

Aminopyralid and Clopyralid Absorption and Translocation in Canada Thistle (*Cirsium arvense*)

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Aminopyralid is a new auxinic herbicide that provides Canada thistle control at lower use rates than clopyralid. Studies were conducted to determine if differences in absorption, translocation, or metabolism account for aminopyralid's greater biological activity. Radiolabeled aminopyralid and clopyralid were applied to individual leaves of rosette-stage Canada thistle plants. Nonionic surfactant was used for the absorption studies because it provided higher aminopyralid absorption than methylated seed oil or crop oil concentrate. Clopyralid was absorbed very rapidly, reaching 72% 24 h after treatment (HAT) and remaining near or above 80% during a 192-h time course. During the same time period, aminopyralid absorption increased from 34 to 60%. Clopyralid translocation out of the treated leaf was significantly higher than aminopyralid, 39% compared with 17%, respectively, 192 HAT. More of applied clopyralid translocated to aboveground tissue 192 HAT (27%) than to roots (12%), whereas aminopyralid translocation was similar in aboveground tissue (10%) and roots (7%) 192 HAT. Neither aminopyralid nor clopyralid was metabolized 192 HAT. Although aminopyralid is effective at lower use rates than clopyralid, clopyralid absorption and translocation were higher in Canada thistle. These results suggest that aminopyralid's chemical structure may provide for greater biological activity at the target site than clopyralid.

Nomenclature: Aminopyralid; clopyralid; Canada thistle, *Cirsium arvense* (L.) Scop. CIRAR.

Key words: Auxinic herbicides, metabolism, herbicide physiology.

Canada thistle is an aggressive perennial weed that causes severe problems in crop, rangeland, pasture, and natural areas in the northern United States and Canada (Donald 1994). It is difficult to control because it produces numerous secondary shoots from adventitious root buds that are common on lateral roots (Nadeau and Vandeborn 1989). Canada thistle spreads easily by seed and by lateral roots that can grow 4 to 6 m per year. Canada thistle is one of very few invasive perennials that are successful invaders in crop and noncrop environments. New patches easily establish from small root pieces spread by tillage.

Canada thistle control can be achieved with a combination of strategies including mechanical control and herbicides (Beck and Sebastian 2000). The most effective herbicides commonly used to control Canada thistle include chlorsulfuron, picloram, and clopyralid. Clopyralid is a pyridine carboxylic acid herbicide that provides Canada thistle control through both soil and foliar activity (Donald 1988; Hall et al. 1985) and selective control of Canada thistle in Brassicaceae (O'Sullivan and Kossatz 1982), Poaceae, and Chenopodiaceae crops. Clopyralid and picloram have limited utility in riparian areas because of ground water advisory statements; therefore, new technology that could be used in riparian environments is needed.

In 2006, Dow Agrosciences received a Section 3 registration for aminopyralid, a new general-use pyridine carboxylic acid herbicide that controls Canada thistle at lower use rates than current standard treatments. Aminopyralid has no groundwater advisory statements, which makes it useful for controlling Canada thistle in riparian areas. Aminopyralid is one of the first herbicides developed specifically for use on rangeland, pasture, noncropland, and natural areas and it

controls many broadleaf species in the Asteraceae, Fabaceae, and Solanaceae families (Carrithers et al. 2005). Aminopyralid applied at 0.11 kg ai ha⁻¹ controlled Canada thistle as well as picloram at 0.42 kg ai ha⁻¹, and provided better control than clopyralid at 0.42 kg ai ha⁻¹, clopyralid + 2,4-D amine (0.32 + 1.68 kg ai ha⁻¹), or dicamba + 2,4-D amine (1.12 + 1.12 kg ai ha⁻¹) 12 mo after treatment (Enloe et al. 2007). Aminopyralid is structurally related to clopyralid with similar pK_a (2.56 and 2.30, respectively) and log K_{ow} (-1.76 and -1.81, respectively), differing only by an amine group on the aromatic ring (Figure 1) and sharing a very similar weed-control spectrum (Senseman 2007).

Although no published information is currently available on aminopyralid absorption and translocation, clopyralid is known to be readily absorbed and translocated by Canada thistle. Devine and Vandeborn (1985) reported 99% absorption 144 h after treatment (HAT), with 29% translocating to roots and 40% translocating above the treated leaf. Overall absorption and translocation of clopyralid was much higher than for chlorsulfuron.

