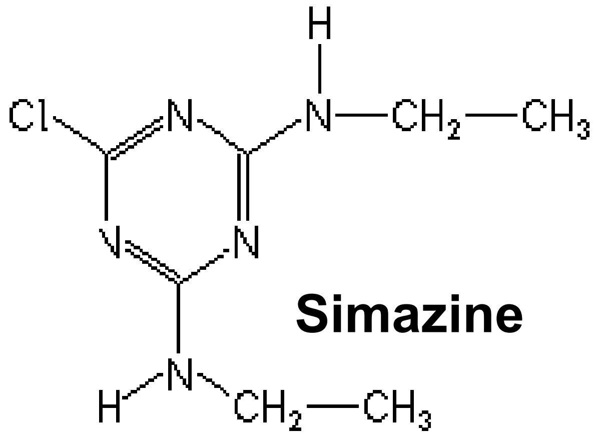
Enjeux phytosanitaires pour l’agriculture et l’environnement

Eds Tec & Doc, ISBN 2-7430-0735-0

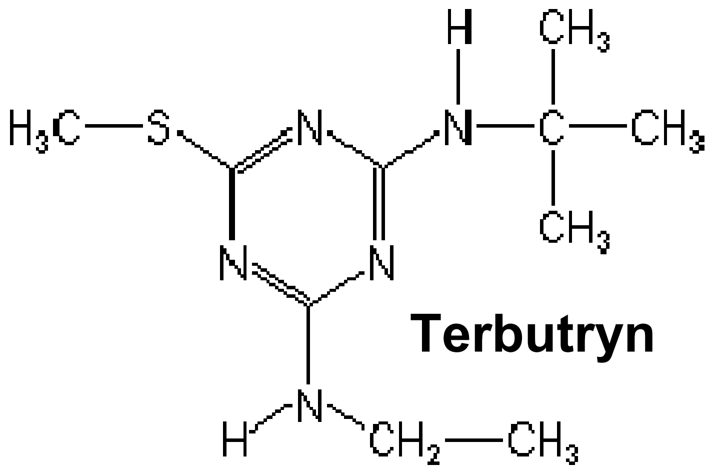
Herbicides / Photosynthèse



Atrazine

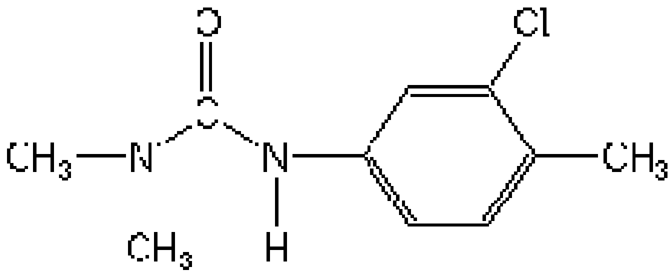


Simazine

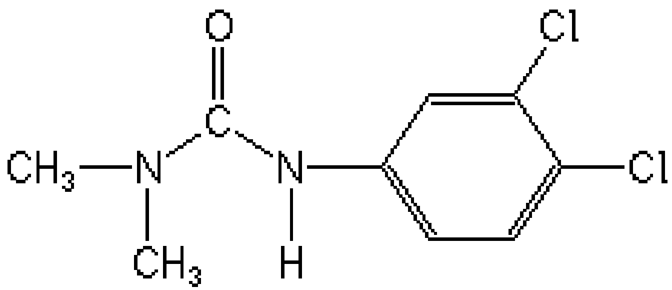


Terbutryn

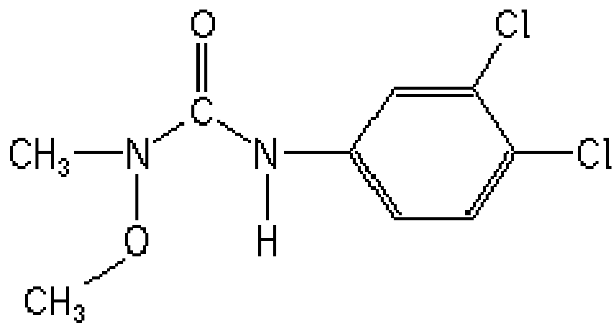
Herbicides inhibiteurs PSII :
Triazines et urées substituées



Chlortoluron



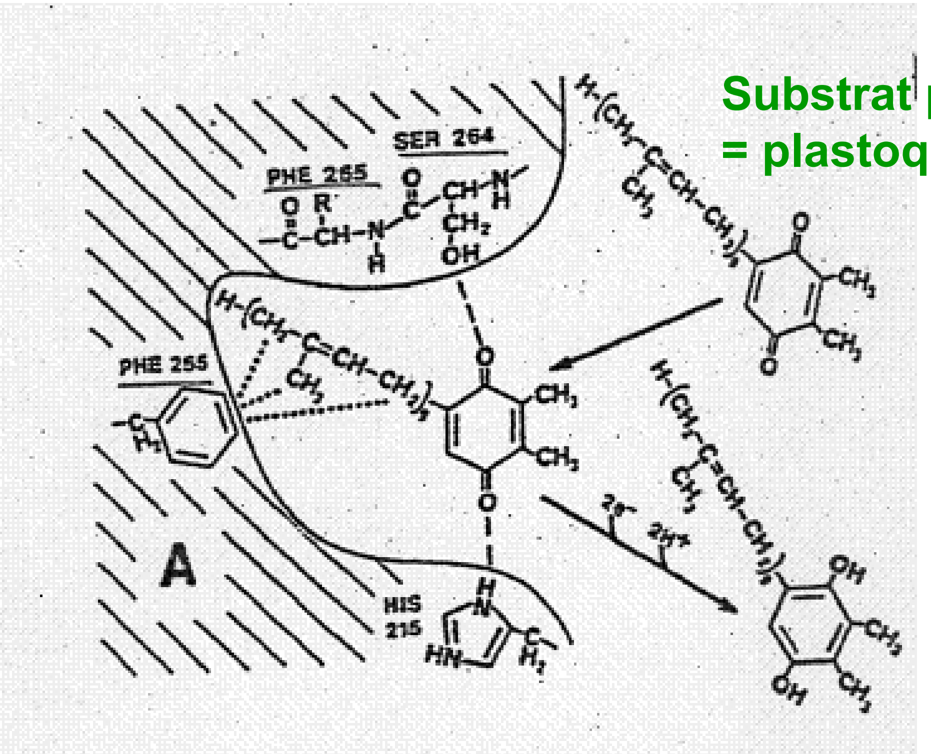
Diuron (DCMU)



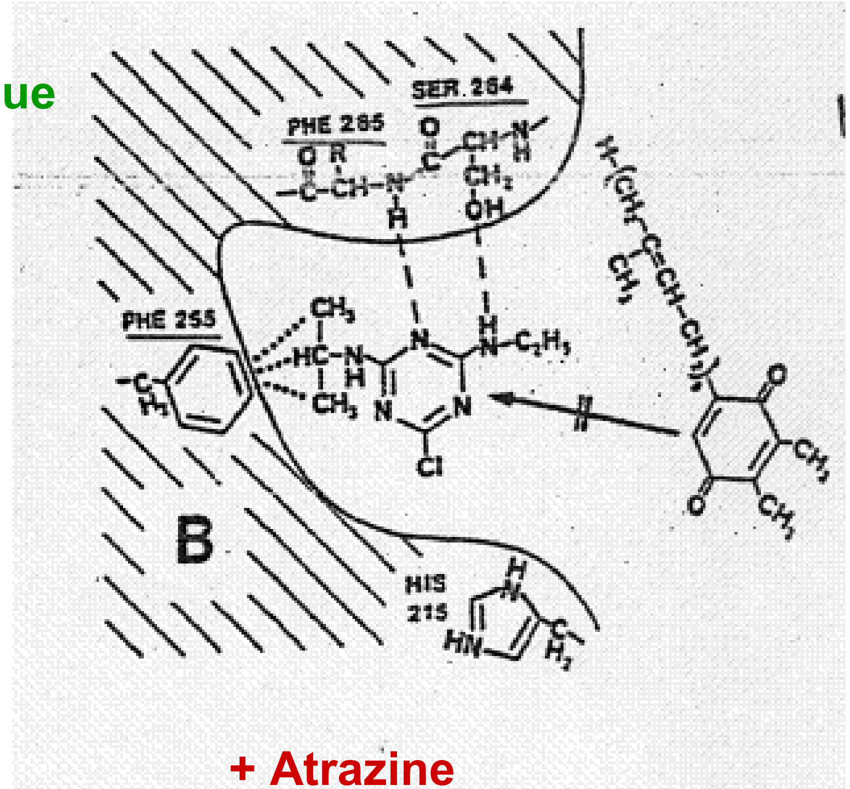
Linuron

Herbicides / Photosynthèse

Cible Atrazine = protéine D1, 32kD (thylakoïdes)

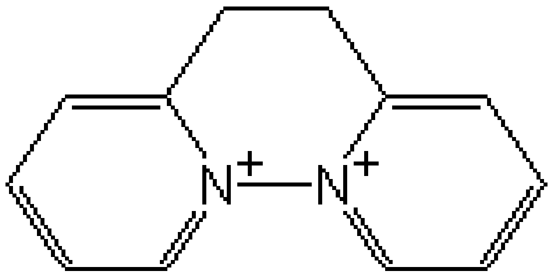


Substrat physiologique
= plastoquinone

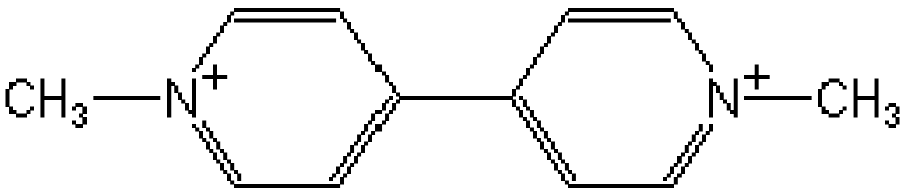


+ Atrazine
=> Inhibition compétitive

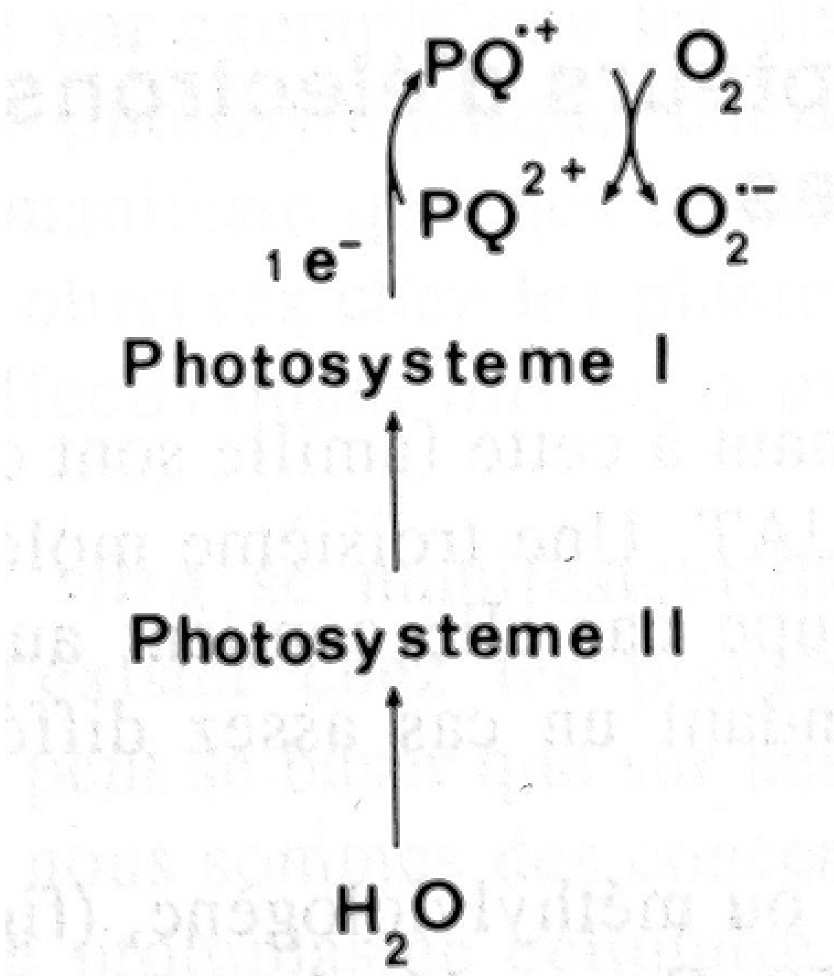
Herbicides accepteurs d'électrons photosynthétiques : bipyridyles



Diquat



Paraquat



Etude de cas : Atrazine / Gronwald *et al.*, 1989

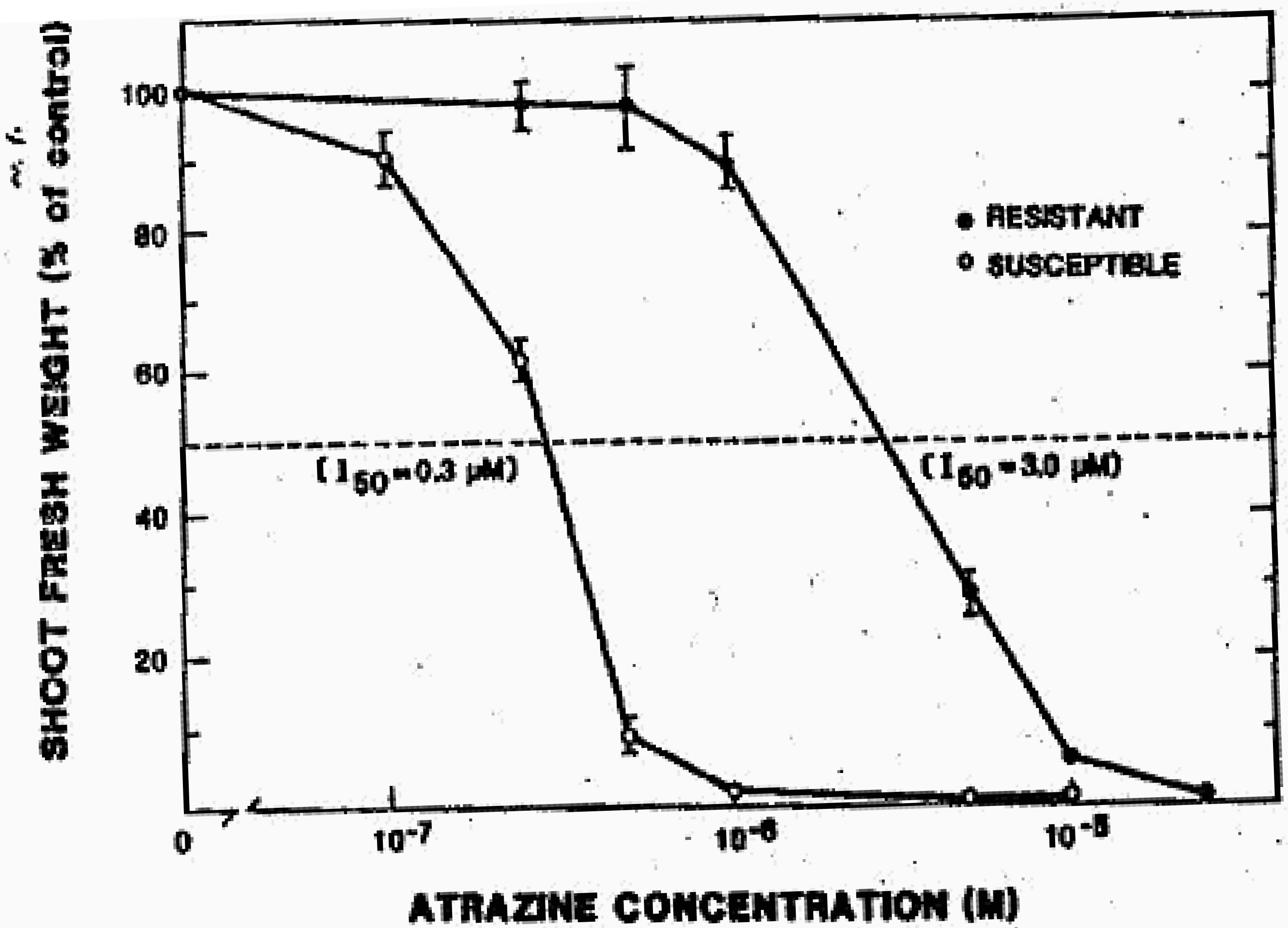


FIG. 1. *Growth response of shoot tissue of susceptible and resistant A. theophrasti biotypes grown in the presence of atrazine. I_{50} values (in parentheses) represent the atrazine concentration required to reduce shoot fresh weight by 50%. Values represent the mean ± SE (n = 16). SE provided when larger than data point. Shoot fresh weights of the untreated resistant and susceptible biotypes at the termination of the experiment where 13.2 ± 0.6 (SE) and 20.0 ± 1.3 g, respectively.*

