Lecture

Inhibition of Pigment Synthesis (Bleaching Herbicides)

1. General Information

Pigments are compounds that strongly absorb light in certain regions of the visible spectrum. Wavelengths of light that are not absorbed are reflected back and therefore appear colored.

Chlorophyll makes plants appear green to the human eye because it is absorbing light in the blue and red spectrum and reflecting green light. Carotenoids are yellow/orange pigments that are almost always associated with chlorophyll. These pigments protect chlorophyll by dissipating the oxidative energy of singlet oxygen ($^1O_2$), i.e. the carotenoid serves as an antioxidant.

Other herbicide modes of action involve the formation of massive amounts of singlet oxygen that destroys plant tissues. Healthy plants undergoing normal rates of photosynthesis do produce some singlet oxygen in the process, and the carotenoids help to prevent any resulting damage.

The herbicides discussed here inhibit the formation of carotenoid pigments or carotenoid and chlorophyll pigments. In both cases, loss of carotenoid pigment results in photo-destruction of chlorophyll and bleaching (whitening) of plant tissue.

2. Mode of Action - Inhibition of Pigment Synthesis (Inhibition of Phytoene Desaturase)

Herbicides with this mode of action inhibit phytoene desaturase (PDS), a key enzyme necessary to produce carotene and carotenoid pigments. Synthesis of carotenoids is initiated from the mevalonic acid pathway. See Figure 8.1; page 2.

Because of the location of the phytoene $\rightarrow$ δ carotene conversion within the pathway (where PDS enzyme is inhibited), only carotenoid synthesis is affected. (see Figure 8.1; page 2)

Since carotenoids function to protect chlorophyll from photooxidation (carotenoids are destroyed chemically in response to singlet oxygen ($^1O_2$)), chlorophyll is indirectly destroyed. Plants truly run out of food reserves and die.

3. Site of Action – Inhibition of Pigment Synthesis (Inhibition of Phytoene Desaturase)

The herbicides in this group act at the chloroplast lamellae, the location of pigment synthesis.