Clopyralid translocation was rapid, with over 50% of applied clopyralid translocating out of Canada thistle treated leaves within 24 HAT (O'Sullivan and Kossatz 1984). Another study found more clopyralid translocation to Canada thistle roots than distal leaves, 33% vs. 15% of applied radioactivity, respectively (Turnbull and Stephenson 1985). There was more translocation to roots and shoots than for 2,4-D. Clopyralid was rapidly absorbed in yellow starthistle (*Centaurea solstitialis* L.), with 75% absorbed 2 HAT (Valenzuela-Valenzuela et al. 2001). Clopyralid translocated primarily to the shoots in yellow starthistle, as 39% of absorbed radioactivity translocated above the treated leaf, 9% moved below the treated leaf, and 1% moved to the roots 96 HAT. Picloram is also a pyridine carboxylic acid, but shows completely different absorption and translocation patterns in Canada thistle compared with clopyralid. Only 12% of applied picloram was absorbed 24 HAT and only 2.2% translocated out of treated leaves (Sharma et al. 1971).

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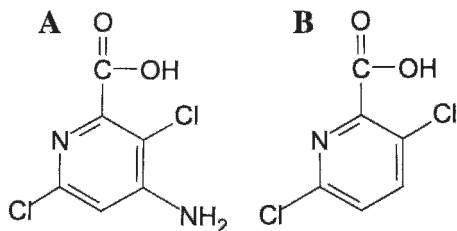


Figure 1. Chemical structures of aminopyralid (A) and clopyralid (B), adapted from Senseman (2007).

Clopyralid metabolism has varied across species. No clopyralid or 2,4-D metabolites were found 9 d after treatment (DAT) in Canada thistle, suggesting that greater clopyralid translocation accounted for its greater biological activity compared with 2,4-D (Turnbull and Stephenson 1985). Clopyralid was metabolized by yellow starthistle within 2 HAT (Valenzuela-Valenzuela et al. 2001), but was not substantially metabolized in hemp dogbane (*Apocynum cannabinum* L.) (Orfanedes et al. 1993). The authors suggested that differences in activity at the target site were responsible for hemp dogbane being more sensitive to fluroxypyr than clopyralid (Orfanedes et al. 1993).

To provide effective control, auxinic herbicides need to translocate to the site of action in sufficient quantities to be phytotoxic. In most species, clopyralid translocates well and has limited metabolism; however, metabolism appears to be species dependent. Because of very similar chemical structures and properties (pK_a and $\log K_{ow}$), aminopyralid may have even better absorption and translocation than clopyralid because it provides Canada thistle control at lower use rates. The objectives of this study were (1) to determine the influence of surfactants on aminopyralid absorption and (2) to compare absorption, translocation, and metabolism of ^{14}C -clopyralid and ^{14}C -aminopyralid in Canada thistle. This information could help to explain why aminopyralid is more effective than clopyralid at lower use rates.

Materials and Methods

Plant Materials. Canada thistle root segments were collected from a wetland noncrop population in fall 2007 and used to vegetatively propagate plants. Root segments were cut to 5 cm, wrapped in moist paper towel, and placed in a growth chamber¹ for 10 d at 24 C/15 C day/night temperature and 12-h photoperiod (approximately 400 $\mu E m^{-2} s^{-1}$). Root segments with emerged shoots were planted horizontally 4 cm deep in 656-ml pots² (6.4 cm diam by 25 cm deep) filled with sand. Pots were watered to maintain normal plant growth. Slow-release fertilizer³ (14-14-14) was added to each pot 5 d after transplanting. Pots were placed outside and exposed to ambient weather conditions during September, and then transferred to a greenhouse.

Surfactants. Plants at the five- to six-leaf rosette stage were returned to the previously described growth chamber conditions and acclimated for 3 d. To determine the effect of different surfactants on aminopyralid absorption, radioactive aminopyralid solutions were prepared with each of the following surfactants: nonionic surfactant⁴ (NIS, 0.25% v/v), methylated seed oil⁴ (MSO, 1% v/v), crop oil concentrate⁴ (COC, 1% v/v),

