Understanding the Mode of Action of Selected Herbicides

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Herbicides are widely used in agriculture and landscape management. Most contemporary herbicides are organic molecules, i.e. contain carbon. These molecules vary in size, shape and elemental composition. The mode of action of a herbicide is fundamentally related to its specific molecular structure. The chemical structure of the herbicide molecule affects the distribution of electrons, hence negative charge, within the molecule. Certain structures, called aromatic or conjugated, possess unusual stability because electrons can be delocalized, and such molecules or their aromatic components may be less reactive than other molecules without aromatic moieties (McMurray 1988).

Herbicides act by interfering with plant growth. Plant growth implies cell division through biochemical processes, such as production of sugars via photosynthesis, synthesis of proteins from amino acids, and synthesis of nucleic acids. These biochemical processes are regulated by naturally occurring hormones, such as auxin. Herbicide molecules interact with the biochemical mechanisms within the plant. Many herbicides in use interfere with only one step of a biochemical pathway, while others have more general biochemical effects. To be bioactive, herbicide molecules must be able to react with biochemical mechanisms in the target plant. It follows that some herbicides could owe their activity to their similarity with naturally occurring plant compounds.

Three fundamental principles guide reactions in organic chemistry, as can be seen in a study of that subject (McMurray 1988). They are steric effects, inductive effects, and resonance. Steric effects refer to the shapes of the reacting molecules. Presence of side chains or rings may allow either a fit with another molecule, or may block approach, thus preventing reaction. Inductive effects refer to the amount and placement of negative charge within the molecule. Such negative charge may cause a herbicide molecule to be attracted to a receptor molecule within a plant. Resonance refers to the stability of reactants or products in a given reaction, and helps determine whether a reaction is energetically favorable. We now review these three fundamental principles as they apply to specific herbicides. For simplicity we consider each of these principles separately, although all three may be involved in a given chemical reaction.

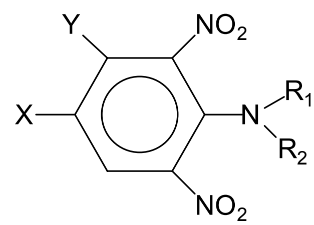
Because of steric considerations, herbicides with similar structures could be expected to have similar modes of action, since they would likely react with the same receptor. Herbicides within certain chemical classes often do have the same mode of action for this reason. An example may be seen in Figure 1, showing the similarity of structure among three dinitroaniline herbicides, all of which interefere with cell division by blocking tubulin synthesis (Cremlyn, 1991). Similarly, the pryidine herbicides clopyralid and picloram have a similar mode of action and similar physicochemical properties (Cremlyn, 1991) (see also "Clopyralid Problems in Mulch and Compost" in these proceedings).

Because of inductive considerations, a herbicide molecule may interact with a receptor molecule within the plant. Location of either full or partial negative charges can be similar to a naturally occurring molecule. This can be seen in Figure 2, where we compare the placement of a full negative and partial negative charges on indole-3-acetic acid, a naturally occurring auxin, with a placement of charges on 2,4-D (Cremlyn, 1991). That herbicide acts as an auxin mimic, stimulating the plant to produce RNA and causing growth abnormalities (Cremlyn, 1991). The cupping and twisting of 2,4-D-affected plants are familiar to people who have used 2,4-D or similar herbicides.

Resonance can confer stability to herbicides or their reaction products. Conversely, the lack of resonance contributors can affect the reactivity of a herbicide molecule. Glyphosate is chemically classified as an organophosphorus (OP) compound, yet it does not have the insecticidal activity or toxicity associated with the organophosphate insecticides. The reason is that although glyphosate has an OP structure at its center, the bond between P and CH_2 (Figure 3) does not readily cleave. In many OP insecticides an aromatic moiety is connected to the P atom, and because electron density can be taken and shared within the aromatic structure, the molecule cleaves easily—an essential feature of OP insecticide compounds (Cremlyn, 1991).

The three principles of steric effects, inductive effects, and resonance are responsible for the similarities among herbicides in their several chemical classes, and for the biochemical interactions of the herbicides themselves. Plant resistance can at times be overcome by switching to a herbicide with a different mode of action, and thus interacts with a different biochemical pathway. On the other hand, it may be possible to substitute a herbicide within the same chemical class to achieve cost savings or because of regulatory issues.

Figure 1. Three dinitroaniline herbicides are used to illustrate structural similarities in a herbicide chemical class.



	X	Y	R1	R2
Oryzalin	SO_2NH_2	H	CH_3H_7	CH_3H_7
Pendimethalin	CH_3	CH_3	H	$CH(C_2H_5)_2$
Trifluralin	F_3C	H	CH_3H_7	CH_3H_7

Figure 2. Distances are similar between partial and full negative charges in indole-3-acetic acid, a naturally occurring auxin shown at left, and 2,4-D shown at right.

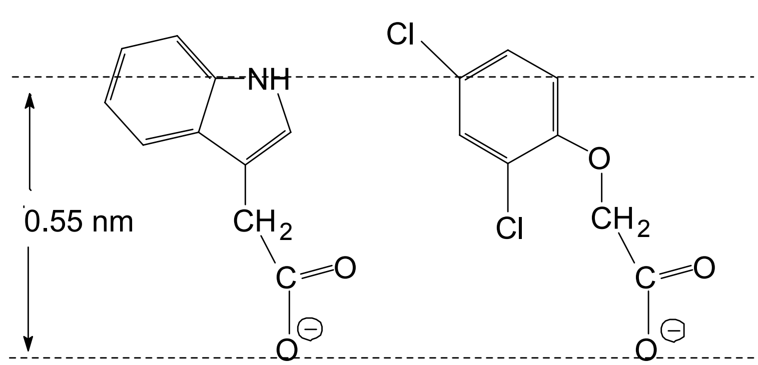
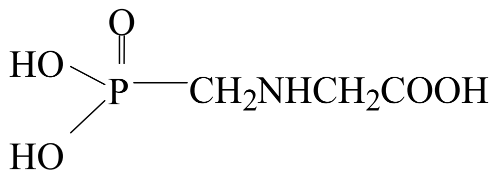


Figure 3. The structure of glyphosate.



References

Cremlyn, R.J. 1991. Agrochemicals: Preparation and mode of action. Wiley & Sons.

McMurray, J. 1988. Organic Chemistry, second edition. Brooks/Cole Publishing Co., Pacific Grove, CA.