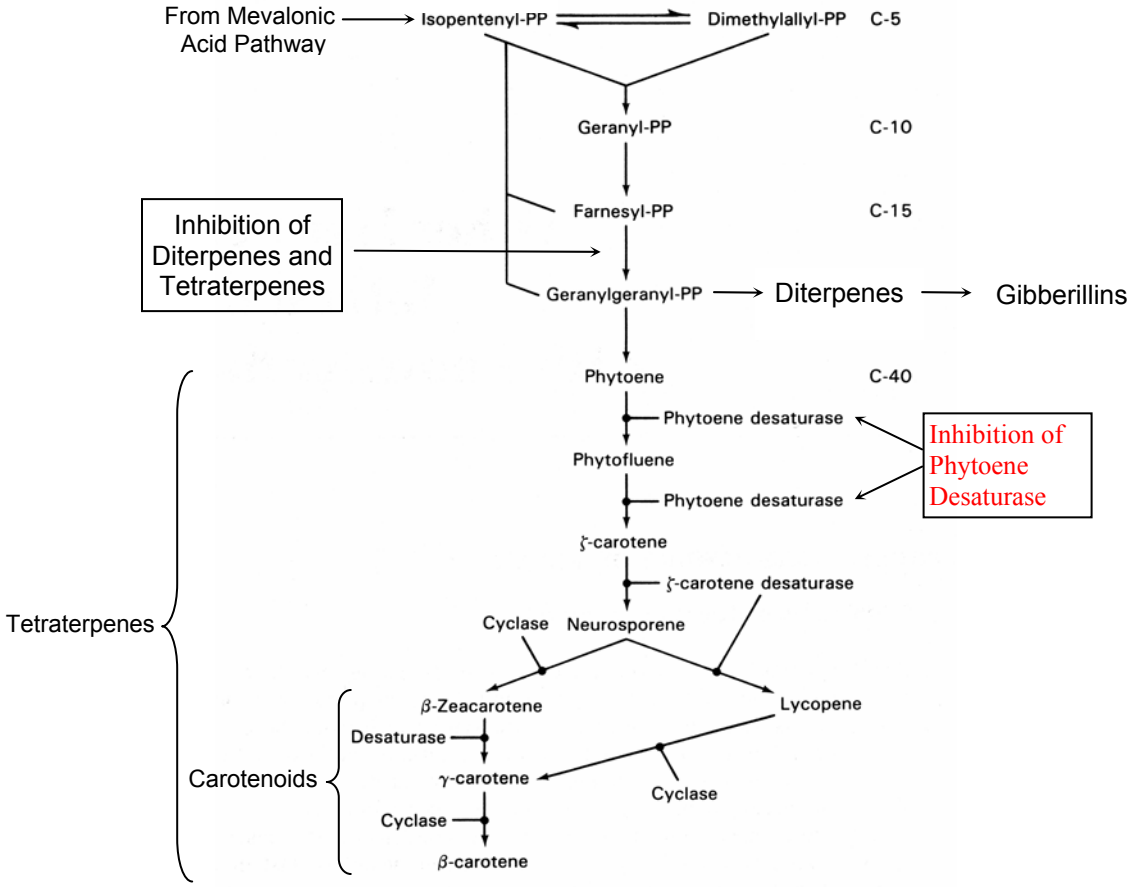


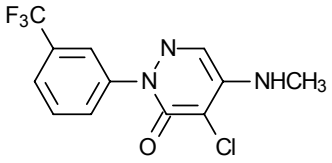
Figure 8.1 Pathway of plastidic carotenoid biosynthesis from mevalonic acid (MVA). The condensation phase from C-5 to C-40 is catalyzed by synthases. The reactions catalyzed by desaturases and by the cyclase are specifically marked.

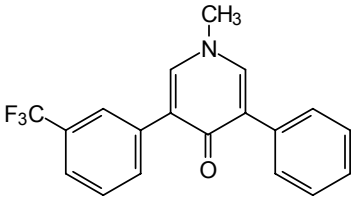
Source: Physiology of Herbicide Action. M.O. Devine, S.O.Duke, and C. Fedtke. 1993. Prentice Hall, NJ.

1. Symptoms – Inhibition of Pigment Synthesis (Inhibition of Phytoene Desaturase)

- bleaching or whitening of the plant – if applied to large weeds or to established vegetation around fields, bleaching is temporary
- veinal bleaching occurs (interveinal areas remain green) – this is because the herbicide has low water solubility and does not move out of the main veins into the interveinal areas of the leaf
- purple margins may be on susceptible plants
- necrosis – if plants are unable to recover

5. Herbicide Family – Inhibition of Pigment Synthesis (Inhibition of Phytoene Desaturase)

Pyridazinones		
Example	 norflurazon (Zorial, Solicam)	phenyl ring bonded to the 2-position of a pyridazinone ring (a 6 member ring with 2 adjacent N's at the 1- and 2-positions; C's at the other 4 positions of the ring and an O bonded to the C at the 3-position; another pyridazinone, pyrazon (Pyramin), inhibits photosynthesis at PS II (see page 55)
Metabolism	plant – not known soil – microbial half-life – 45-180 d	
Absorption & Translocation	absorbed readily by roots and translocated acropetally in the xylem	
Selectivity	selective – not known	
Herbicide Use	controls grasses, sedges, and broadleaf weeds used PRE in almonds, apples, apricots, avocados, blackberries, blueberries, cherries, hops, rights-of-ways, citrus, cotton, peanuts, ornamentals	

Non-family		
Example	 fluridone (Sonar)	aquatic herbicide used to control submersed and emersed vascular plants in ponds, lakes, and drainage canals
Metabolism	plant – not metabolized appreciably soil – microbial and photodegradation half-life – 20 d (aerobic pond water); 9 months (anaerobic pond water); 90 d (hydrosoil)	

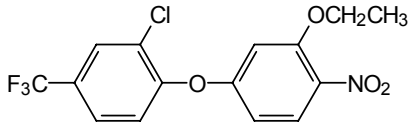
Absorption & Translocation	absorbed from water by plant shoots and from hydrosoil by roots translocation from roots upward
Selectivity	selective – not known; differential metabolism??
Herbicide Use	aquatic herbicide can be applied to water surface or subsurface or as a bottom application in ponds, lakes, reservoirs, drainage canals, irrigation canals, rivers symptoms: white or pink growing points 7 to 10 d; 30-90 d required before weeds die; does not control algae and floating aquatics, and cattails are partially affected

6. General Comments – Inhibition of Pigment Synthesis (Inhibition of Phytoene Desautrase)

Norflurazon was first synthesized by Ebner and Schuler in Belgium. It was introduced for agricultural use in the U.S. in 1968.