Résistance Atrazine / Gronwald *et al.*, 1989

croissance

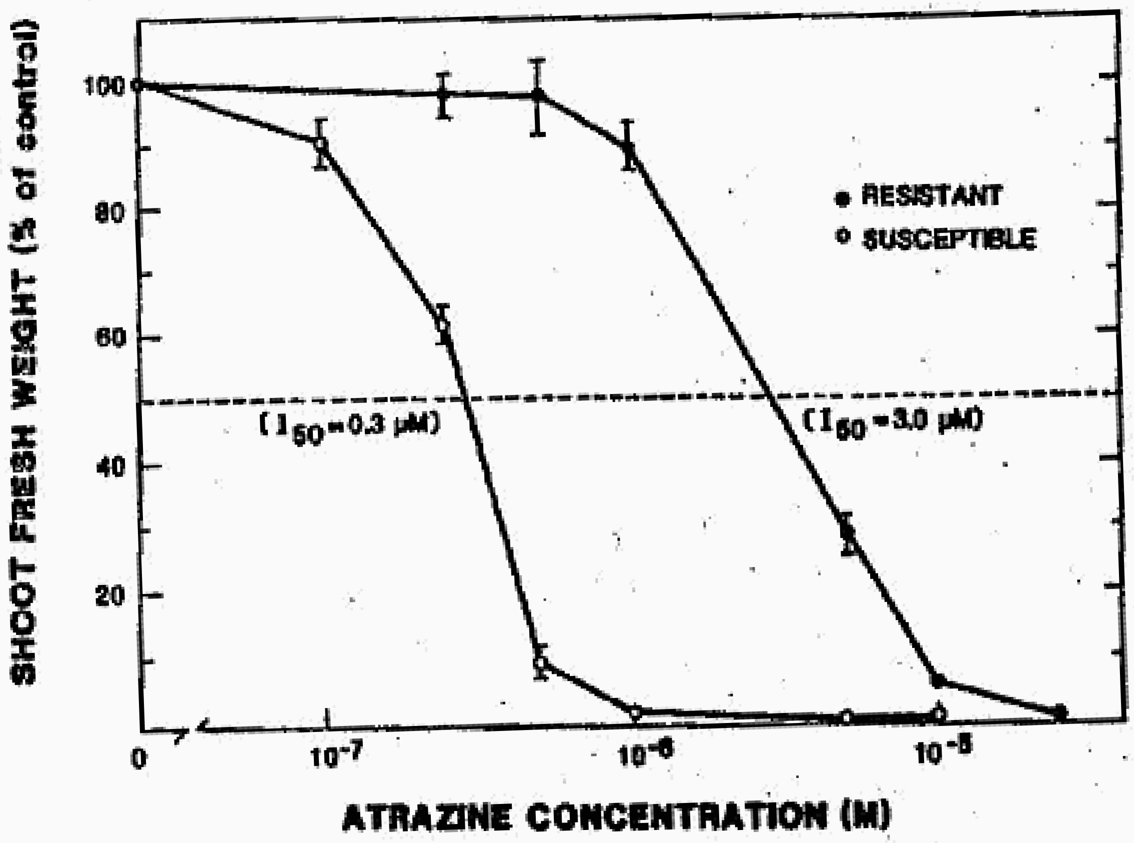
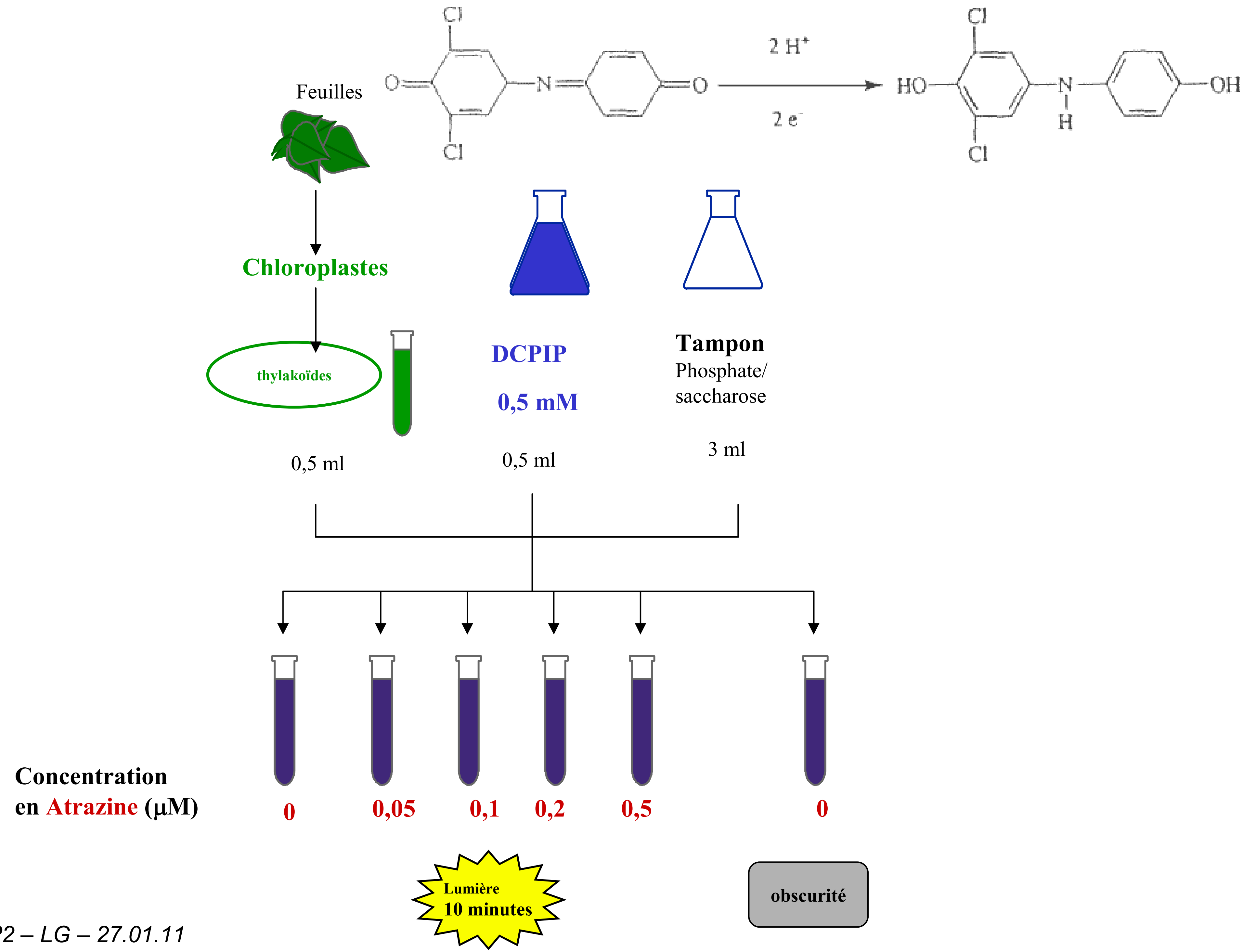


FIG. 1. *Growth response of shoot tissue of susceptible and resistant A. theophrasti biotypes grown in the presence of atrazine. I_{50} values (in parentheses) represent the atrazine concentration required to reduce shoot fresh weight by 50%. Values represent the mean ± SE (n = 16). SE provided when larger than data point. Shoot fresh weights of the untreated resistant and susceptible biotypes at the termination of the experiment where 13.2 ± 0.6 (SE) and 20.0 ± 1.3 g, respectively.*

I_{50} S= 0,3 µM
I_{50} R = 3 µM

FT = 10

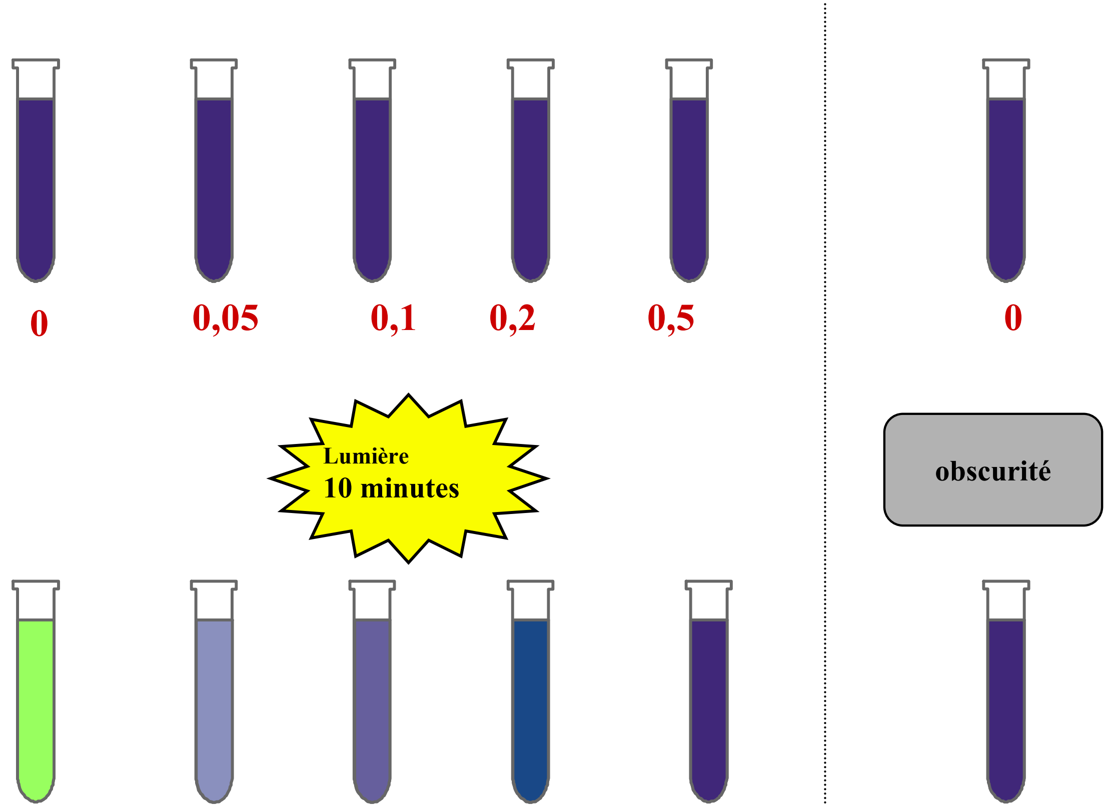
Atrazine / mesure activité *in vitro*



Atrazine / mesure activité *in vitro*

Concentration
en Atrazine (µM)

0	0,05	0,1	0,2	0,5	0



DO 600nm					
0	0,15	0,33	0,56	0,7	0,8

=> I_{50} ?

Résistance Atrazine / Gronwald *et al.*, 1989

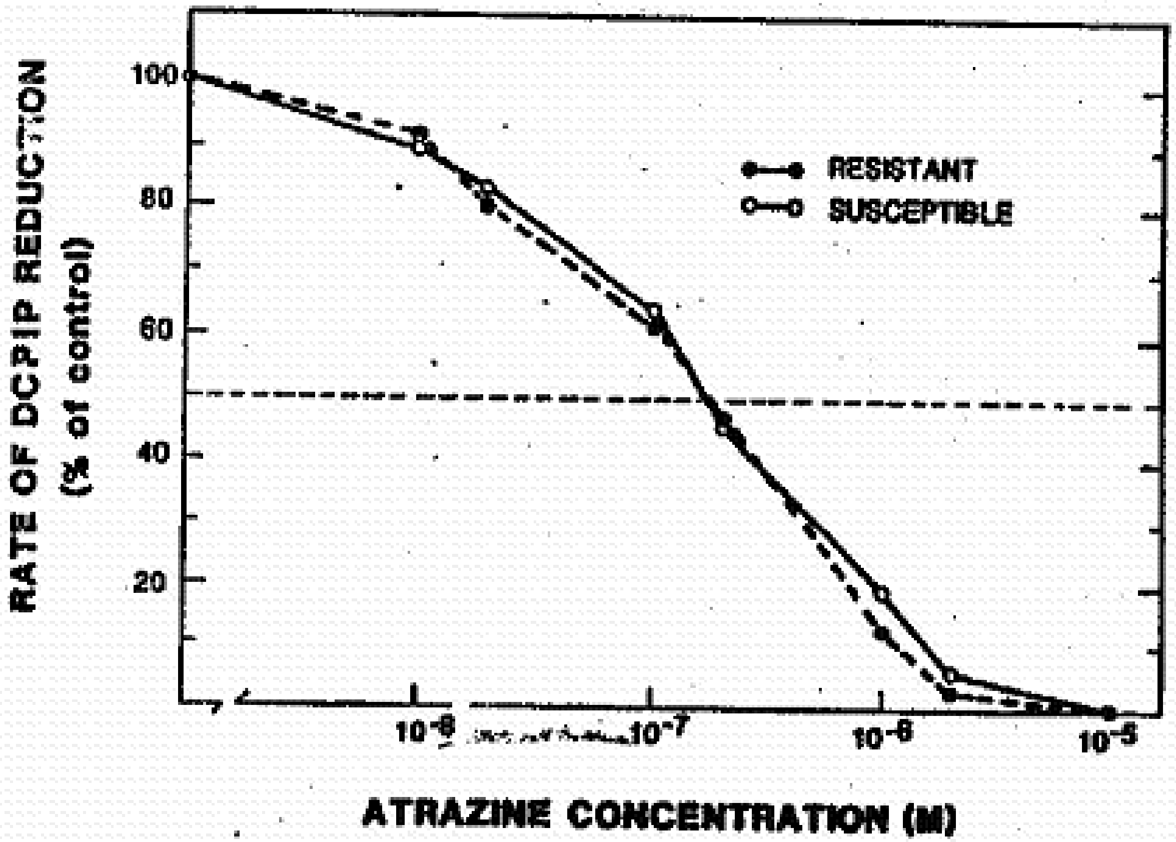


FIG. 2. *Effect of atrazine on DCPIP reduction in chloroplast thylakoids isolated from atrazine-resistant and susceptible biotypes. The atrazine concentration required to reduce the rate of DCPIP reduction by 50% (I_{50}) was 0.18 µM for chloroplasts isolated from both resistant and susceptible biotypes.*

Résistance Atrazine / Gronwald *et al.*, 1989

Activité cible

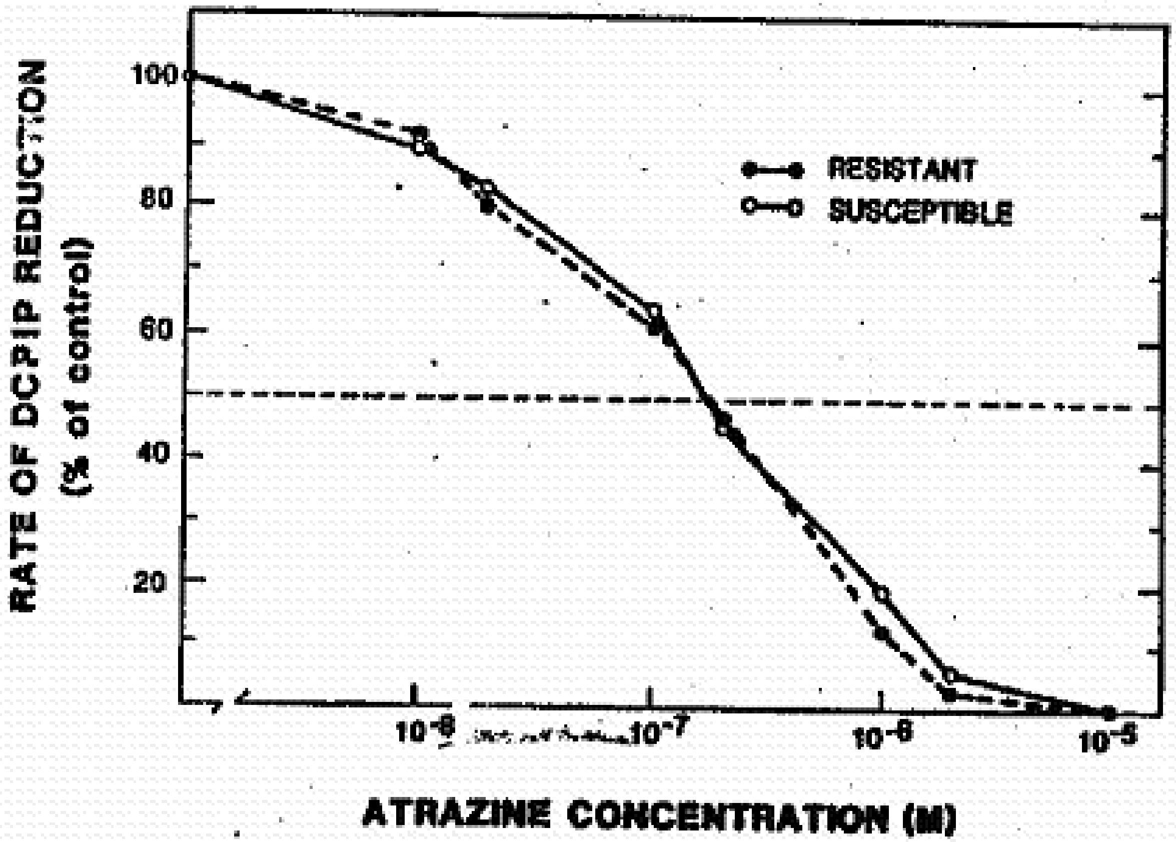
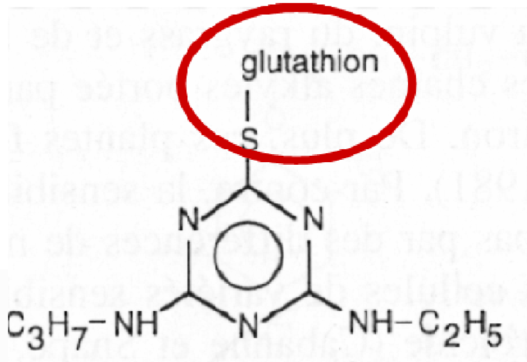


FIG. 2. *Effect of atrazine on DCPIP reduction in chloroplast thylakoids isolated from atrazine-resistant and susceptible biotypes. The atrazine concentration required to reduce the rate of DCPIP reduction by 50% (I_{50}) was 0.18 µM for chloroplasts isolated from both resistant and susceptible biotypes.*

I_{50} S= I_{50} R = 0,18 µM

Pas de tolérance de la cible (prot.D1)

Résistance Atrazine / Gronwald *et al.*, 1989



S

TABLE 1

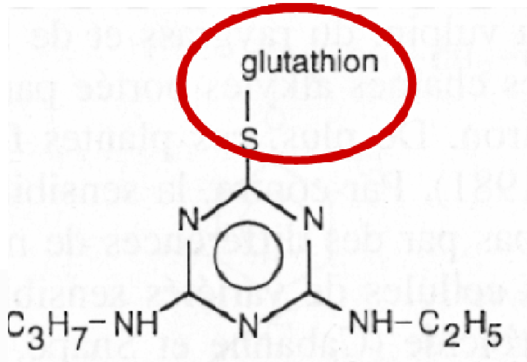
Levels of Atrazine and GS-Atrazine in Various Tissues of the Susceptible Abutilon theophrasti Biotype 0, 1, 6, and 24 hr after Pretreatment with [^{14}C]Atrazine

Tissue	Incubation period (hr)[a] 0 Atrazine	0 GS-Atrazine	1 Atrazine	1 GS-Atrazine	6 Atrazine	6 GS-Atrazine	24 Atrazine	24 GS-Atrazine
	nmol/g fresh wt[b]							
Leaf	15.6 ± 3.4	3.8 ± 1.1	13.8 ± 2.3	6.3 ± 1.8	12.9 ± 2.1	8.6 ± 1.9	11.8 ± 1.3	8.4 ± 1.2
Stem	22.5 ± 1.4	1.6 ± 0.3	11.1 ± 0.5	2.8 ± 0.4	5.0 ± 0.4	2.3 ± 0.2	3.6 ± 0.3	2.3 ± 0.1
Root	17.6 ± 0.6	0.5 ± 0.2	3.1 ± 0.1	0.7 ± 0.1	2.2 ± 0.1	0.6 ± 0.1	1.6 ± 0.1	0.4 ± 0.1
Total	55.7	5.9	28.0	9.8	20.1	11.5	17.0	11.1
Percentage of total radiolabel as GS-atrazine	9.6		25.9		36.4		39.5	

[a] After 3-hr pretreatment with 30 μ*M* [^{14}C]atrazine. See Materials and Methods for details.

[b] Values represent the mean ± SE for three experiments (*n* = 7). The mean fresh weight of leaf, stem (including petiole and cotyledons), and root tissue was 0.58, 0.29, and 0.32 g, respectively.

Résistance Atrazine / Gronwald *et al.*, 1989



S

TABLE 1

Levels of Atrazine and GS-Atrazine in Various Tissues of the Susceptible Abutilon theophrasti Biotype 0, 1, 6, and 24 hr after Pretreatment with [¹⁴C]Atrazine

Tissue	Incubation period (hr)[a] 0: Atrazine	0: GS-Atrazine	1: Atrazine	1: GS-Atrazine	6: Atrazine	6: GS-Atrazine	24: Atrazine	24: GS-Atrazine
	nmol/g fresh wt[b]							
Leaf	15.6 ± 3.4	3.8 ± 1.1	13.8 ± 2.3	6.3 ± 1.8	12.9 ± 2.1	8.6 ± 1.9	11.8 ± 1.3	8.4 ± 1.2
Stem	22.5 ± 1.4	1.6 ± 0.3	11.1 ± 0.5	2.8 ± 0.4	5.0 ± 0.4	2.3 ± 0.2	3.6 ± 0.3	2.3 ± 0.1
Root	17.6 ± 0.6	0.5 ± 0.2	3.1 ± 0.1	0.7 ± 0.1	2.2 ± 0.1	0.6 ± 0.1	1.6 ± 0.1	0.4 ± 0.1
Total	55.7	5.9	28.0	9.8	20.1	11.5	17.0	11.1
Percentage of total radiolabel as GS-atrazine	9.6		25.9		36.4		39.5	

[a] After 3-hr pretreatment with 30 μM [^{14}C]atrazine. See Materials and Methods for details.

[b] Values represent the mean ± SE for three experiments (n = 7). The mean fresh weight of leaf, stem (including petiole and cotyledons), and root tissue was 0.58, 0.29, and 0.32 g, respectively.

Résistance Atrazine / Gronwald *et al.*, 1989

R

TABLE 2

Levels of Atrazine and GS-Atrazine in Various Tissues of the Resistant Abutilon theophrasti Biotype 0, 1, 6, and 24 hr after Pretreatment with [^{14}C]Atrazine

Tissue	Incubation period (hr)[a] 0: Atrazine	0: GS-Atrazine	1: Atrazine	1: GS-Atrazine	6: Atrazine	6: GS-Atrazine	24: Atrazine	24: GS-Atrazine
	nmol/g fresh wt[b]							
Leaf	5.9 ± 1.2	8.2 ± 2.3	5.7 ± 0.6	9.2 ± 1.4	6.6 ± 0.9	9.1 ± 1.0	7.1 ± 1.3	10.3 ± 1.3
Stem	16.9 ± 1.4	15.0 ± 1.9	8.6 ± 1.1	15.9 ± 1.2	9.6 ± 1.3	15.9 ± 1.4	9.3 ± 1.3	11.3 ± 1.2
Root	18.0 ± 1.1	1.4 ± 0.2	3.3 ± 0.5	1.3 ± 0.2	1.8 ± 0.2	1.4 ± 0.1	1.3 ± 0.1	1.2 ± 0.1
Total	40.8	24.6	17.6	26.4	18.0	26.4	17.7	22.8
Percentage of total radiolabel as GS-atrazine	37.6		60.0		59.5		56.3	

[a] After 3-hr pretreatment with 30 μM [^{14}C]atrazine. See Materials and Methods for details.
[b] Values represent the mean ± SE for three experiments ($n = 7$). The mean fresh weight of leaf, stem (including petioles and cotyledons), and root tissue was 0.54, 0.28, and 0.27 g, respectively.