NIS + ammonium sulfate (AMS) (0.25% v/v + 1.2% w/v), and NIS + urea ammonium nitrate (0.25% v/v + 1% v/v). Each different radiolabeled treatment was applied to a unique leaf on one plant as 20 discrete, 0.5- μ l droplets distributed across both sides of the adaxial surface midvein. Each 10- μ l treatment contained 4,170 Bq. The radiolabeled aminopyralid solutions contained [2,6- ^{14}C]aminopyralid⁵ (specific activity 9.03×10^5 kBq mmol⁻¹), commercially formulated aminopyralid,⁶ and each respective surfactant. Total aminopyralid concentration in application solutions was 2.7 mM, equivalent to a 0.12 kg ha⁻¹ application rate. Plants were returned to the growth chamber after treatment. The experimental design was a randomized complete block with four replications and the experiment was repeated. Treated leaves were excised 96 HAT and washed in 5 ml of 10% (by vol) aqueous methanol with 0.25% NIS. Unabsorbed ^{14}C in the leaf wash solution was quantified by liquid scintillation spectroscopy⁷ (LSS) with scintillation fluid⁸ and used to calculate absorption as a percentage of total radioactivity applied.

Absorption, Translocation, and Root Exudation. Plants at the five- to six-leaf rosette stage were acclimated in a growth chamber for 3 d as described previously. The youngest fully expanded leaf on each plant was covered with aluminum foil and the remainder of the plant was oversprayed with commercially formulated aminopyralid at 0.12 kg ha⁻¹ with 0.25% v/v NIS or commercially formulated clopyralid⁹ at 0.42 kg ha⁻¹ with 0.25% v/v NIS in a pressured spray chamber¹⁰ calibrated to deliver 187 L ha⁻¹ at 206 kPa.

After foliar herbicide applications, radiolabeled solutions were applied to the foil-protected leaf adaxial surface as described previously and each 10- μ l treatment contained 4,170 Bq. The radiolabeled aminopyralid solution was prepared as described previously using 0.25% v/v NIS. Total aminopyralid concentration in the application solution was 2.7 mM, equivalent to a 0.12 kg ai ha⁻¹ application rate. The radiolabeled clopyralid solution contained [2,6- ^{14}C]clopyralid¹¹ (specific activity 1.103×10^6 kBq mmol⁻¹), commercially formulated clopyralid, and 0.25% v/v NIS. Total clopyralid concentration in the application solution was 11.7 mM, equivalent to a 0.42 kg ha⁻¹ application rate. Plants were returned to the growth chamber after treatment.

Plants were harvested 24, 48, 96, and 192 HAT. The treated leaf was excised and washed in 5 ml of 10% (by vol) aqueous methanol with 0.25% NIS. Unabsorbed ^{14}C in the leaf wash solution was quantified by LSS with scintillation fluid. Plants were further divided into shoot above the treated leaf, shoot below the treated leaf, crown, and root. Plant parts were oven dried at 60 C for 48 h, weighed, combusted in a biological oxidizer,¹² and resulting $^{14}CO_2$ was trapped in 10 ml of ^{14}C trapping cocktail.¹³ Radioactive content was quantified by LSS. Radioactivity exuded by roots was determined by adding 250 ml of water to the sand-rooting medium. After shaking and settling, 5 ml of the solution was quantified by LSS with scintillation fluid.

The experimental design was a randomized complete block with three replications and the experiment was repeated. Herbicide absorption was calculated as the total quantity of ^{14}C applied minus that recovered in the leaf wash. Translocation out of the treated leaf was calculated as percentage of applied by determining the total radioactivity recovered in all plant parts other than the treated leaf and

dividing by the total radioactivity applied. The shoot above and below the treated leaf and the crown were combined and referred to as aboveground plant parts. Root-exuded radioactivity was included in total translocation to the root.

Metabolism. For determination of aminopyralid and clopyralid metabolism, plants were treated with foliar and radioactive herbicide applications as described in the absorption and translocation experiment, with the exception that each 10- μ l radioactive treatment solution contained 8.3 kBq. The total aboveground portion of the plants was harvested at 24, 48, 96, and 192 HAT. Plant tissue was ground using a mechanical tissue homogenizer¹⁴ in 90% acetone (v/v). Homogenized tissue was centrifuge filtered, rinsed, and centrifuged twice with 90% acetone, and then acetone was evaporated from the filtrate. Pelleted plant material was combusted in a biological oxidizer, ¹⁴CO₂ trapped in 10 ml of ¹⁴C trapping cocktail, and radioactive content was quantified by LSS. Samples of the filtrate were analyzed by high-performance liquid chromatography (HPLC)¹⁵ using a C8¹⁶ column coupled with in-line ¹⁴C detection.¹⁷ Mobile phases for clopyralid were (A) 90% water : 10% acetonitrile with 0.05% phosphoric acid (v/v), and (B) 70% water : 30% acetonitrile with 0.05% phosphoric acid (v/v). Mobile phases for aminopyralid were (A) 99.9% water : 0.1% acetonitrile with 0.05% phosphoric acid (v/v), and (B) 70% water : 30% acetonitrile with 0.05% phosphoric acid (v/v). The compounds were fractionated with a gradient from 0% B to 100% B over 10 min and held at 100% B for 10 min. The experimental design was a randomized complete block with three replications and the experiment was repeated.