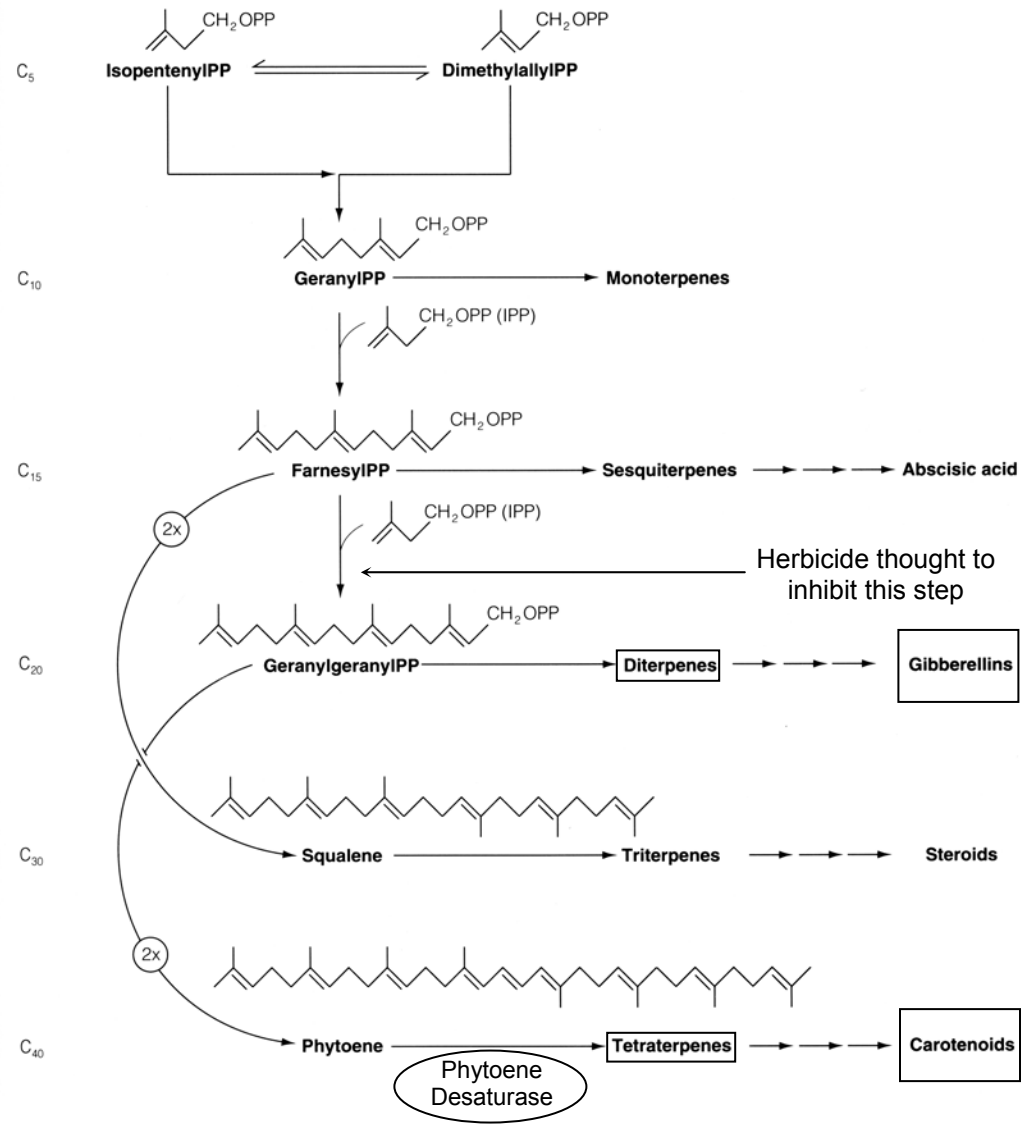
In contrast to norflurazon (Zorial/Solicam), the pyridazinone herbicide pyrazon (Pyramin) is a photosynthesis inhibitor.

There is some disagreement on the mode of action of oxyfluorfen, a diphenylether herbicide. Some authorities classify it as a PPOase inhibior, while others claim it is a carotenoid biosynthesis inhibitor that acts similar to norflurazon. For the latter hypothesis, the difference in mode of action from other diphenyethers is attributed to the lack of a carboxyl group attached to the diphenylether base structure.



oxyfluorfen (Goal)

7. Mode of Action – Inhibition of Pigment Synthesis (Inhibition of Diterpenes and Tetraterpenes)



Source: Taiz, L. and E. Zeiger. **Plant Physiology**. 1991. Benjamin Cummings Publishing, CA.

Herbicides with this mode of action inhibit formation of diterpene and tetraterpene compounds in the plant. Herbicides act in the same pathway (mevalonic acid) discussed previously for the phytoene desaturase inhibitors. Diterpenes in plants are precursors to gibberellins.

Tetraterpenes are the precursors to beta carotene (carotenoids). Herbicides block the conversion from farnesyl-pyrophosphate → geranylgeranyl-pyrophosphate, but the specific

enzyme is unknown. This step in the pathway is much earlier than described for the phytoene desaturase inhibitors and consequently carotenoid synthesis is inhibited.

In addition, the conversion of farnesyl-pyrophosphate → geranylgeranyl-pyrophosphate prevents production of diterpenes. One diterpene that is not produced is gibberellic acid, which explains the stunting of plants treated with these herbicides. Also, phytol (a diterpene) is a component of the "tail" of chlorophyll molecules, hence chlorophyll production is also inhibited.