Résistance Atrazine / Gronwald *et al.*, 1989

R

TABLE 2
Levels of Atrazine and GS-Atrazine in Various Tissues of the Resistant Abutilon theophrasti Biotype 0, 1, 6, and 24 hr after Pretreatment with [^{14}C]Atrazine

Tissue	Incubation period (hr)[a] 0 Atrazine	0 GS-Atrazine	1 Atrazine	1 GS-Atrazine	6 Atrazine	6 GS-Atrazine	24 Atrazine	24 GS-Atrazine
	nmol/g fresh wt[b]							
Leaf	5.9 ± 1.2	8.2 ± 2.3	5.7 ± 0.6	9.2 ± 1.4	6.6 ± 0.9	9.1 ± 1.0	7.1 ± 1.3	10.3 ± 1.3
Stem	16.9 ± 1.4	15.0 ± 1.9	8.6 ± 1.1	15.9 ± 1.2	9.6 ± 1.3	15.9 ± 1.4	9.3 ± 1.3	11.3 ± 1.2
Root	18.0 ± 1.1	1.4 ± 0.2	3.3 ± 0.5	1.3 ± 0.2	1.8 ± 0.2	1.4 ± 0.1	1.3 ± 0.1	1.2 ± 0.1
Total	40.8	24.6	17.6	26.4	18.0	26.4	17.7	22.8
Percentage of total radiolabel as GS-atrazine	37.6		60.0		59.5		56.3	

[a] After 3-hr pretreatment with 30 μM [^{14}C]atrazine. See Materials and Methods for details.
[b] Values represent the mean ± SE for three experiments (n = 7). The mean fresh weight of leaf, stem (including petioles and cotyledons), and root tissue was 0.54, 0.28, and 0.27 g, respectively.

Capacité de détoxication accrue (complexes- GSH) dans plantes résistantes

Résistance Atrazine

Plant Physiol. (1993) 103: 911–917

A Serine-to-Threonine Substitution in the Triazine Herbicide-Binding Protein in Potato Cells Results in Atrazine Resistance without Impairing Productivity[1]

Reid J. Smeda[2], Paul M. Hasegawa, Peter B. Goldsbrough, Narendra K. Singh[3], and Stephen C. Weller*
Department of Horticulture, Purdue University, West Lafayette, Indiana 47907–1165

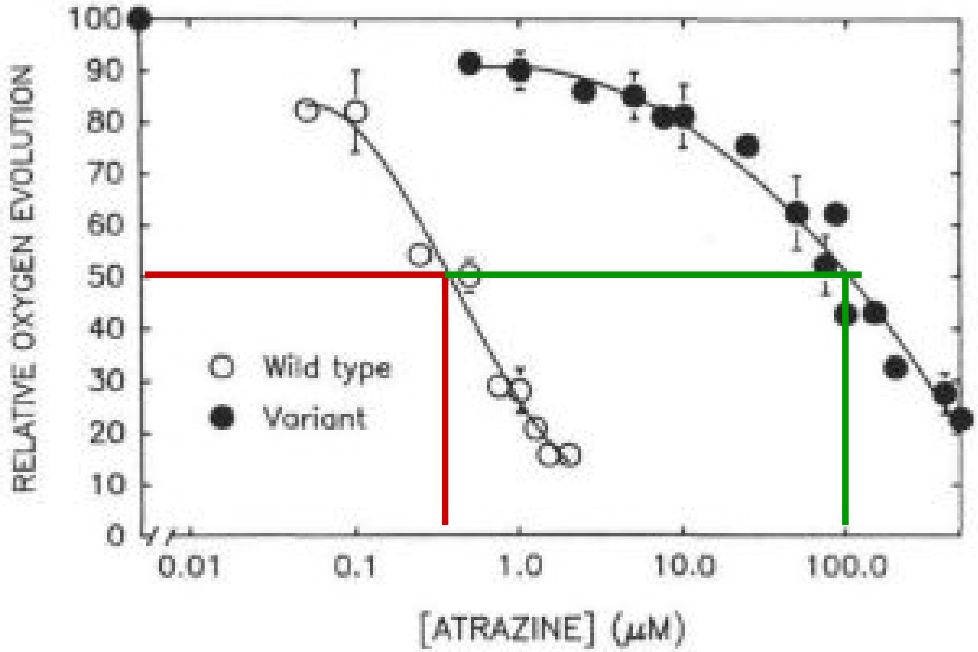


Figure 2. Atrazine inhibition of photosynthetic electron transport in wild-type and variant potato cells. The rate of electron transport was measured within 90 s of herbicide addition. Each point is the mean of four observations, and vertical bars represent the SE. Rates of oxygen evolution for wild-type and variant cells in medium lacking atrazine were 126.6 and 141.1 μmol of O_2 mg^{-1} of Chl h^{-1}, respectively.

I_{50} wt = 0,6 μM
I_{50} R = 100 μM

Facteur de tolérance = 167

Résistance Atrazine / Smeda *et al.*, 1993

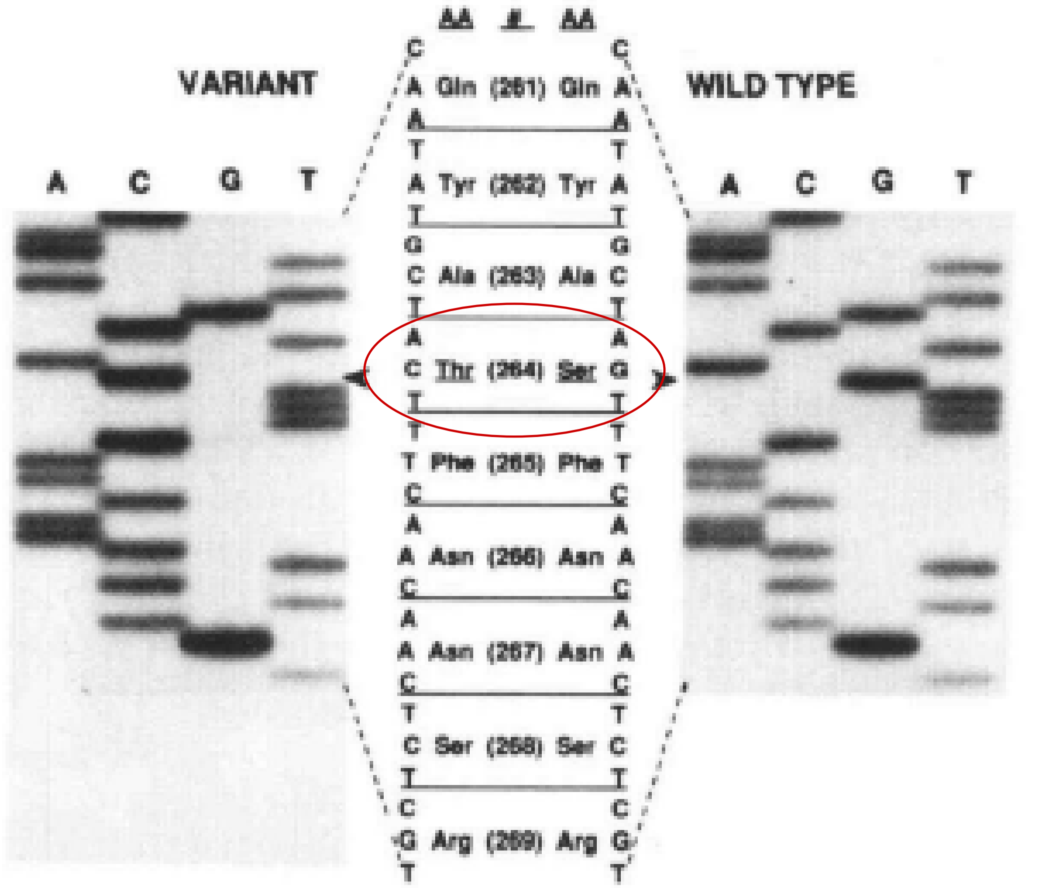
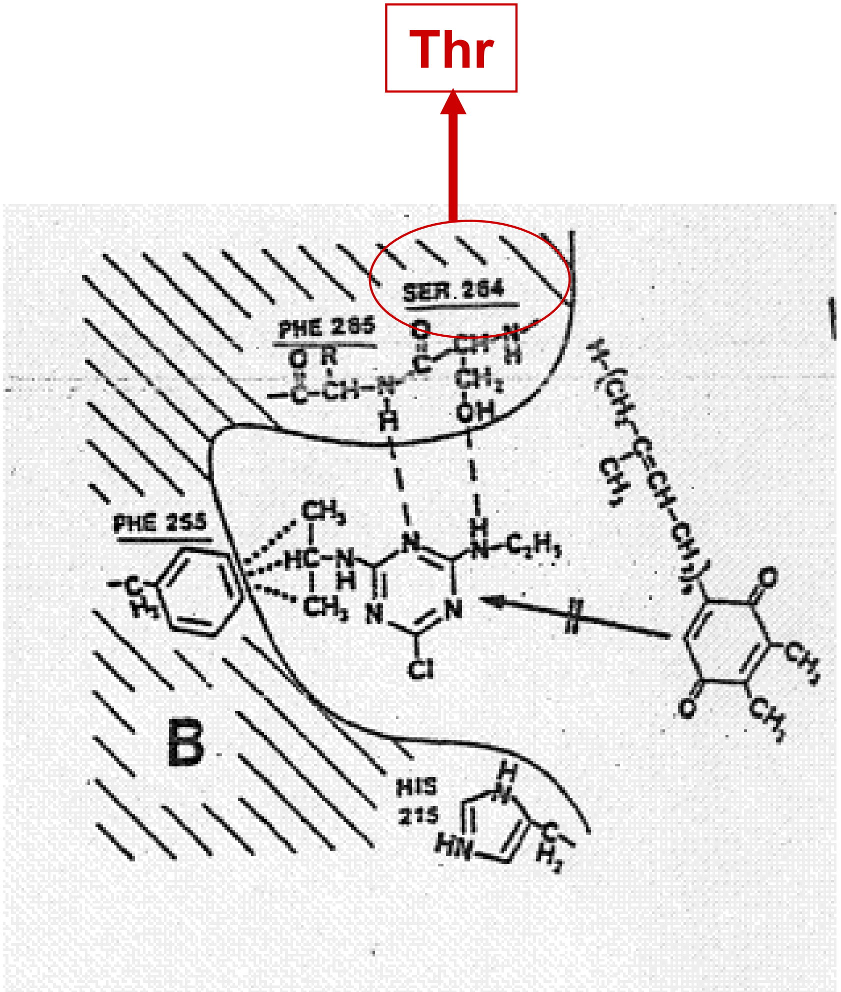
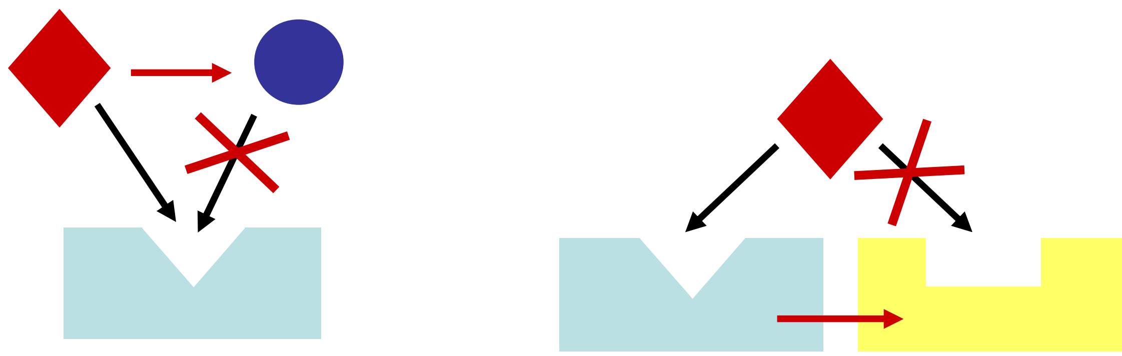


Figure 6. Autoradiogram of *psbA* DNA-sequencing gels for wild-type and variant cells. The only site for divergence was at the amino acid Ser at position 264 where a G residue was substituted by a C residue. This observation was confirmed by sequencing four unique plasmid target ctDNA inserts.

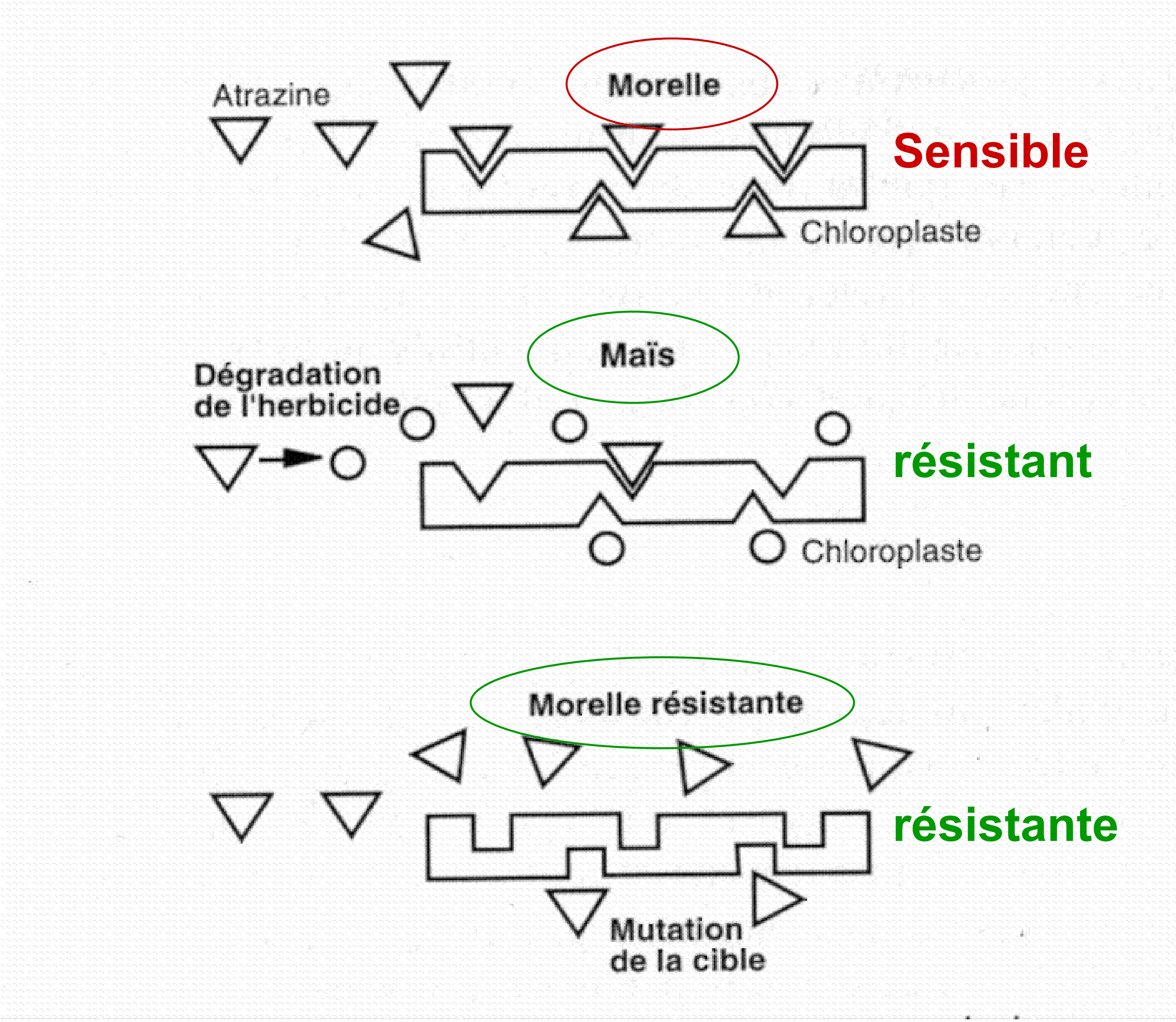


Résistance Atrazine - Bilan I_{50} / cible

A. theophrasti	**Sensible** **Résistant**	**I_{50} = 0,18 µM** **I_{50} = 0,18 µM**	 **Détoxication** (GST)
S. tuberosum	**Sensible** **Résistant**	**I_{50} = 0,6 µM** **I_{50} = 100 µM**	 **Cible** (Prot.D1)
Epinard	**Sensible**	**I_{50} = 0,2- 0,3 µM**	
Maïs	**Résistant**	**I_{50} = 0,3 µM**	**Détoxication** (GST)



Résistance Atrazine



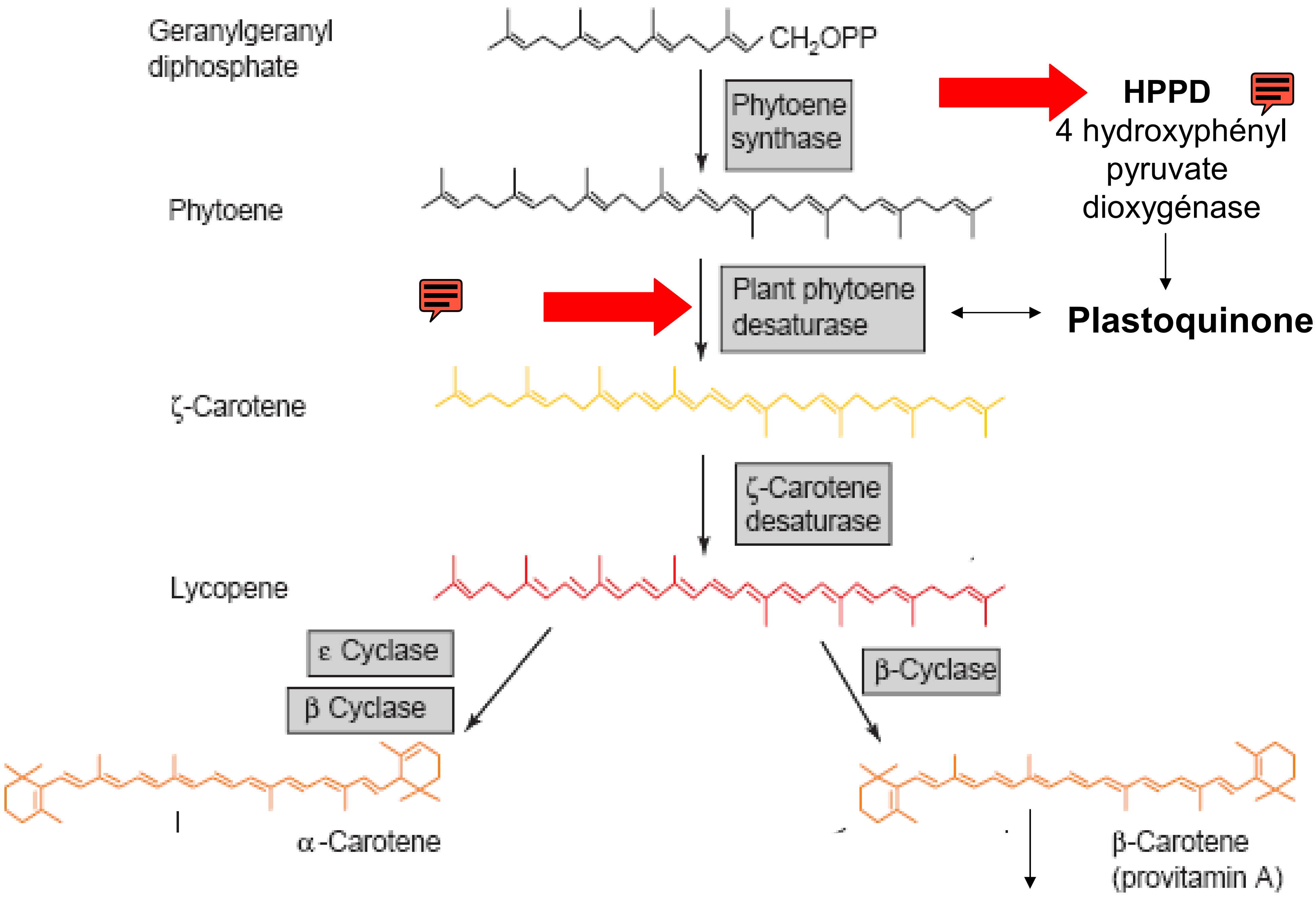
Herbicide Resistance Action Committee
Classification of herbicides