Data Analysis. Data from the surfactant and absorption/translocation experiments were subjected to Levene's test for homogeneity of variance between the two runs of each experiment to determine whether data could be pooled. Analysis of variance was performed on data from the surfactant experiment in SAS PROC GLM (SAS 2004) and treatment means were compared using Fisher's Protected LSD ($P \leq 0.05$). Absorption and translocation data were analyzed using nonlinear and linear regression in SigmaPlot 9.0.¹⁸ Means and standard errors are presented for absorption and translocation data, with regressions calculated from raw data.

Results and Discussion

Surfactants. Data from the two runs were pooled on the basis of a test for homogeneity of variance. Surfactant type was significant ($P < 0.0001$) and absorption was higher with NIS than with MSO, COC, or no surfactant (Figure 2). Adding AMS with NIS improved aminopyralid absorption compared with NIS alone; however, given that NIS alone provided reasonably good absorption and has been used alone in field research (Enloe et al. 2007), it was chosen as the surfactant for the absorption and translocation experiments. The addition of an ammonium ion to spray solutions tends to increase absorption of weak acid herbicides by reducing the pH of the cell wall and enabling acid trapping (Gronwald et al. 1993; Kirkwood 1993). This process has been clearly demonstrated for imidazolinone and sulfonylurea herbicides at the cellular level (Gronwald et al. 1993; Kirkwood 1993). For this process to work most effectively, the herbicide needs to have a pKa

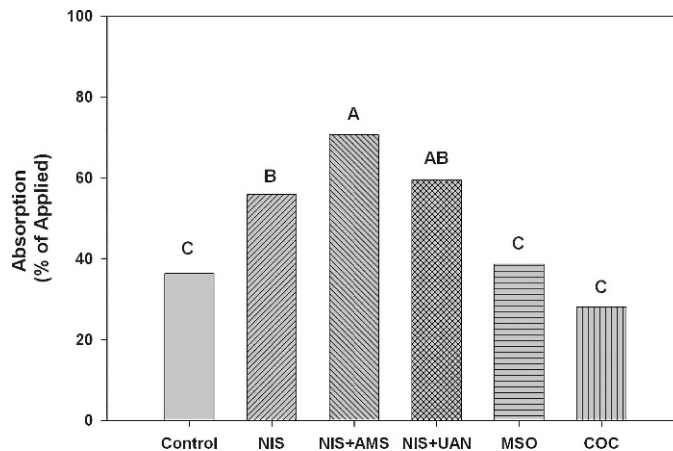


Figure 2. Absorption of ¹⁴C-labeled aminopyralid into treated leaves of Canada thistle 96 h after treatment as a percentage of total applied radioactivity when applied with no surfactant (control), 0.25% (v/v) nonionic surfactant (NIS), NIS + 1.2% (w/v) ammonium sulfate (AMS), NIS + 1% (v/v) urea ammonium nitrate (UAN), 1% (v/v) methylated seed oil (MSO), and 1% (v/v) crop oil concentrate (COC). Means followed by the same letter are not significantly different ($P \leq 0.05$).

within physiological range (Kirkwood 1993). If the pKa of the ionizable group is too acidic, in theory the ammonium ion should have no effect. Aminopyralid's pKa is 2.56 (Senseman 2007), which is lower than the necessary physiological range described by Kirkwood (1993); however, even a slight reduction in cell wall pH might facilitate plasma membrane penetration, providing access to the phloem and creating the concentration gradient necessary to drive both foliar and cellular absorption and long-distance translocation.

Absorption, Translocation, and Root Exudation. Levene's test indicated that the two experiments could be pooled for analysis. Combining radioactivity from the leaf wash with the total radioactivity found in the plant accounted for 86% (standard error [SE] 1.1%) of the total radioactivity applied for both herbicides. Clopyralid had significantly higher foliar absorption than aminopyralid 192 HAT, 80% compared with 60%, respectively (Figure 3). Clopyralid absorption was nearly complete 24 HAT, whereas aminopyralid absorption was much slower and did not reach its maximum level until 96 HAT (Figure 3).