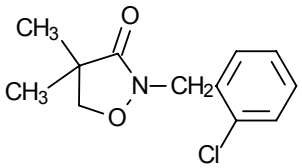
8. Site of Action – Inhibition of Pigment Synthesis (Inhibition of Diterpenes and Tetraterpenes)

The herbicides in this group act at the chloroplast lamellae, the location of pigment synthesis. The precise enzyme(s) inhibited is unknown.

9. Symptoms – Inhibition of Pigment Synthesis (Inhibition of Diterpenes and Tetraterpenes)

- bleaching or whitening of the plant – if applied to large weeds or to established vegetation around fields, bleaching is temporary
- interveinal bleaching occurs – this is because the herbicide has high water solubility and moves readily out of main veins into the interveinal area of the leaf.
- purple margins may be seen on susceptible plants
- stunting of plants
- necrosis if plants are unable to recover

10. Herbicide Family – Inhibition of Pigment Synthesis (Inhibition of Diterpenes and Tetraterpenes)

Isoxazolidinones		
Example	 clomazone (Command, Commence)	a bleacher herbicide; volatility issue with past problems in Midwest, Arkansas, and Tennessee; "tells on you"; formulation was changed from an EC to a micro-encapsulated (ME) formulation to address the volatility issue

Metabolism	plant – oxidative cleavage soil – microbial half-life – 24 d
Absorption & Translocation	readily absorbed by roots and shoots (grass coleoptiles and broadleaf hypocotyls) and translocated in xylem to foliage not highly absorbed when applied to foliage; translocated poorly in phloem
Selectivity	selective – not known; differential metabolism??
Herbicide Use	controls grasses and broadleaf weeds used PRE or PPI in soybeans, peppers, succulent peas, sweet potatoes, sugarcane, rice control of velvetleaf is why the herbicide is popular in the Midwest

11. General Comments – Inhibition of Pigment Synthesis (Inhibition of Diterpenes and Tetraterpenes)

Clomazone was developed in the early 1980's and sold commercially as Command in 1985. It has since gained registration for use on numerous crops in the U.S.

12. Mode of Action – Inhibition of Pigment Synthesis (Pigment Inhibitors with Unknown Target Site)

This mode of action is represented by only one herbicide, amitrole. The enzyme inhibited is not known, but it is presumed to work on one of the earlier steps in the terpene synthesis pathway.

Phytoene, carotenes, lycopene, and phytofluene all accumulate, indicating that any number of enzymes may be involved. Carotenoid synthesis is not strongly inhibited, and it has been proposed that amitrole has several modes of action including inhibition of catalase (the enzyme responsible for breaking down toxic hydrogen peroxide), inhibition of histidine synthesis (histidine is an amino acid), and inhibited purine synthesis (purines are basic components of nucleic acids in RNA and DNA).

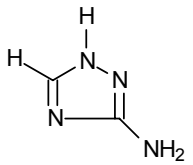
13. Site of Action – Inhibition of Pigment Synthesis (Unknown Target Site)

The site of action is not truly known. Many sites may actually be involved.

14. Symptoms – Inhibition of Pigment Synthesis (Unknown Target Site)

- bleaching in leaves and shoots – primarily in meristems and developing leaves
- wilting and necrosis in treated plants

15. Herbicide Family – Inhibition of Pigment Synthesis (Unknown Target Site)

<table>
<tr><td colspan="3">Triazoles</td></tr>
<tr><td>Example</td><td> 
amitrol (Amitrol, Amizol)</td><td>Restricted Use Pesticide (oncogen); 5 member ring with 3 N’s and 2 C’s</td></tr>
<tr><td>Metabolism</td><td colspan="2">plant – conjugation
soil – not available
half-life – 14 d</td></tr>
<tr><td>Absorption & Translocation</td><td colspan="2">rapid absorption by roots and leaves

highly mobile in xylem and phloem</td></tr>
<tr><td>Selectivity</td><td colspan="2">non selective – weed response due to differential metabolism, herbicide placement, and dosage</td></tr>
<tr><td>Herbicide Use</td><td colspan="2">controls annual and perennial grasses and broadleafs
used POST in noncrop areas, railroad rights-of-ways, roadsides, fence rows, utility installation
PD in hardwood nurseries</td></tr>
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16. General Comments – Inhibition of Pigment Synthesis (Unknown Target Site)

Amitrol was first reported in 1953 and introduced to the U.S. by Union Carbide in 1954.

17. References

Ahrens, W. Herbicide Handbook, seventh edition. 1994. Weed Science Society of America, Champaign, IL.

Anderson, W.P. Weed Science – Principles and Applications, third edition. 1996. West Publishing, NY.

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