(Cf Autre système de classification **WSSA** "Weed Science Society of America »)

http://www.plantprotection.org/HRAC/ http://www.wssa.net/

A **(1)** / Inhibition **ACCase**	**H** **(10)** / Inhibition **Glutamine Synthase**
B **(2)** / Inhibition **ALS** (AHAS)	**I** **(18)** / inhibition of **Dihydroptéorate (DHP) synthase**
C1 **(5)**, **C2** **(7)**, **C3** **(6)** / inhibition **PSII** **(prot. D1)**	**K1** **(3)**, **K2** **(23)**,**K3** **(15)** / inhibition **divisions cellulaires** (microtubules, VLCFA)
D **(22)** / capture électrons **PSI**	**L** **(20, 21,26)** / inhibition synthèse **paroi cellulaire** (cellulose)
E **(14)** / inhibition **Protox**	**M** **(24)** / agents découplants (disruption membranaire)
F1 **(12)** / inhibition **Phytoène désaturase** (PDS)	**N** **(8, 26)** / inhibition synthèse lipides (sauf ACCase)
F2 **(27)** / inhibition **HPPD**	**O** **(4)** / herbicides auxiniques **P** **(19)** / inhibition transport auxine
G **(9)** / inhibition **EPSP Synthase**	**R,S,Z** **(17, 25 à 27)** / mode d'action inconnu

Herbicides / Pigments chloroplastiques

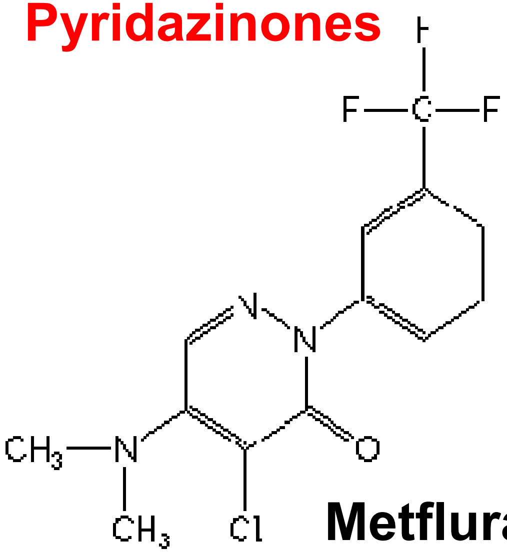


Guliano et al., 2000

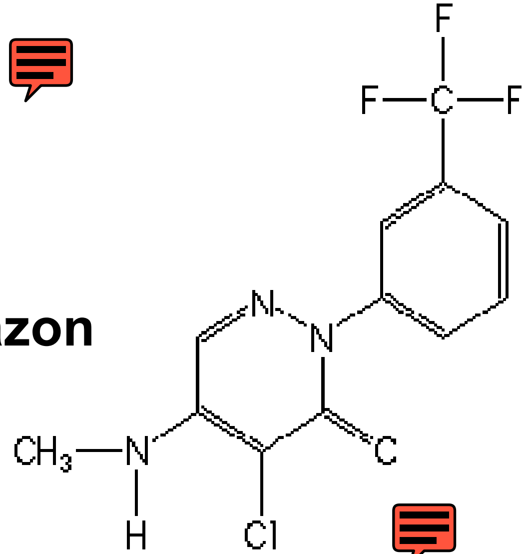
Herbicides / Pigments chloroplastiques

Pyridazinones

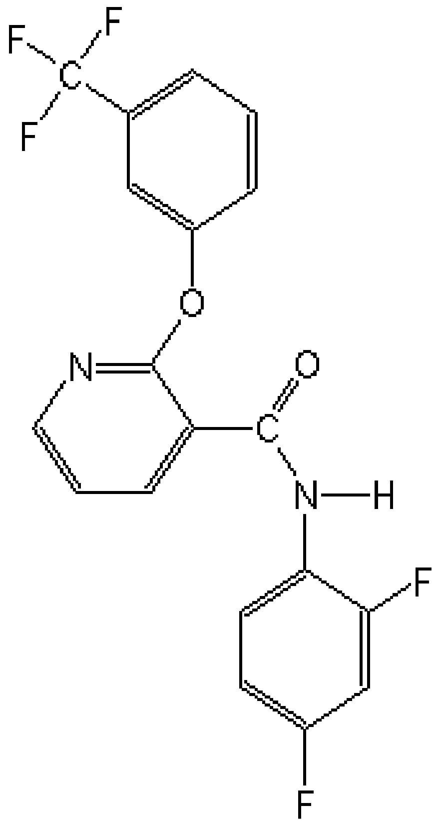
caroténoïdes



Metflurazon



Norflurazon



Diflufenican
(anilide)

⇨ Phytoène désaturase

Herbicides / Pigments chloroplastiques

PESTICIDE BIOCHEMISTRY AND PHYSIOLOGY 52, 33–44 (1995)

**Herbicides inhibiteurs
de la synthèse des caroténoïdes**

Substituted Tetrahydropyrimidinones: A New Herbicidal Class of Compounds Inducing Chlorosis by Inhibition of Phytoene Desaturation

1. Biological and Biochemical Results[1]

PETER BABCZINSKI, GERHARD SANDMANN,* ROBERT R. SCHMIDT, KOZO SHIOKAWA,†
AND KAZUOMI YASUI†

TABLE 3
Carotenoid Composition of Anacystis as Influenced by Compound 1

	(μg mg^{-1} dry wt)			
Compound 1	Zeaxanthin	β-Cryptoxanthin	β-Carotene	Phytoene
Absent (control)	3.11	0.13	2.79	0.00
5×10^{-8} *M*	2.06	0.09	2.49	0.50
10^{-7} *M*	1.68	0.06	1.42	0.78
2×10^{-7} *M*	0.65	0.05	0.99	1.16

Babzynski et al., 1995

Herbicides / Pigments chloroplastiques

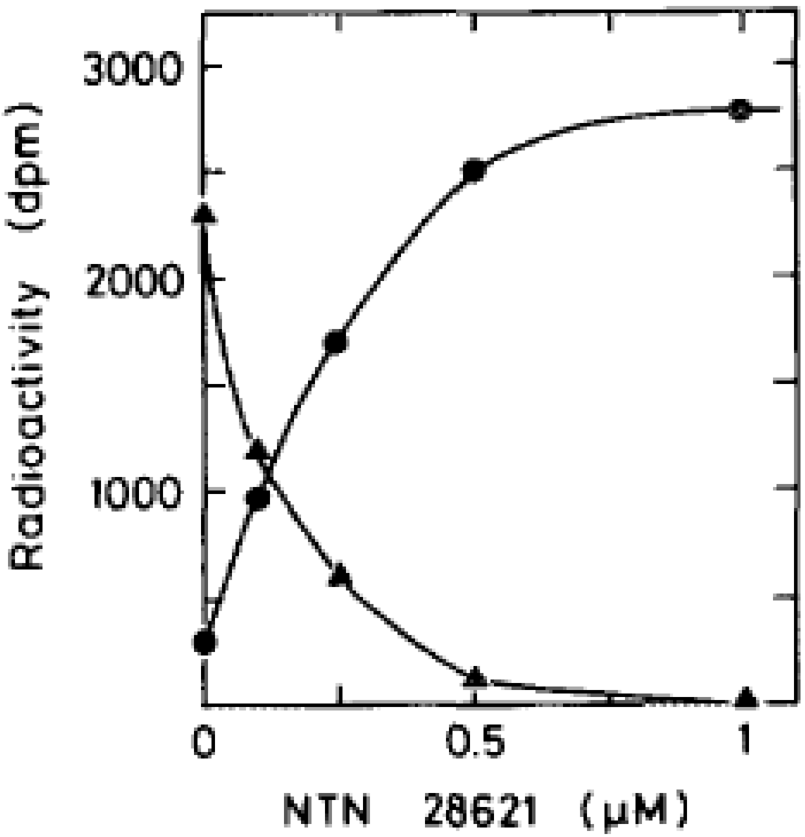


FIG. 4. *In vitro formation of phytoene and β-carotene from [^{14}C]geranylgeranyl pyrophosphate by Anacystis membranes. Incubations as described under Materials and Methods in the presence of thylakoids equivalent to 120 μg chlorophyll (2 hr) and various concentrations of compound 1.* ●, *Phytoene,* ▲, *β-carotene. NTN 28621 = cpd. 1.*

Babzynski et al., 1995

Herbicides / Pigments chloroplastiques

⇨ Herbicides blanchissants (« bleaching herbicides »)

Kim et al, 2004

Fig. 1. White/green-mixed tissue of the 3rd leaf induced by a drenching treatment (100 ml per 350 cm^2) of 26.6 μM fluridone at the 40% growth of the 3rd leaf of corn. G, Green part; PG, pale green part; W, white part.

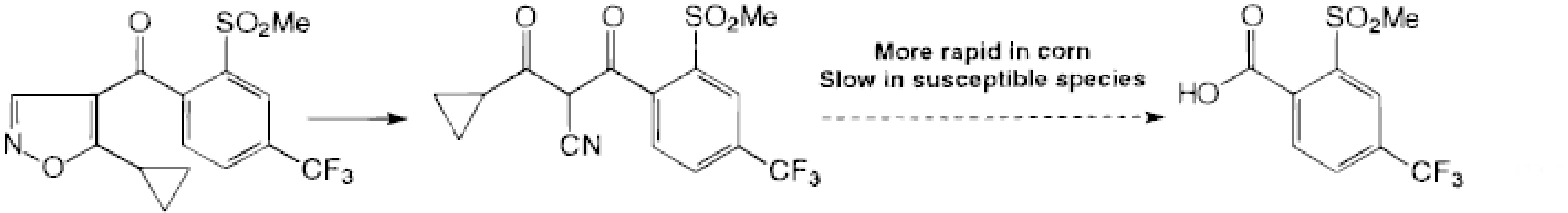
Table 1
Photosynthetic pigment contents in each part of white/green mixed corn leaf induced by a drenching treatment of fluridone on the soil surface

Leaf part	Photosynthetic pigments (μg g fresh weight^{-1})		
	Total chlorophylls (*A*)	Carotenoids (*B*)	*A*/*B*
G	3236.5 ± 38.3	461.3 ± 12.6	7.02
PG	948.9 ± 67.8	143.9 ± 9.5	6.60
W	18.5 ± 2.6	2.6 ± 0.2	7.16

Herbicides / Pigments chloroplastiques

Herbicides inhibiteurs de la synthèse des caroténoïdes

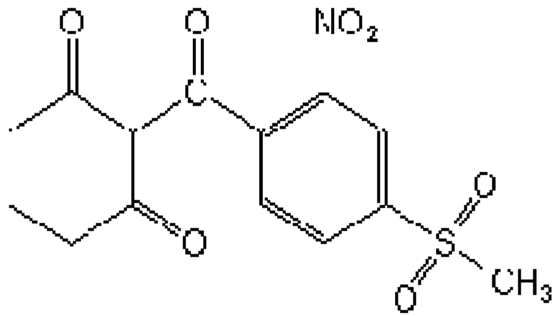
Métabolisation ⇨ Activation
Proherbicide ⇨ Herbicide



Isoxaflutole — diketonitrile — benzoic acid

(cyclopropylisoxazoles)

⇨ HPPD



Mésotrione
(benzoylcyclohexanedione)

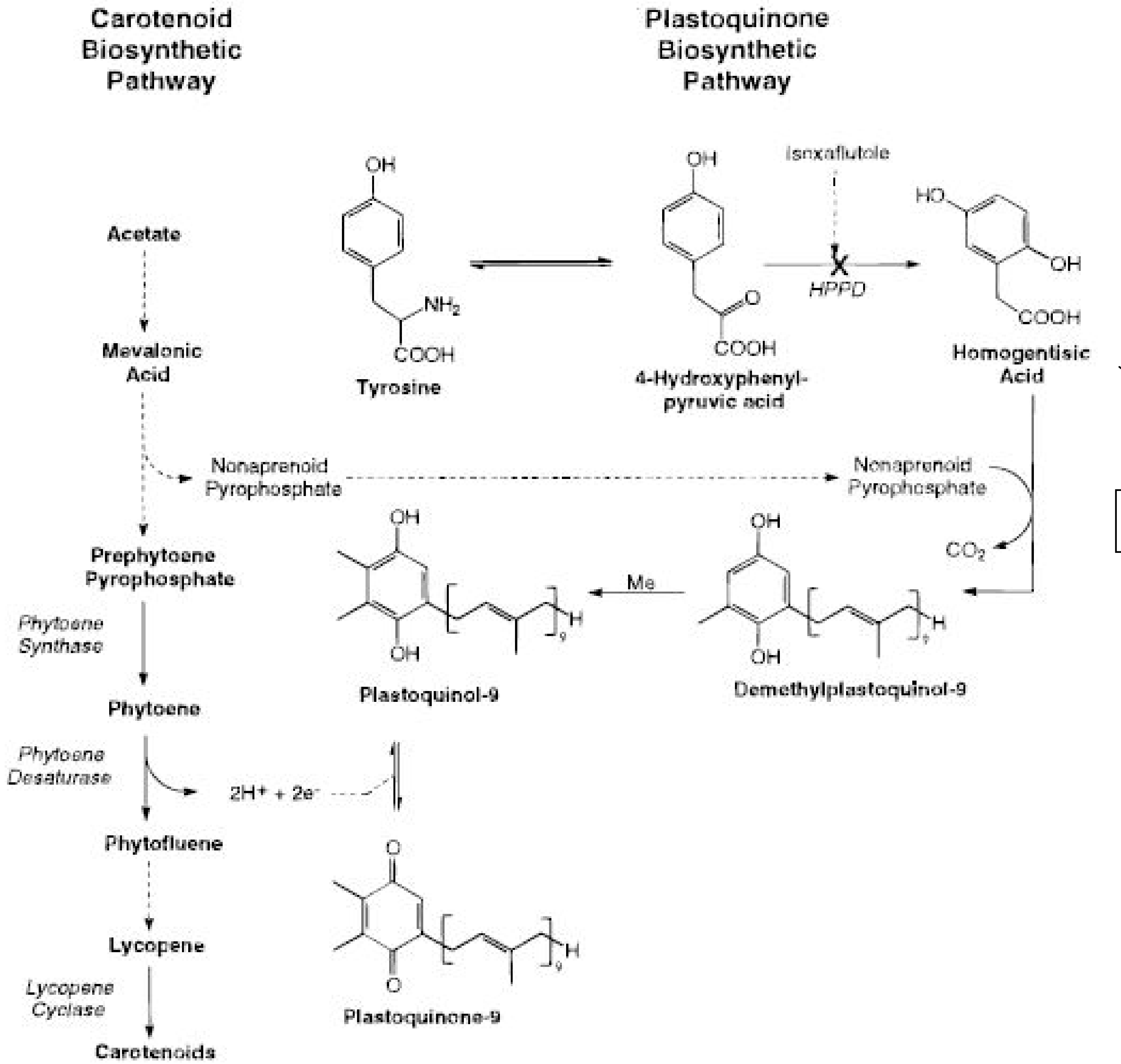


FIG. 6. The integration of the carotenoid and plastoquinone biosynthetic pathways.

α - tocophérol

Pallett *et al.* (1998)

Pest Management Science *Pest Manag Sci* 57:120–128 (2001)

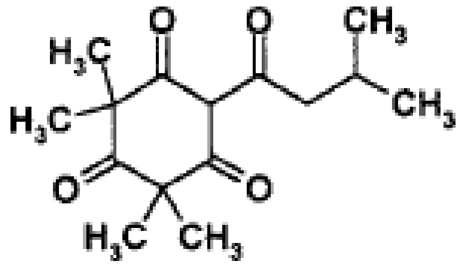
Mesotrione: a new selective herbicide for use in maize†

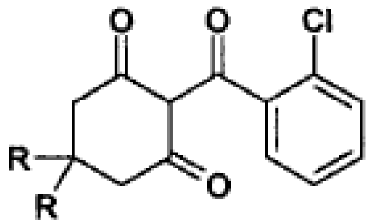
Glynn Mitchell,[1]* David W Bartlett,[1] Torquil EM Fraser,[1] Tim R Hawkes,[1] David C Holt,[1] Jane K Townson[1] and Rex A Wichert[2]
[1] *Zeneca Agrochemicals, Jealott's Hill International Research Centre, Bracknell, Berkshire RG42 6ET, UK*
[2] *Zeneca Ag Products, Western Research Center, 1200 South 47th Street, Richmond, CA 94804, USA*

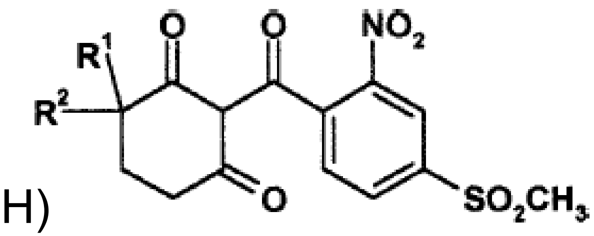
-1977 : *Callistemon citrinus (Myrtacées)* => **leptospermone**

-1980 => Brevet sur potentiel herbicide

-1982 => nouvelle classe d'herbicides:
Les **benzoylcyclohexanediones**







Mésotrione (R1=R2=H)

Herbicides / Pigments chloroplastiques

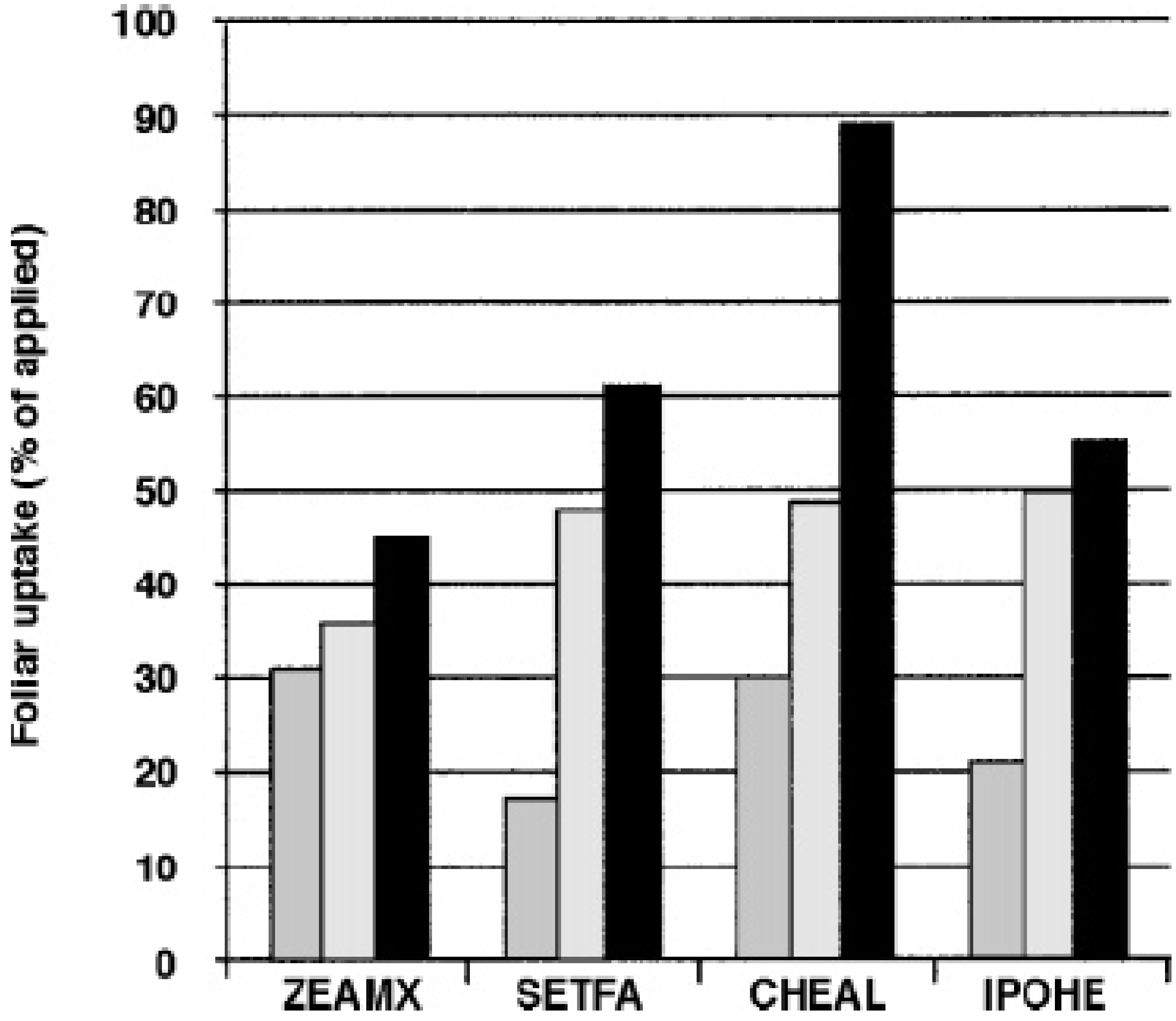


Figure 7. Uptake of radiolabelled mesotrione into single treated leaf of *Zea mays* (ZEAMX), *Setaria faberi* (SETFA), *Chenopodium album* (CHEAL), and *Ipomoea hederacea* (IPOHE). ▩ = 1 h, □ = 6 h, ■ = 24 h.

Mitchell *et al.*, 2001

Herbicides / Pigments chloroplastiques

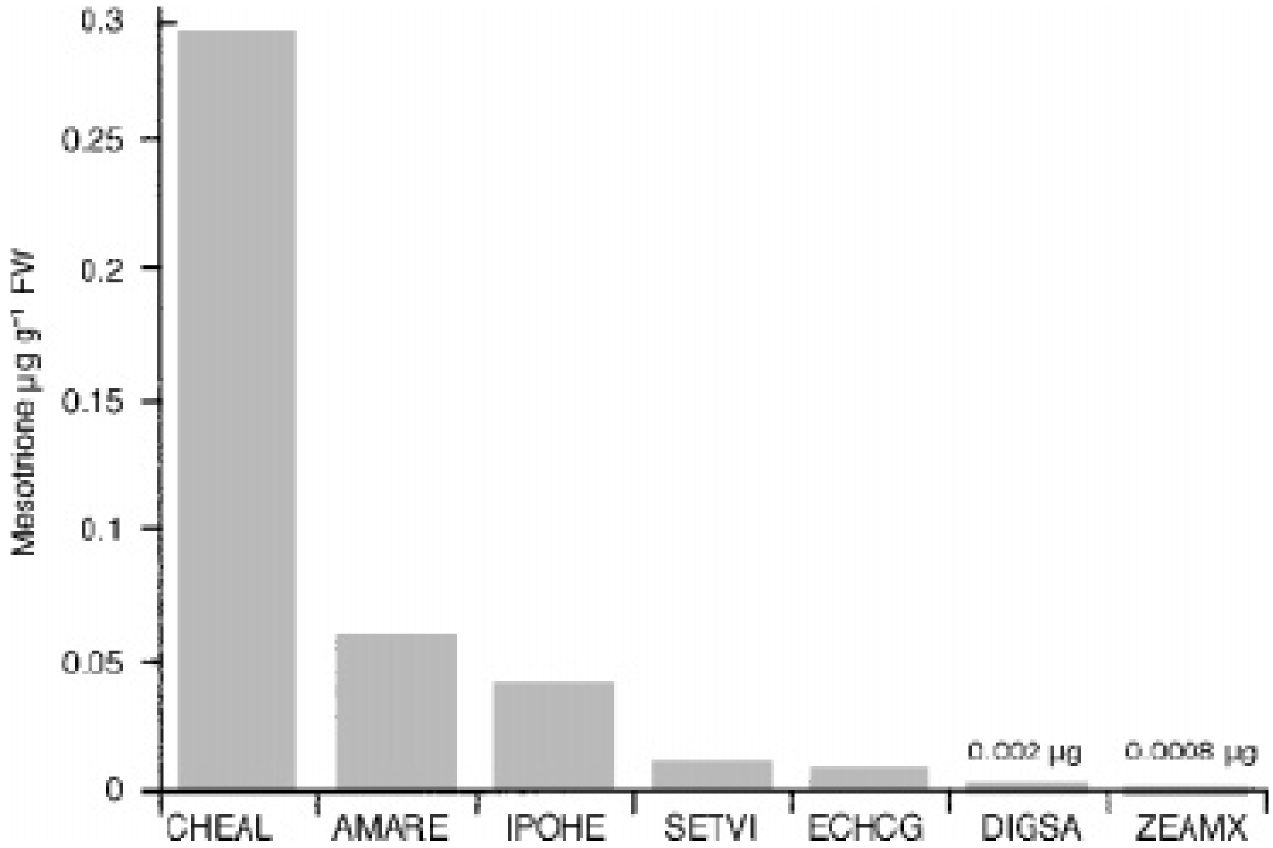


Figure 8. Differential metabolism of mesotrione in maize (ZEAMX) and the weed species *Chenopodium album* (CHEAL), *Amaranthus retroflexus* (AMARE), *Ipomoea hederacea* (IPOHE), *Setaria viridis* (SETVI), *Echinochloa crus-galli* (ECHCG) and *Digitaria sanguinalis* (DIGSA). Recoveries from whole shoots treated with ^{14}C-mesotrione 7 days after application.

Mitchell *et al.*, 2001

Herbicides / Pigments chloroplastiques

http://www.syngenta-agro.fr/synweb/galerie/Documents/Notice/CALLISTO.pdf

TD Isoxaflutole / Pallett *et al.* (1998)

PESTICIDE BIOCHEMISTRY AND PHYSIOLOGY 62, 113–124 (1998)
ARTICLE NO. PB982378

The Mode of Action of Isoxaflutole

I. Physiological Effects, Metabolism, and Selectivity

K. E. Pallett, J. P. Little, M. Sheekey, and P. Veerasekaran

Plant Science Research Department, Rhône-Poulenc Agriculture Limited, Fyfield Road, Ongar, Essex, CM5 0HW, United Kingdom

Isoxaflutole / Pallett *et al.* (1998)

TABLE 1

The Recovery of Isoxaflutole in Corn and *A. theophrasti* Following Treatment of Roots to [^{14}C]Isoxaflutole ($0.5\ \mu g\ ml^{-1}$) in Hydroponic Medium

Species	Treatment period (h)	^{14}C extracted[a] ($\mu g\ g^{-1}$)		% Isoxaflutole equivalent detected		
		Roots	Shoots	Nutrient medium	Roots	Shoots
Corn	3	0.31	0.58	99	43	4
	6	0.22	1.08	98	34	2
	12	0.21	2.26	93	21	0
	24	0.18	3.06	87	9	0
A. theophrasti	3	0.25	0.61	100	65	19
	6	0.27	1.12	94	51	7
	12	0.26	2.78	88	32	2
	24	0.22	3.34	81	14	0

[a] For each extraction, nine plants from three replicates were combined and ^{14}C from shoots and roots was extracted separately. The results are expressed as microgram equivalent of isoxaflutole per gram fresh wt of tissue (113,240 dpm is equivalent to 1 μg of isoxaflutole). Isoxaflutole in the extracts was separated by radio-TLC and identified by cochromatography with the authentic standard.

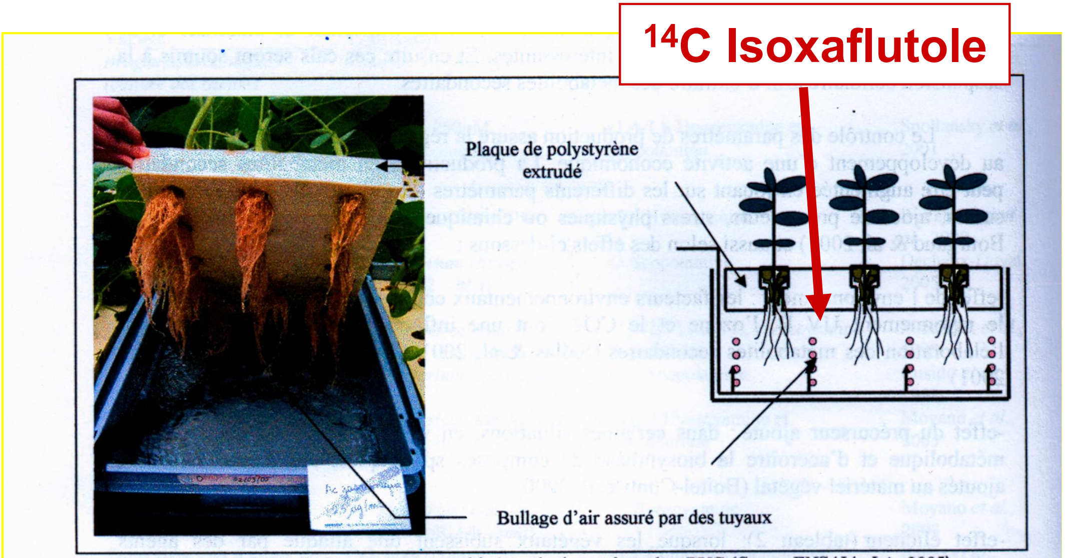


Planche 1: Photo et schéma de *Datura innoxia* cultivés en hydroponie en bac PVC (*Serres ENSAIA, Juin 2005*)

Isoxaflutole / Pallett *et al.* (1998)

Herbicide racinaire

TABLE 1
The Recovery of Isoxaflutole in Corn and *A. theophrasti* Following Treatment of Roots to [^{14}C]Isoxaflutole ($0.5\ \mu g\ ml^{-1}$) in Hydroponic Medium

Species	Treatment period (h)	^{14}C extracted[a] ($\mu g\ g^{-1}$) Roots	Shoots	% Isoxaflutole equivalent detected Nutrient medium	Roots	Shoots
Corn	3	0.31	0.58	99	43	4
	6	0.22	1.08	98	34	2
	12	0.21	2.26	93	21	0
	24	0.18	3	87	9	0
A. theophrasti	3	0.25	0.61	100	65	19
	6	0.27	1.12	94	51	7
	12	0.26	2.78	88	32	2
	24	0.22	3	81	14	0

Corn **= plante résistante (R)** — **=94,4% ^{14}C**

A. theophrasti **= plante sensible (S)** — **=93,8% ^{14}C**

[a] For each extraction, nine plants from three replicates were combined and ^{14}C from shoots and roots was extracted separately. The results are expressed as microgram equivalent of isoxaflutole per gram fresh wt of tissue (113,240 dpm is equivalent to 1 μg of isoxaflutole). Isoxaflutole in the extracts was separated by radio-TLC and identified by cochromatography with the authentic standard.

-Pas de différence entre R et S
-Herbicide systémique ascendant (xylème)
=> Accumulation dans les parties aériennes
⇒Cible probable dans chloroplastes

-L'isoxaflutole est rapidement métabolisé après absorption racinaire

^{14}C Isoxaflutole

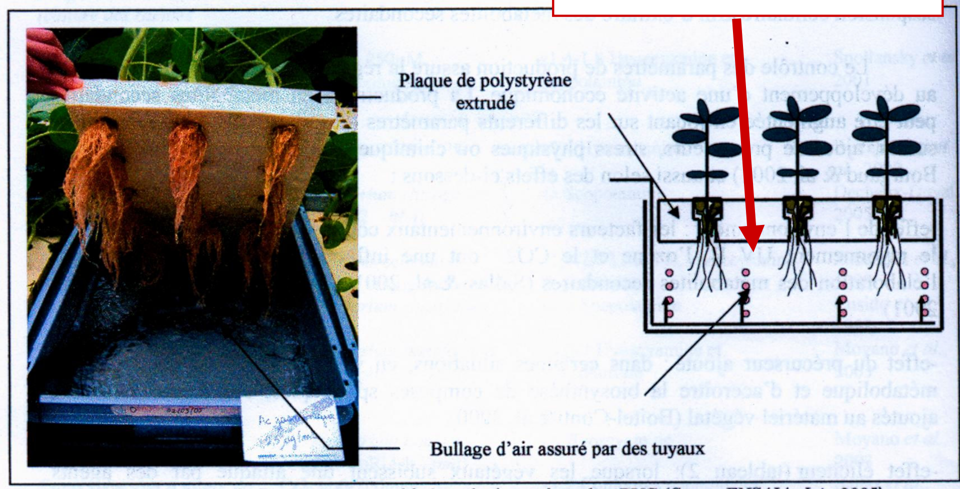


Planche 1: Photo et schéma de *Datura innoxia* cultivés en hydroponie en bac PVC (*Serres ENSAIA, Juin 2005*)

Isoxaflutole / Pallett *et al.* (1998)

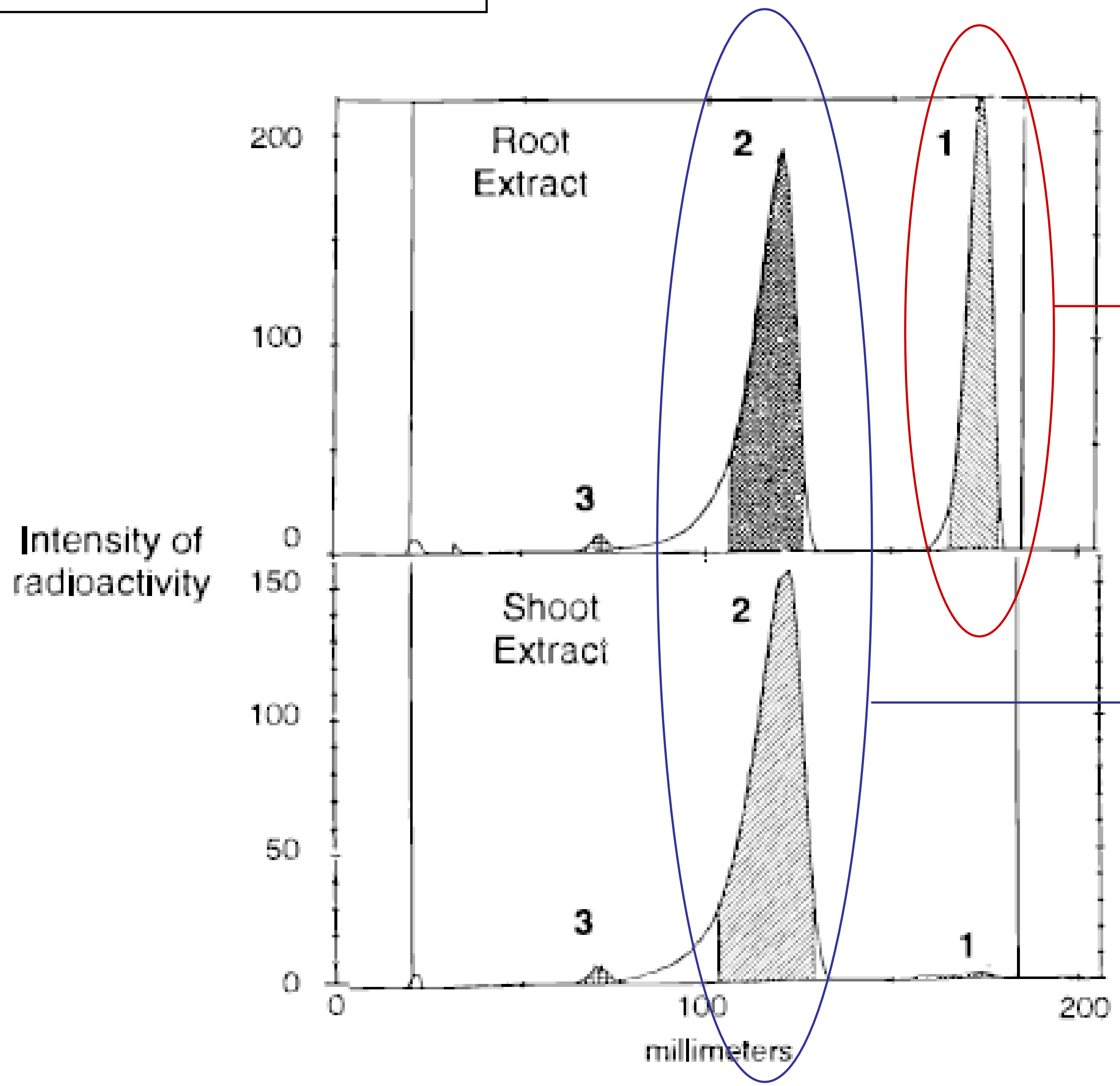
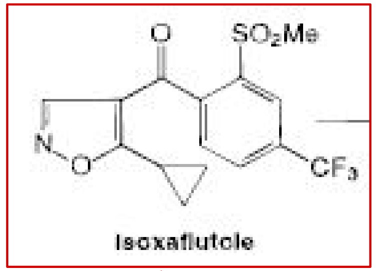
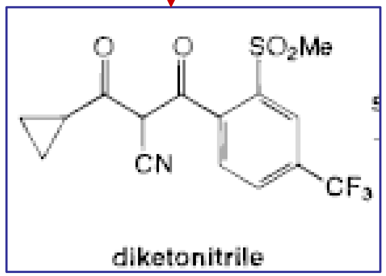


FIG. 1. Radioactivity traces of thin-layer chromatographic separations of [^{14}C]isoxaflutole and its metabolites formed in root and shoots of *corn* seedlings (cv. P3394) following a 3-h treatment of roots to [*phenyl*-U-^{14}C]isoxaflutole (0.5 μg ml $^{-1}$) in hydroponic medium. Root and shoot extracts were separated by TLC with solvent system A. The TLC plates were analyzed using phosphorimaging. The intensity of radioactive peaks is measured as photostimulated luminescence (PSL) which is in proportion to the intensity of radioactivity measured as dpm using LSC counting. Peak 1, isoxaflutole; peak 2, diketonitrile; peak 3, benzoic acid.



TLC
LC-MS



Isoxaflutole / Pallett *et al.* (1998)

TABLE 2

Identity of ^{14}C-Labeled Products in the Shoot Extracts of Corn, *Ipomoea* spp., and *A. theophrasti* Following a 1-Day Exposure of Roots to [*phenyl*- U -^{14}C] Isoxaflutole (56,620 dpm ml^{-1} Equivalent to 0.5 µg ml^{-1}) via the Hydroponic Medium

	Corn **R**		*Ipomoea* spp. **RS**		*A. theophrasti* **S**	
	1 day	1 + 6 days[a]	1 day	1 + 6 days	1 day	1 + 6 days
^{14}C extracted[b]						
% Total ^{14}C in shoot tissue	95	87	92	85	94	91
µg equivalent g^{-1} shoot	3.46	3.03	2.47	2.21	1.32	1.62
% Distribution of metabolites in shoots						
Diketonitrile	80	29	77	57	89	82
Benzoic acid	13	59	12	31	0	12
Unidentified	7	12	11	12	11	6

[a] After a 1-day exposure period the roots were transferred to fresh untreated medium and the plants were grown for a further 6 days period.

[b] Each value is the mean of three replicates. Each replicate consisted of nine shoots from each species. The results are expressed as microgram equivalent of isoxaflutole or DKN per gram fresh wt of tissue (113240 dpm is equivalent to 1 µg of isoxaflutole). The DKN and benzoic acid in the extracts were separated by radio-TLC and identified by cochromatography with the standards.

La sensibilité à l'isoxaflutole est corrélée avec le taux de DKN dans les parties aériennes

Métabolisation ≠ Détoxication !!

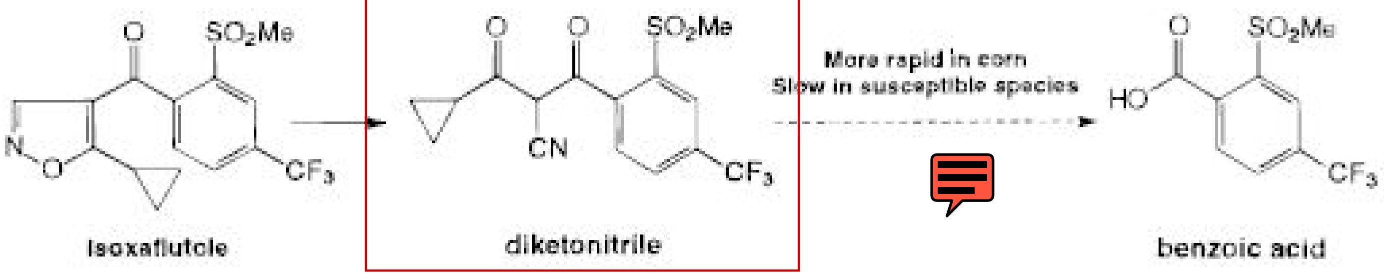


FIG. 2. The degradation of isoxaflutole in plants.

Isoxaflutole / Pallett *et al.* (1998)

3 pots de 10 plantules par traitement / 30% humidité / couche superficielle (0,5 cm)+ ^{14}C Isoxaflutole

TABLE 3

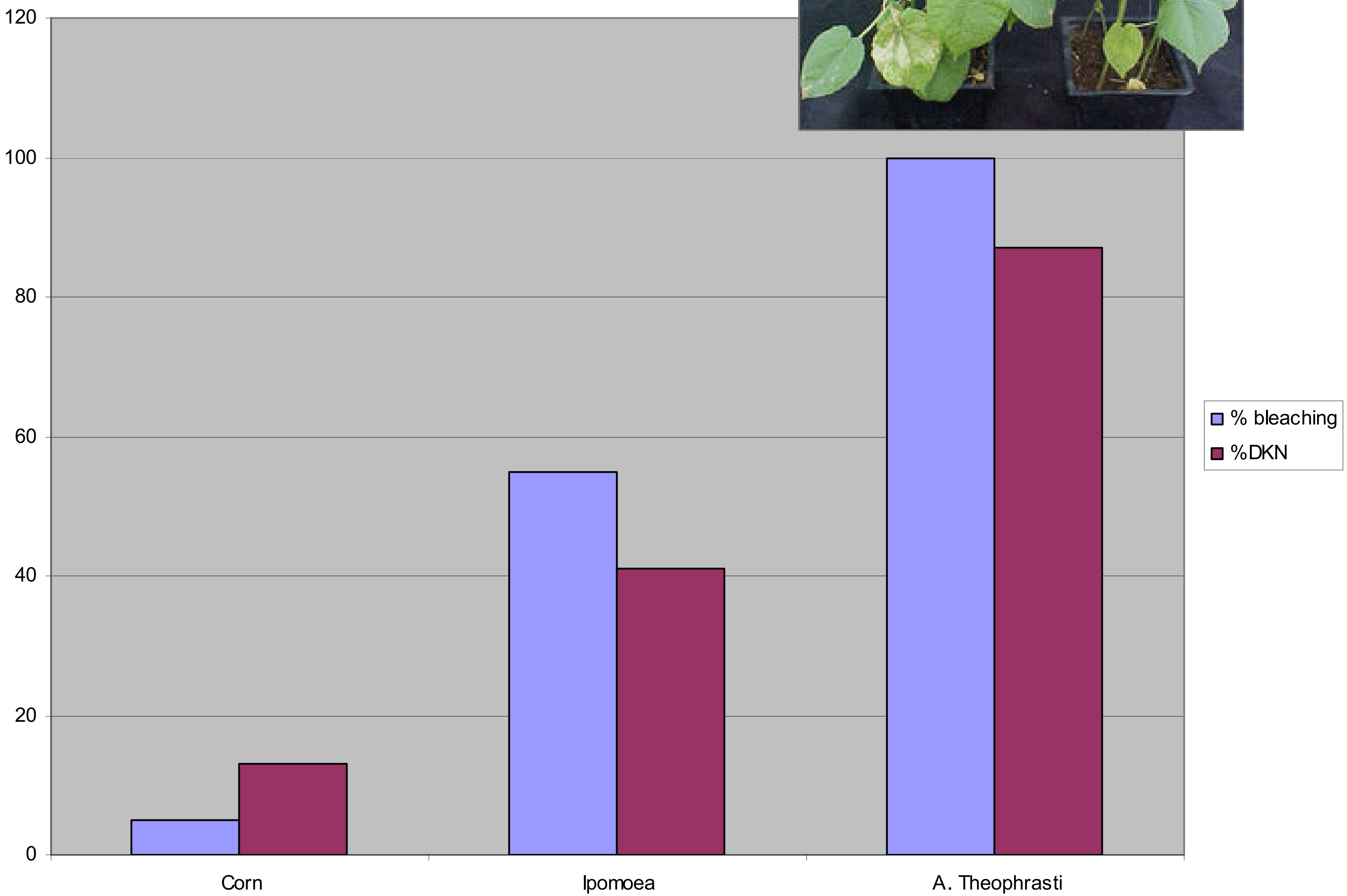
The Relationship between Injury and the Levels of Distribution of [^{14}C]Diketonitrile (DKN) in Corn, *Ipomoea* spp., and *A. theophrasti* Seedlings 10 days after Preemergence Treatment of [^{14}C]Isoxaflutole to the Surface 0.5 cm of the Soil Surface Equivalent to 250 g ha^{-1}

Assessment 10 days after treatment	Corn	*Ipomoea* spp	*A. theophrasti*
Shoot injury (% bleaching)	5	55	100
Total ^{14}C extracted (dpm $shoot^{-1}$)[a]	10,290	7835	6765
% Remaining as DKN			
Mature leaves	8	33	91
Young leaves	13	41	87

[a] 113,240 dpm is equivalent to 1 µg of isoxaflutole or DKN.

Confirmation résultats précédents dans un système plus proche des conditions normales d’utilisation
+ lien avec symptômes morphologiques de phytotoxicité (=> « bleaching »)

Isoxaflutole / Pallett *et al.* (1998)



Isoxaflutole / Pallett *et al.* (1998)

TABLE 4
Pigment Analysis of *E. crus-galli* Leaves Following Postemergence Treatment with Isoxaflutole and Diflufenican

	Leaf pigment content ($\mu g\ g^{-1}$ fresh wt)		
	Untreated	Isoxaflutole ($32\ g\ ha^{-1}$)	Diflufenican ($125\ g\ ha^{-1}$)
β-Carotene	78.5	4.7	17.8
Violaxanthin	57.7	4.6	7.0
Antheraxanthin	8.0	1.6	2.5
Lutein	102.0	12.9	27.2
Neoxanthins[a]	22.8	2.6	5.7
Phytoenes[a]	0.0	7.5	31.6
Chlorophyll a	1157.8	84.6	281.7
Chlorophyll b	252.5	26.0	63.9

Note. After 4 days, the leaves were excised and extracted as described by Barry and Pallett (10). The carotenoid and chlorophyll profiles of the leaves were determined by HPLC (11). Data are means of four replicates.

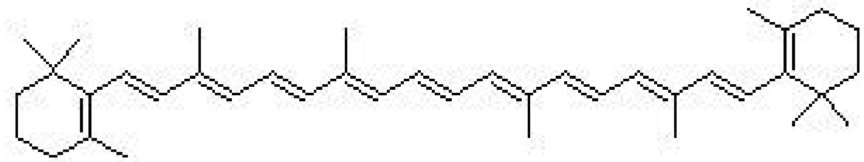
[a] Mixture of *cis*- and *trans*- isomers.

$\mu g.g^{-1}$ FW	Témoin	Isoxaflutole $32\ g.ha^{-1}$	Diflufénican $125\ g.ha^{-1}$
Phytoène	0	7,5	31,6
β Carotène	78,5	4,7 (6 %) *Dim 94%*	17,8
Xanthophylles	190,5	21,7 (11,4%) *Dim 88,6%*	42,4
Chlorophylles	1410,3	110,6 (7,8%) *Dim 92,2%*	345,6

⇨Accumulation phytoène = substrat de l'enzyme Phytoène désaturase (PDS), indétectable dans témoin

anthéraxanthine

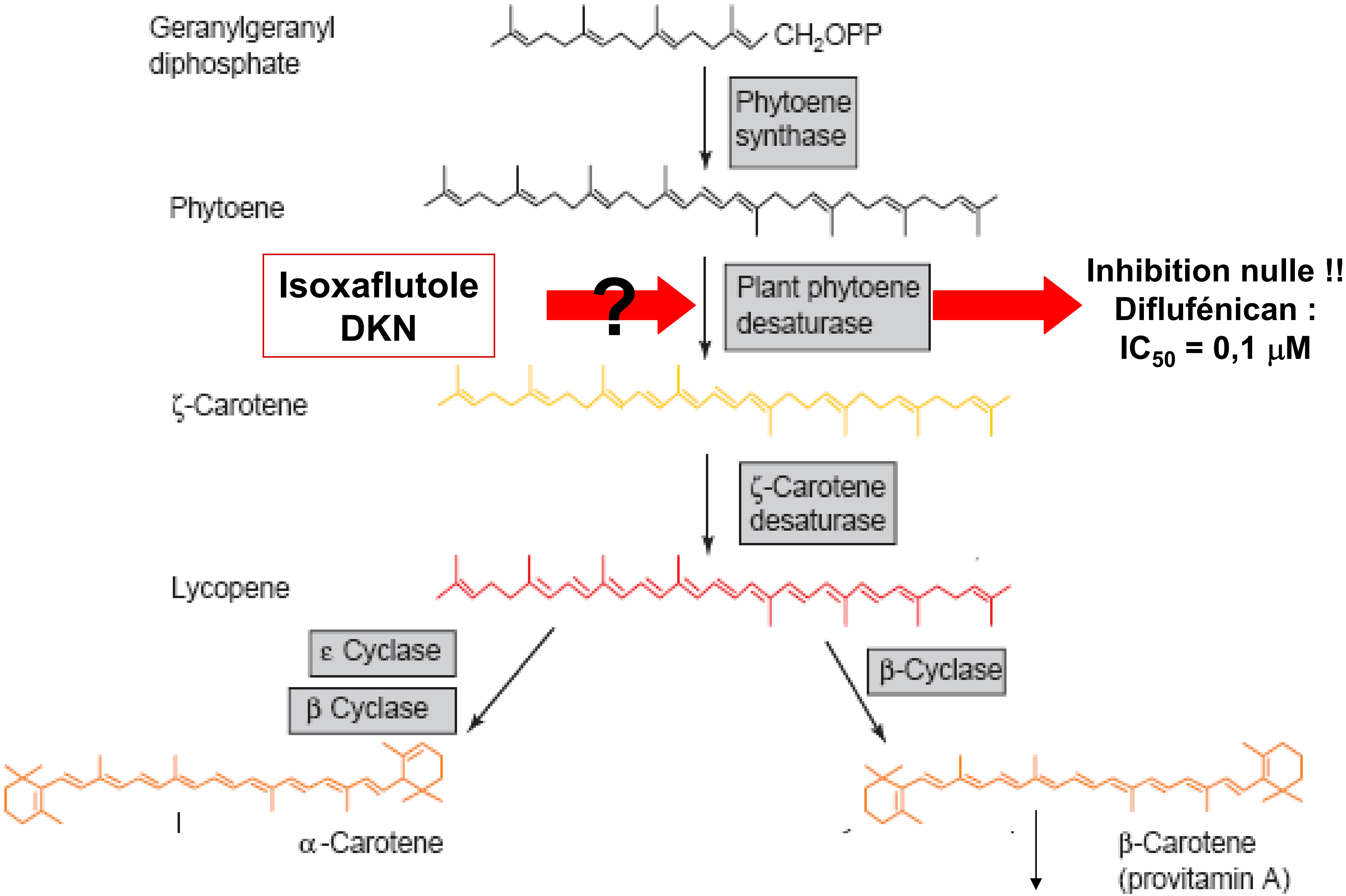
phytoène



β carotène

Herbicides / Pigments chloroplastiques

Herbicides inhibiteurs de la synthèse des caroténoïdes



Guliano et al., 2000

Xanthophylles

Isoxaflutole / Pallett *et al.* (1998)

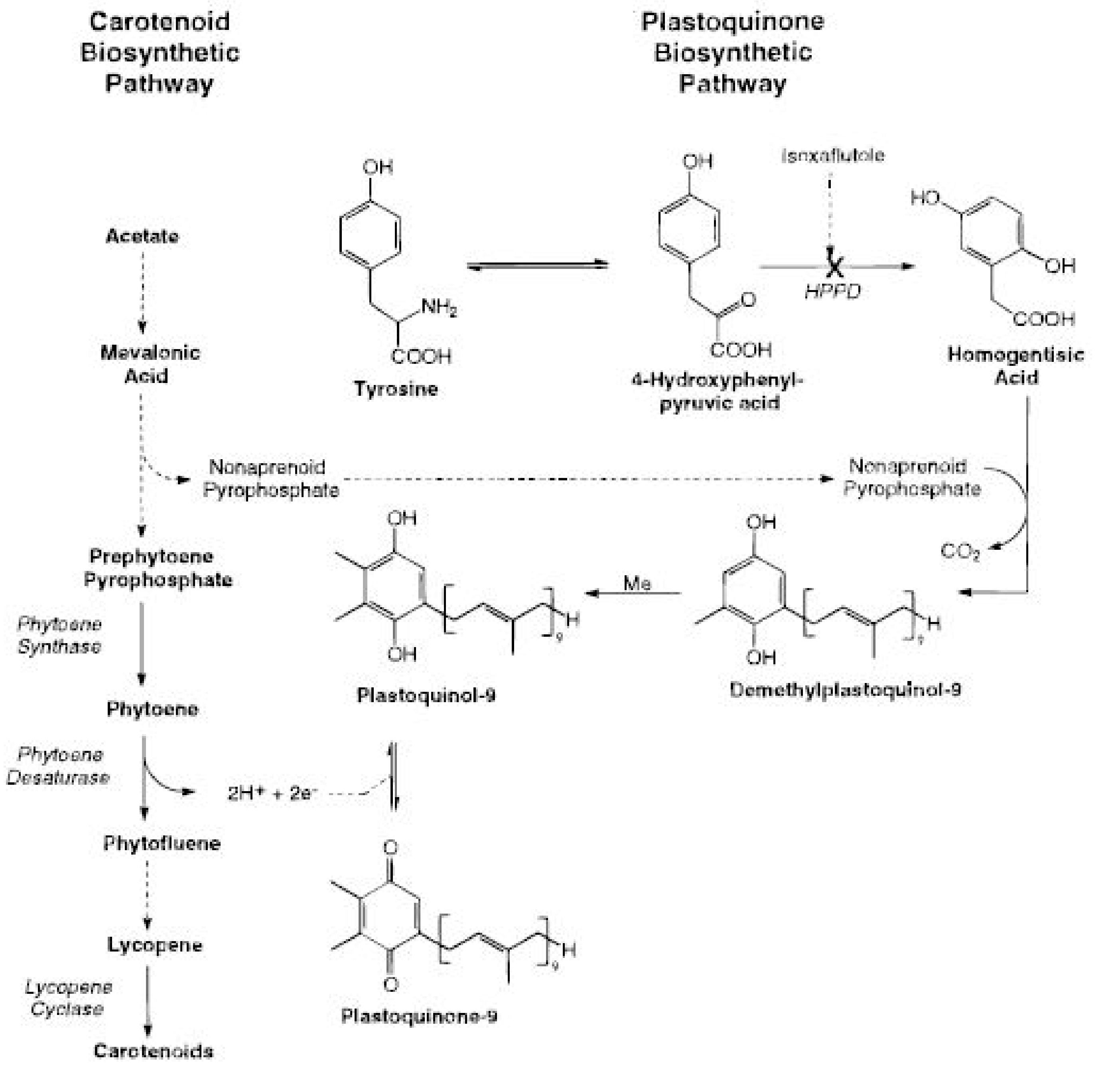


FIG. 6. The integration of the carotenoid and plastoquinone biosynthetic pathways.

Isoxaflutole / Pallett *et al.* (1998)

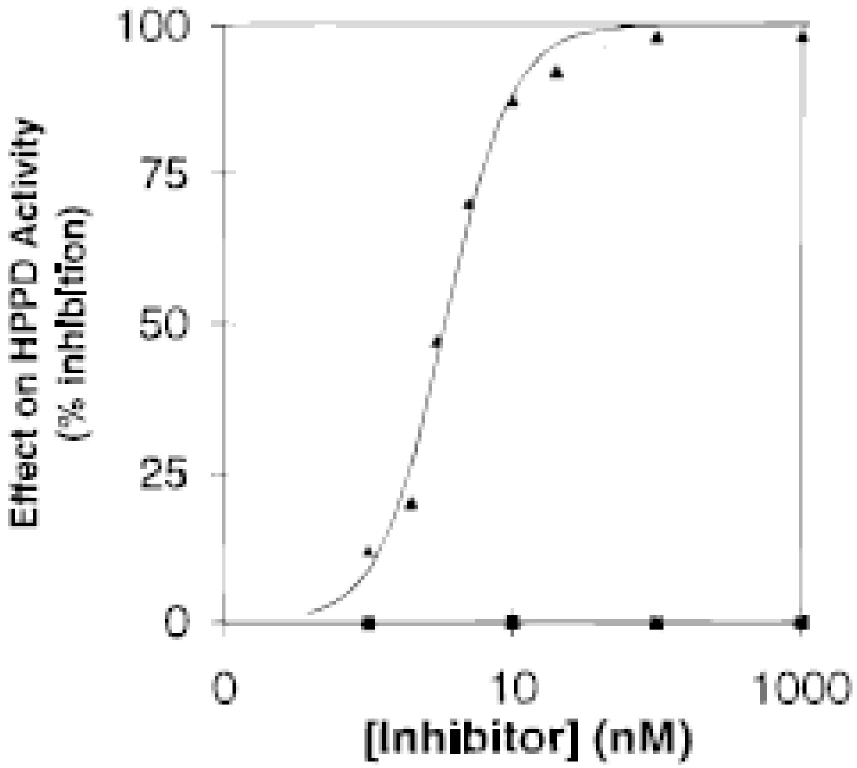


FIG. 4. The inhibition of carrot cell HPPD activity isoxaflutole (■) and by the diketonitrile derivative of isoxaflutole (▲). Enzyme activity was determined by measuring the accumulation of the product of the reaction, homogentisic acid, by its UV absorption after separation of reaction constituents by reverse-phase HPLC (9).

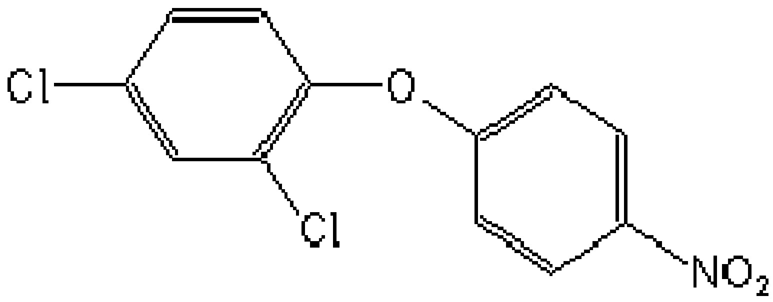
Test HPPD in vitro
⇨Effet nul de l'isoxaflutole
⇨DKN : IC $_{50}$ = 5 nM

Herbicides / Pigments chloroplastiques

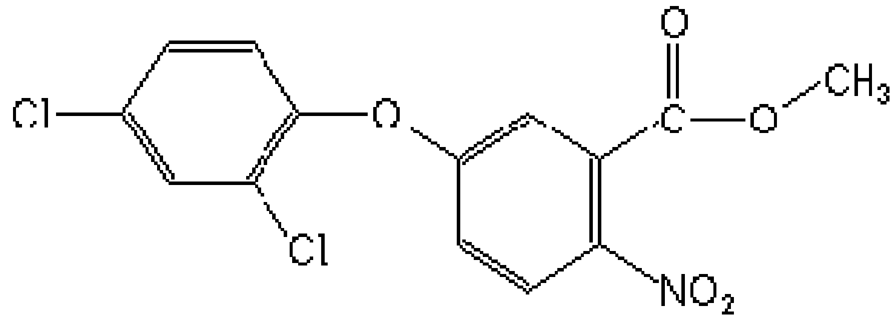
Herbicides inhibiteurs de la synthèse des chlorophylles

⇨Protox

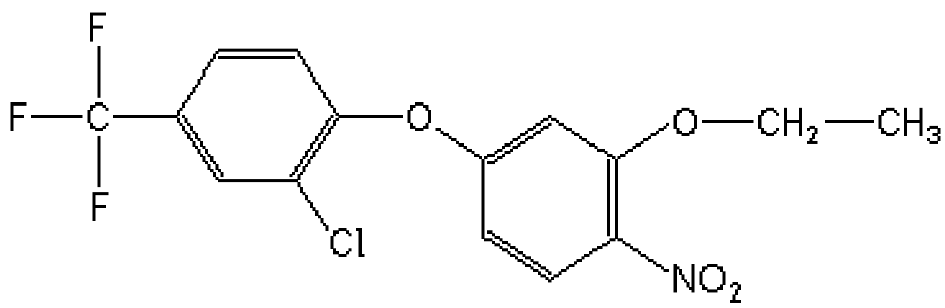
Diphényl-éthers



Nitrofene

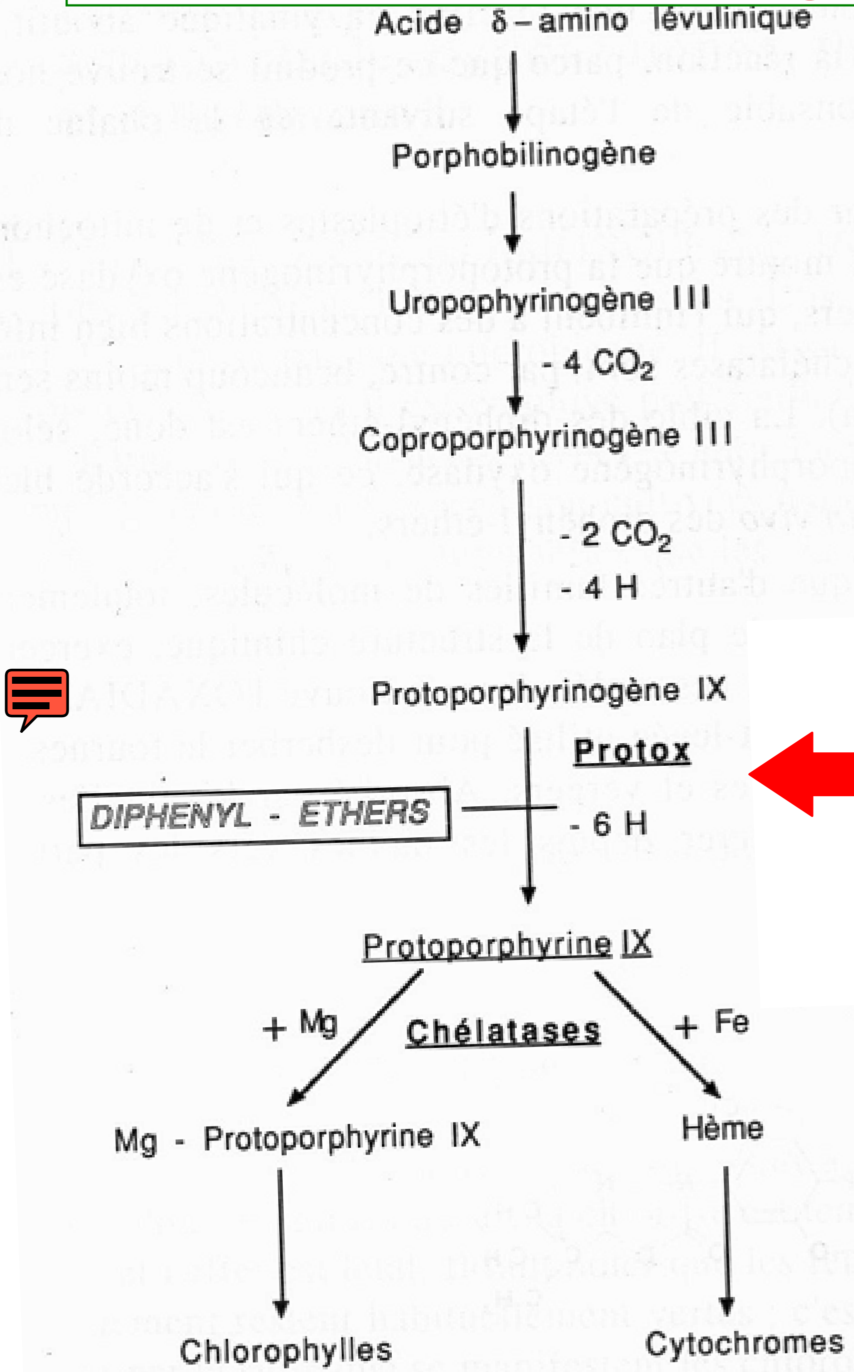


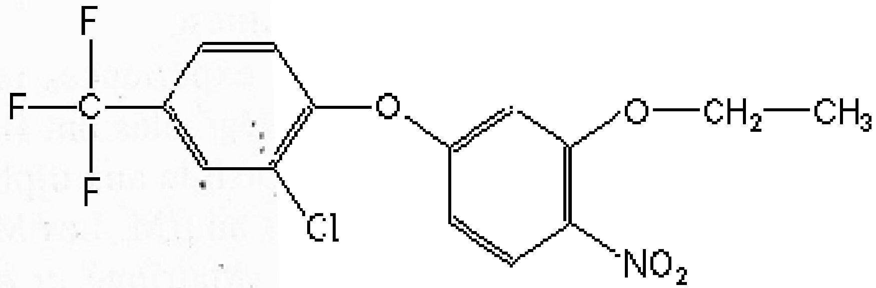
Bifenox



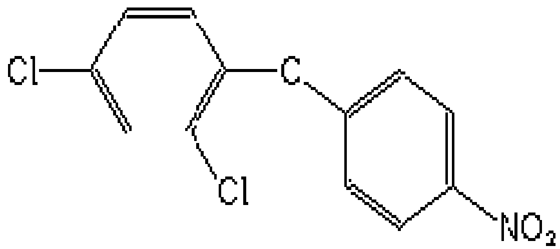
Oxyfluorfene

Herbicides / Pigments chloroplastiques

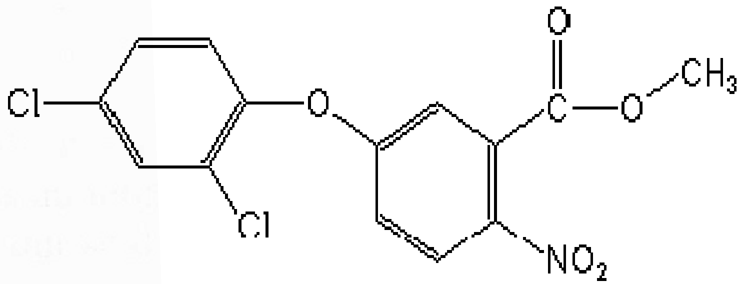




Oxyfluorfene



Nitrofene



Bifenox

Herbicide Resistance Action Committee
Classification of herbicides

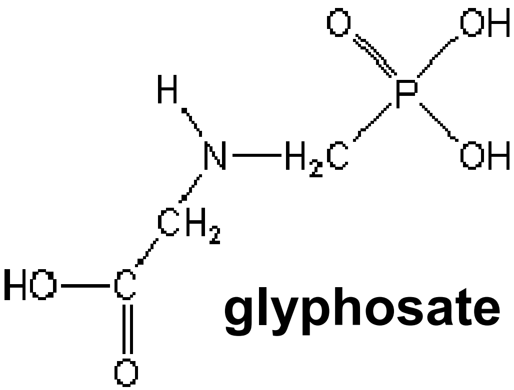
(Cf Autre système de classification **WSSA** "Weed Science Society of America »)

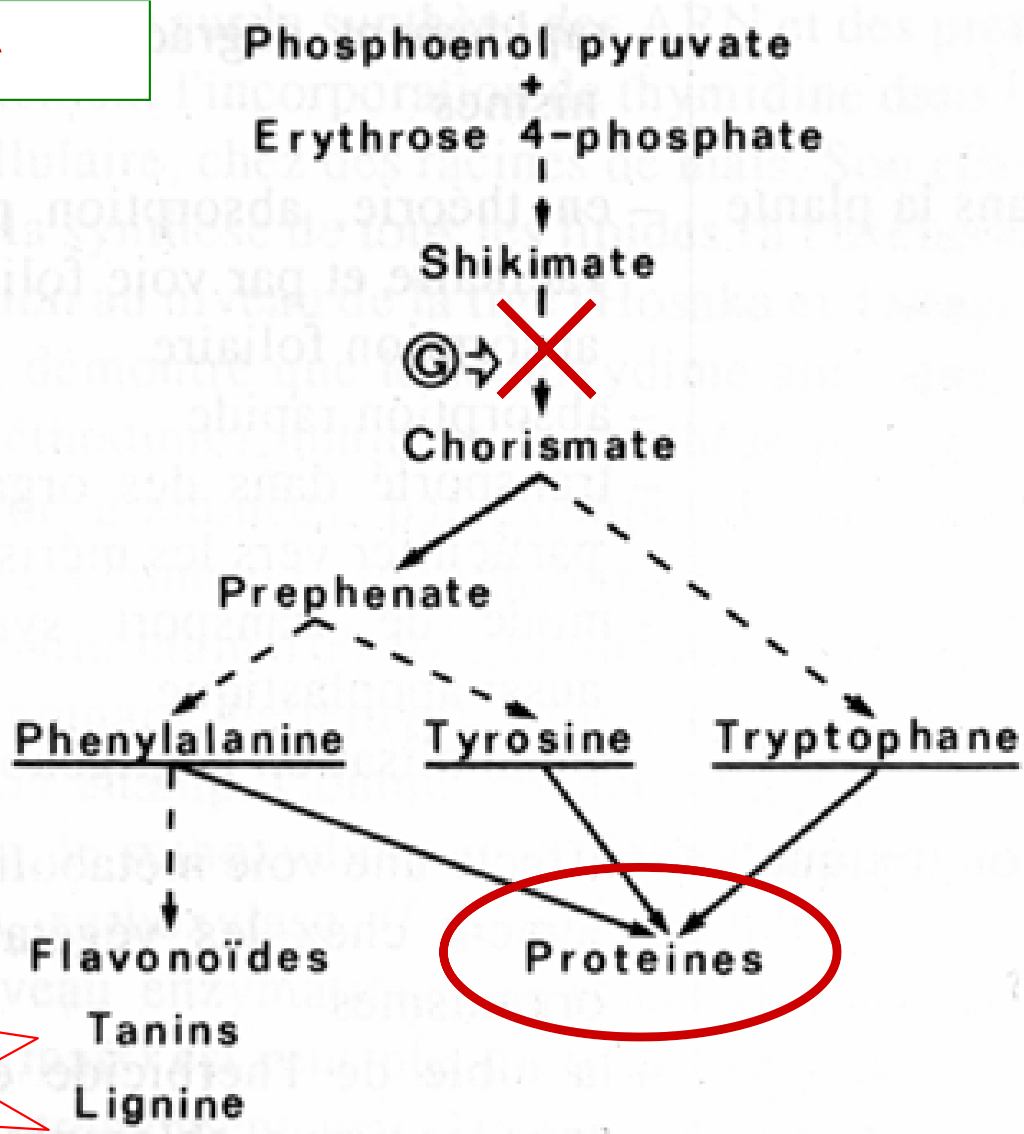
http://www.plantprotection.org/HRAC/ **http://www.wssa.net/**

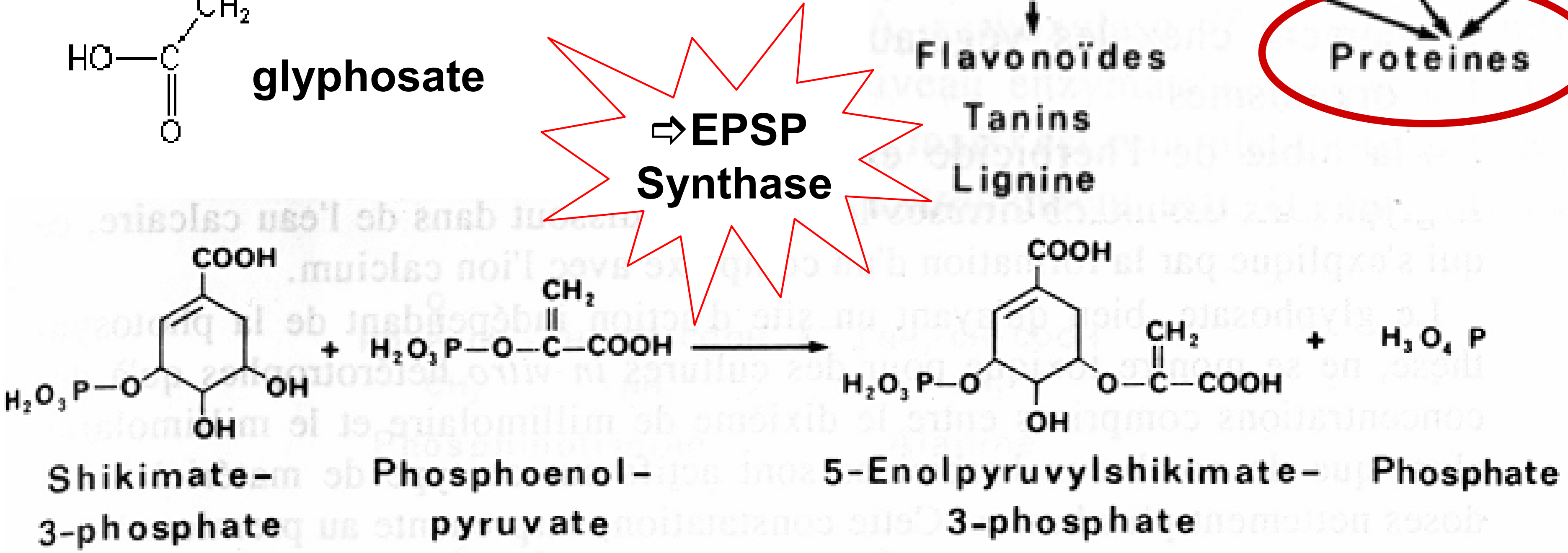
A (1) / Inhibition **ACCase**	**H (10)** / Inhibition **Glutamine Synthase**
B (2) / Inhibition **ALS** (AHAS)	**I (18)** / inhibition of **Dihydroptéorate (DHP) synthase**
C1 (5), C2 (7), C3 (6) / inhibition **PSII (prot. D1)**	**K1 (3), K2 (23),K3 (15)** / inhibition **divisions cellulaires** (microtubules, VLCFA)
D (22) / capture électrons **PSI**	**L (20, 21,26)** / inhibition synthèse **paroi cellulaire** (cellulose)
E (14) / inhibition **Protox**	**M (24)** / agents découplants (disruption membranaire)
F1 (12) / inhibition **Phytoène désaturase** (PDS)	**N (8, 26)** / inhibition synthèse lipides (sauf ACCase)
F2 (27) / inhibition **HPPD**	**O (4)** / herbicides auxiniques **P (19)** / inhibition transport auxine
G (9) / inhibition **EPSP Synthase**	**R,S,Z (17, 25 à 27)** / mode d'action inconnu

Herbicides / Acides aminés

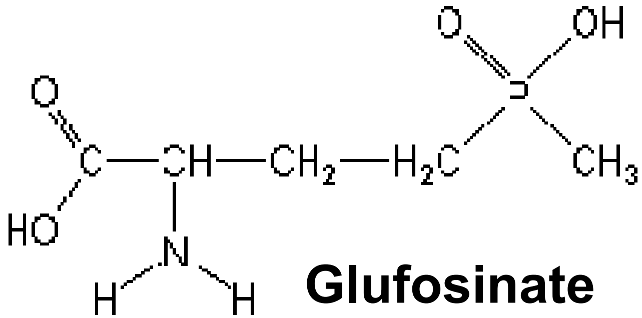
ROUNDUP 3Plus
Formulation : concentré à diluer
Composition : glyphosate (sel d'isopropylar
AMM : 9300241
Monsanto Agriculture France SAS, 69 Bror







Herbicides / Acides aminés



Glufosinate

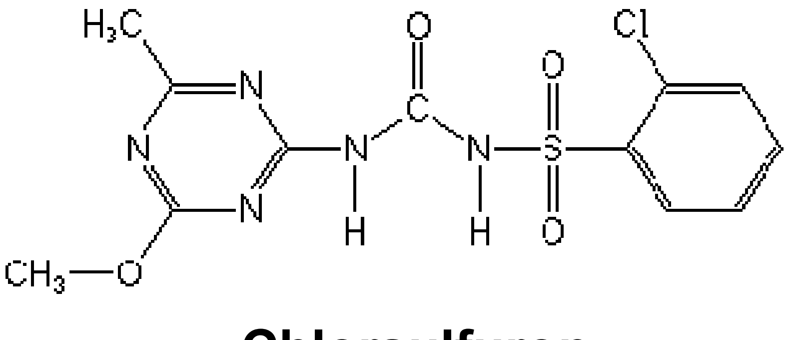
⇨Glutamine Synthétase

$$\begin{array}{l} COO^- \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CHNH_3^+ \\ | \\ COO^- \end{array} \quad + NH_4^+ + ATP \longrightarrow \begin{array}{l} CO\text{-}NH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CHNH_3^+ \\ | \\ COO^- \end{array} \quad + ADP + Pi$$

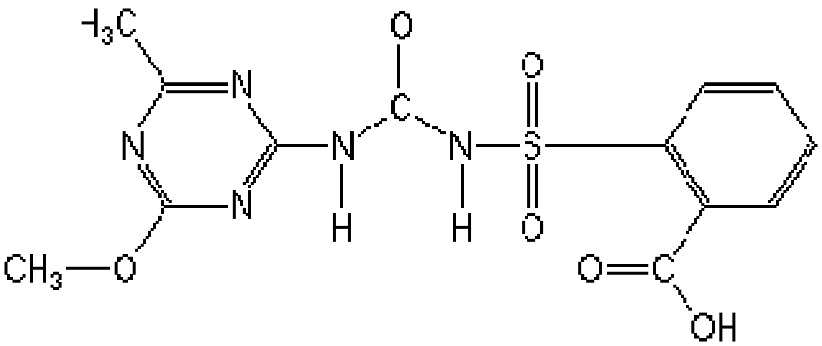
Herbicides / Acides aminés

⇨ **Acétolactate Synthase**

Sulfonylurées

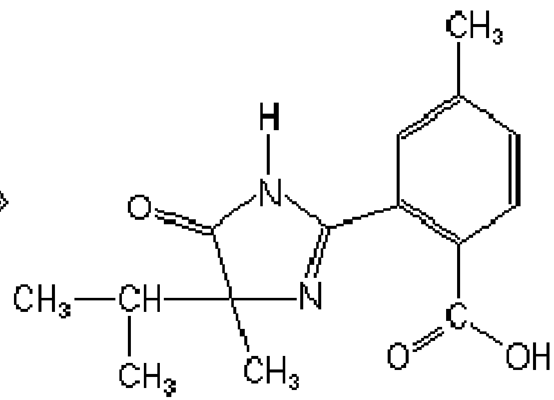


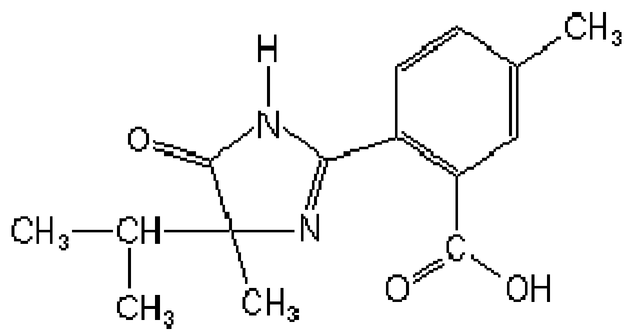
Chlorsulfuron



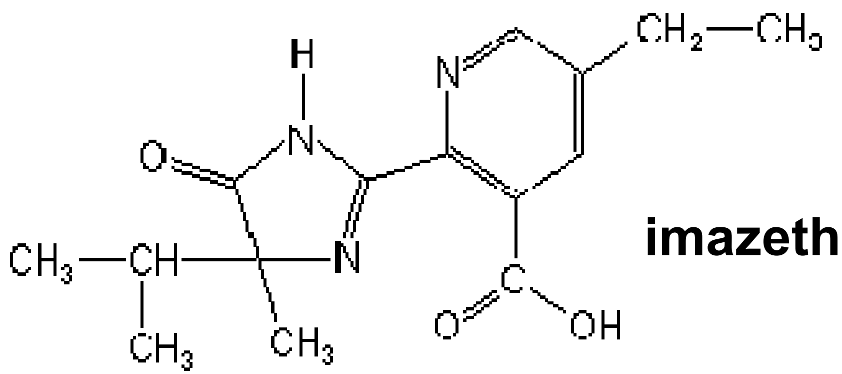
Metsulfuron

Imidazolinones





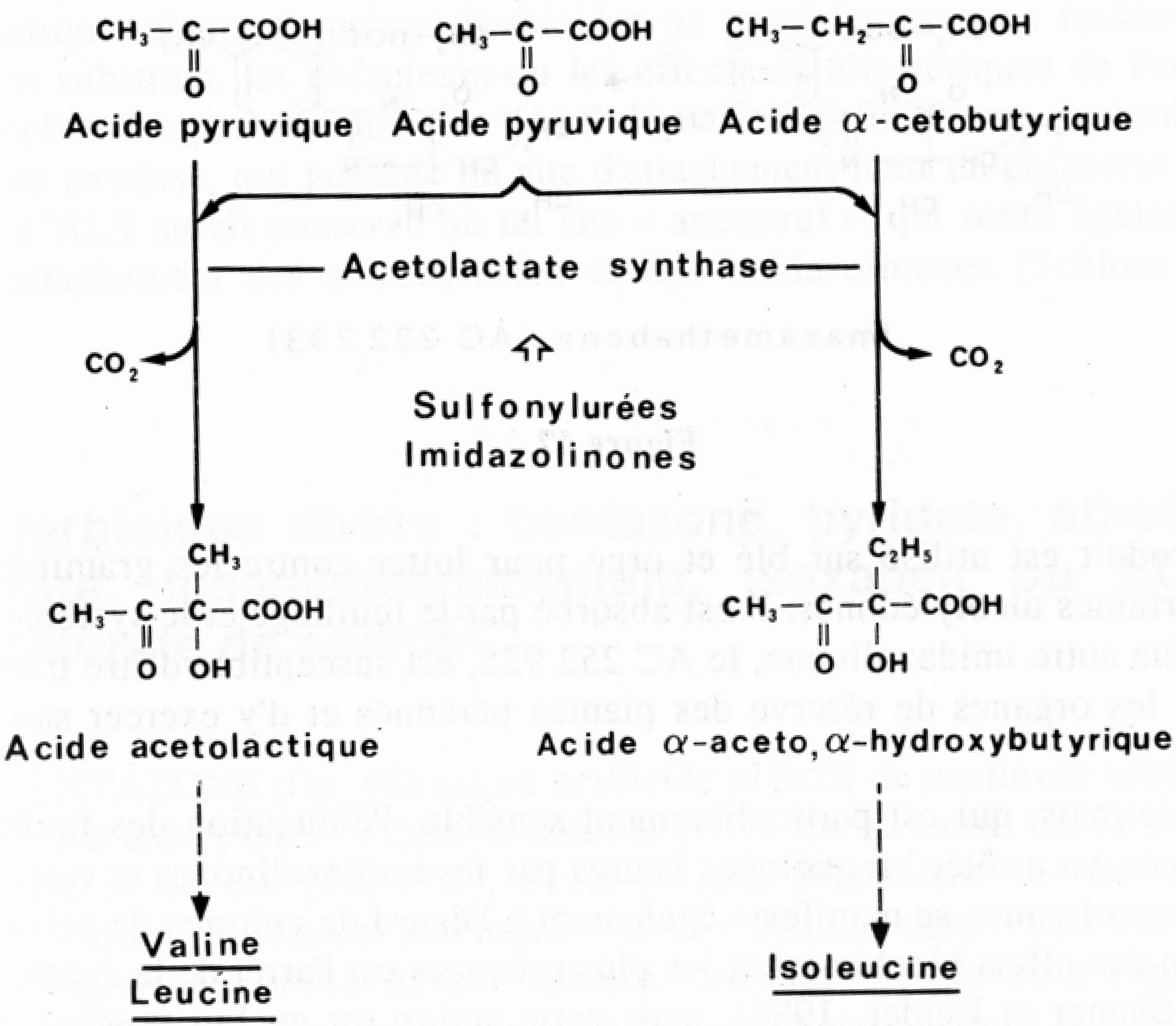
Imazamethabenz



imazethapyr

Herbicides / Acides aminés

⇨ALS



Acétolactate synthase (ALS) = acétohydroxyacid synthase (AHAS)

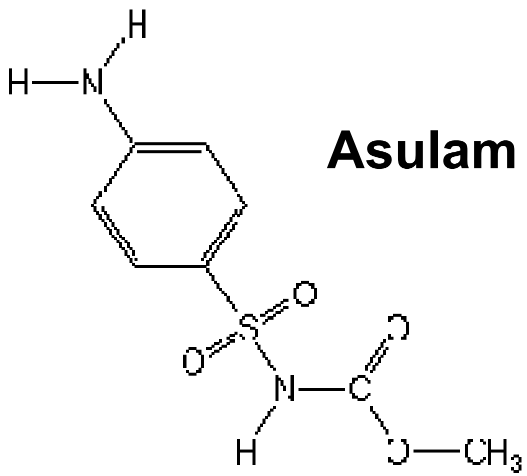
Herbicides / Divisions cellulaires

Herbicides antimitotiques

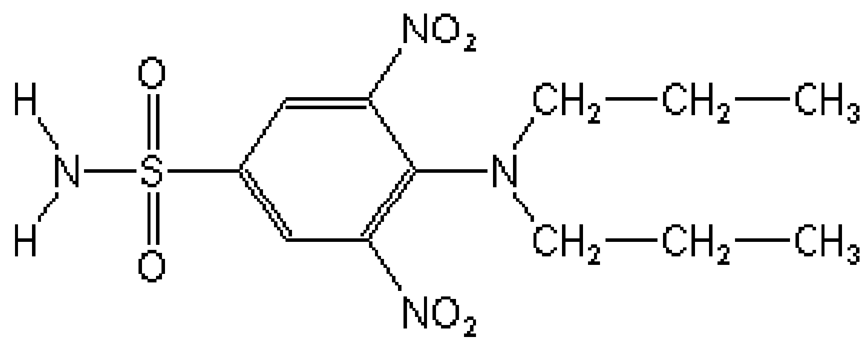
⇨ **tubuline**

Carbamates

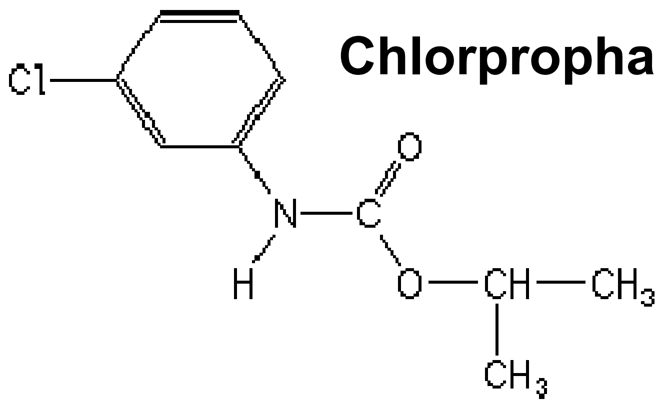
Dinitroanilines



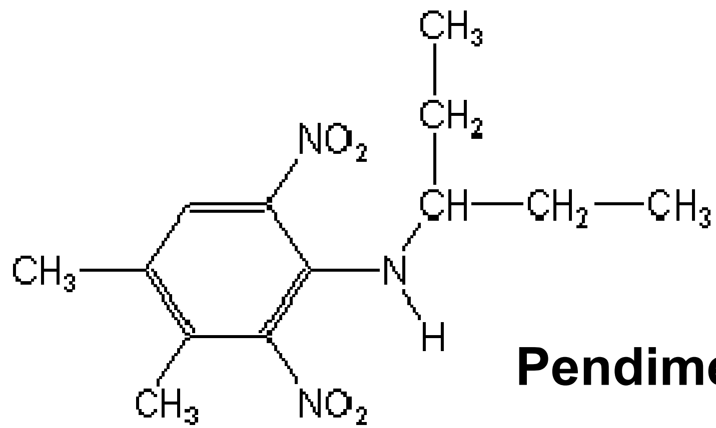
Asulam



Oryzalin

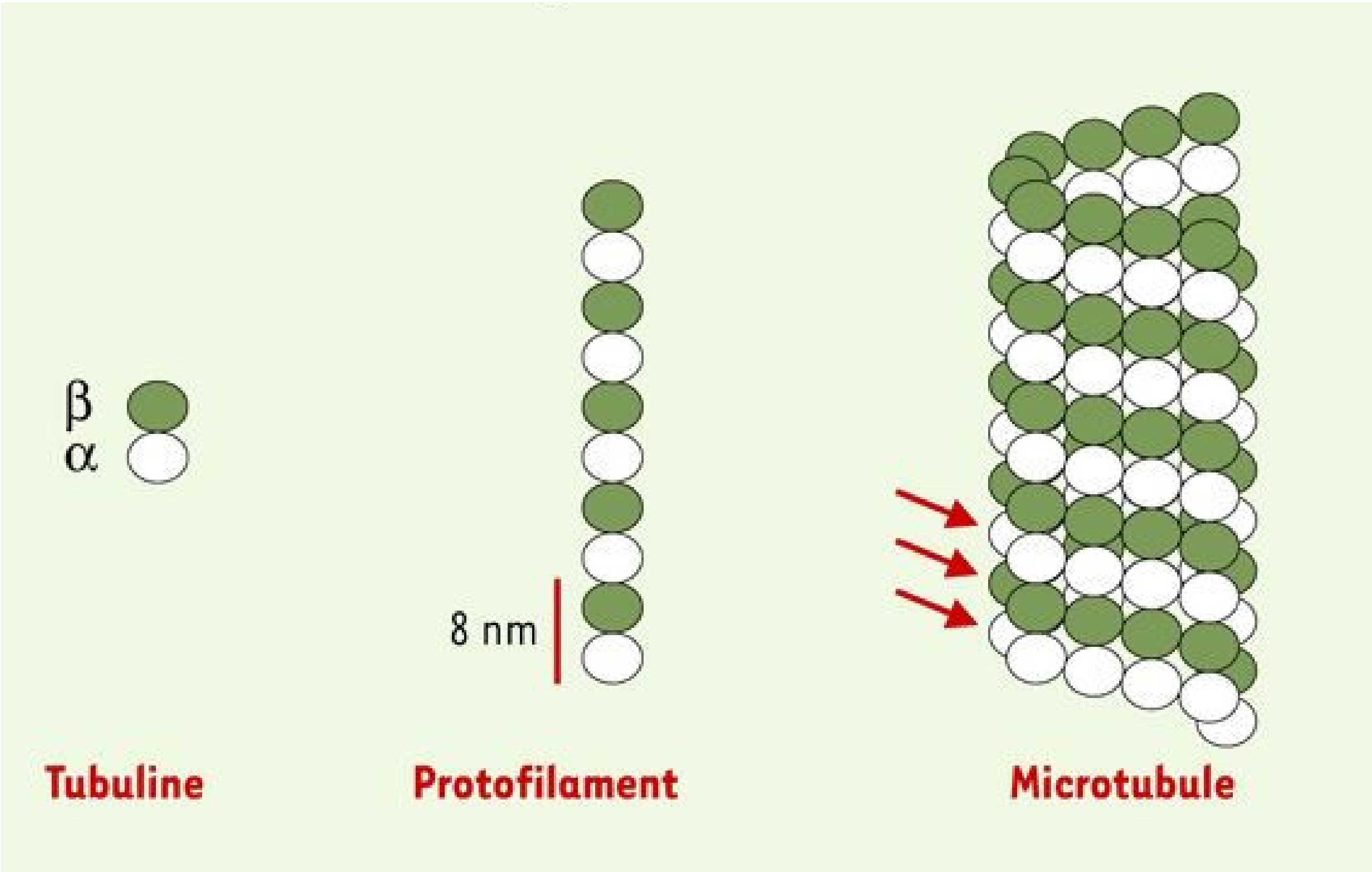


Chlorprophame



Pendimethalin

Herbicides / Divisions cellulaires



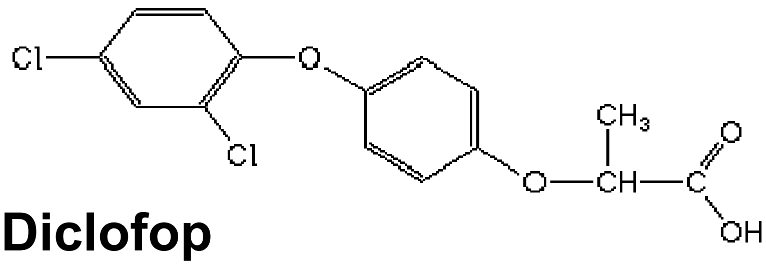
Herbicides / Acides Gras

« Fop's »

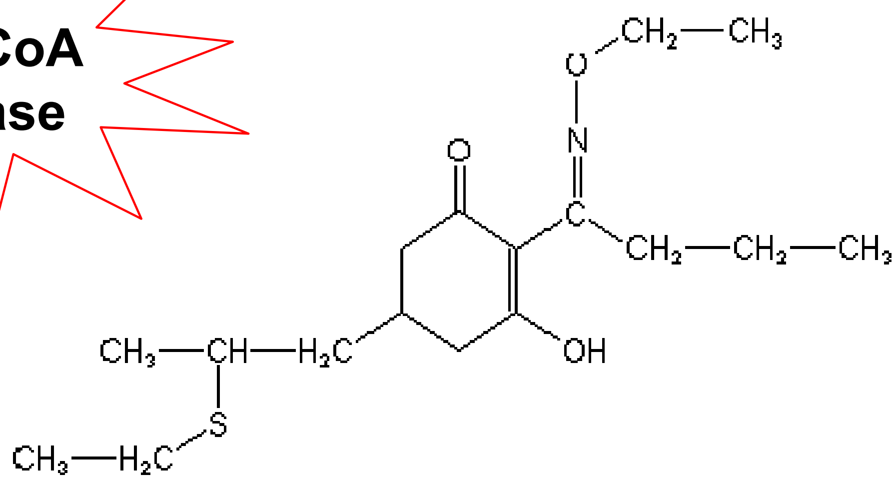
Aryloxyphenoxypropionates

⇨ Acétyl-CoA Carboxylase

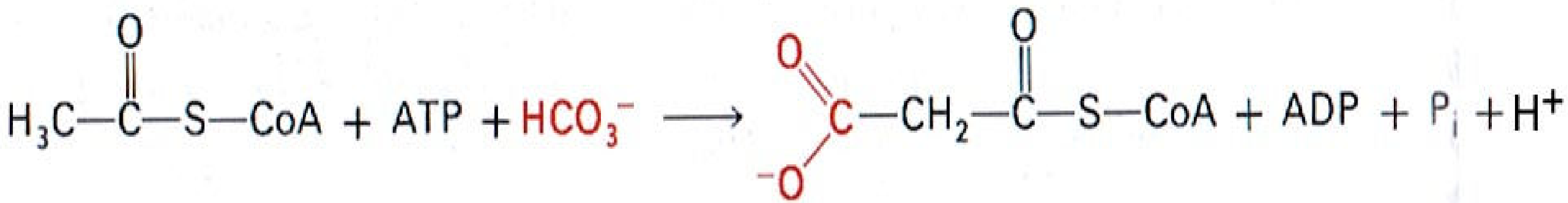
Cyclohexanediones



Diclofop



Sethoxydime

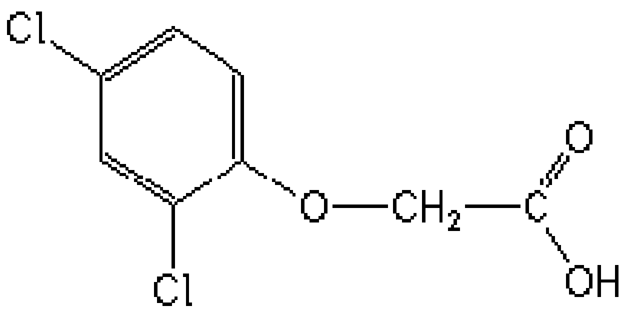


Acétyl CoA **Malonyl CoA**

Herbicides / Hormones végétales

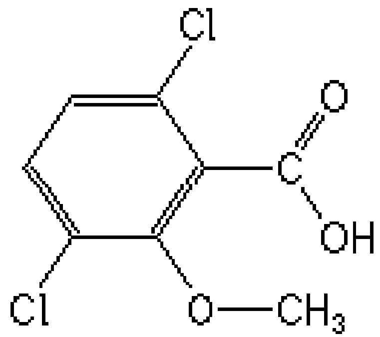
Herbicides auxiniques

Acides phénoxyacétiques



(2,4-dichlorophenoxy)acetic acid
= 2,4 D

Acides benzoïques



Dicamba

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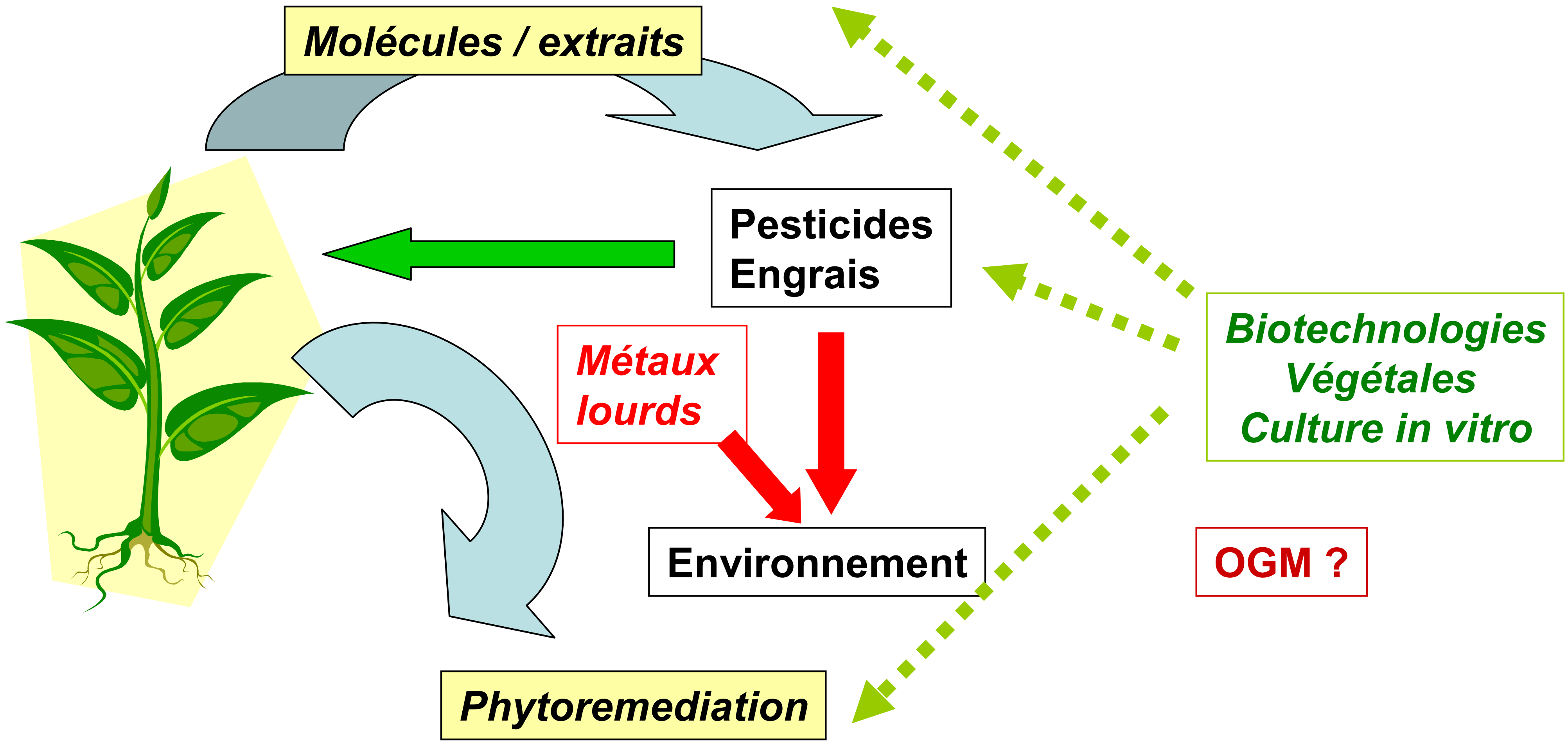

Molécules / extraits
Pesticides
Engrais
Métaux
lourds
Environnement
Phytoremediation
Biotechnologies
Végétales
Culture in vitro
OGM ?