Significantly more clopyralid translocated out of the treated leaf than aminopyralid (Figure 4A). Clopyralid translocation was described best with a nonlinear equation; it appeared to reach maximum translocation out of the treated leaf 48 HAT (Figure 4A). In contrast, aminopyralid translocation was best described by a linear equation and did not appear to reach an asymptote. Given these trends, it is possible that more aminopyralid would translocate out of the treated leaf than clopyralid over a longer time period; however, in the field aminopyralid causes rapid leaf and stem desiccation so it would seem unlikely that translocation could continue. Even when provided with ideal growing conditions and minimal moisture stress, Canada thistle plants used in these experiments developed significant injury symptoms 192 HAT after aminopyralid and clopyralid applications (data not shown).

More clopyralid translocated to aboveground than to belowground plant parts (Figure 4B). Maximum clopyralid root translocation occurred 24 HAT, whereas maximum aboveground translocation occurred 48 HAT (Figure 4B).

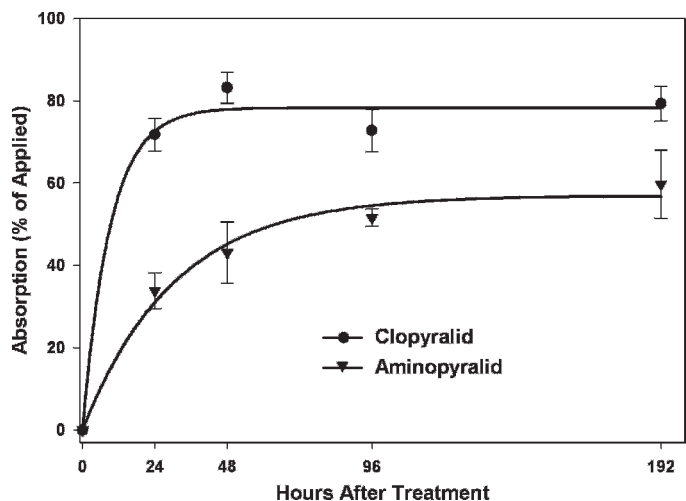


Figure 3. Total absorption of ^{14}C -labeled clopyralid and aminopyralid into treated leaves of Canada thistle. Data points are means and standard errors. Clopyralid regression ($P < 0.0001$): $y = 78.3(1 - e^{-0.11x})$. Aminopyralid regression ($P < 0.0001$): $y = 56.9(1 - e^{-0.03x})$.

This phenomenon has been observed in other perennial plants, including imazapyr in leafy spurge (*Euphorbia esula* L.) (Nissen et al. 1995). Aminopyralid translocation to aboveground tissue was not significantly different from translocation to roots (Figure 4B), and translocation to both was less for aminopyralid than for clopyralid. Root exudation was similar for both herbicides throughout the time course, with 2.9% (SE 1.3%) of applied aminopyralid exuding from the roots 192 HAT, compared with 4.8% (SE 1.3%) of applied clopyralid.

Although aminopyralid is effective at lower use rates than clopyralid (Enloe et al. 2007), much less aminopyralid was absorbed and translocated out of treated leaves. The higher biological activity of clopyralid compared with 2,4-D was attributed to greater translocation (Turnbull and Stephenson 1985), which does not explain the higher biological activity of aminopyralid compared with clopyralid.

Metabolism. Extractable aminopyralid and clopyralid were not metabolized 192 HAT (Figure 5). A maximum of 2% of applied radioactivity from both compounds was detected as nonextractable radioactivity in pelleted plant material. This is consistent with a previous report that no clopyralid metabolites were found 9 DAT in Canada thistle (Turnbull and Stephenson 1985). Given that aminopyralid has a chemical structure very similar to clopyralid, it seems reasonable that aminopyralid would not be metabolized by Canada thistle. Although no soluble metabolites were detected 192 HAT, it is possible that some metabolism could have been detected with a longer sampling window; however, herbicide injury was clearly visible 192 HAT (data not shown). Proteins that conjugate indole-3-acetic acid (IAA) and other endogenous auxins in response to excess auxin and auxinic herbicides, such as *GH3* in soybeans [*Glycine max* (L.) Merr.], do not recognize dicamba or 2,4-D as substrates (Kelley and Riechers 2007), so these proteins likely would not recognize aminopyralid or clopyralid as substrates. Neither aminopyralid nor clopyralid was metabolized as indicated by HPLC retention time, so conjugation was not occurring.

Recent advances in understanding auxin perception and auxinic herbicide mode of action have shown that auxin

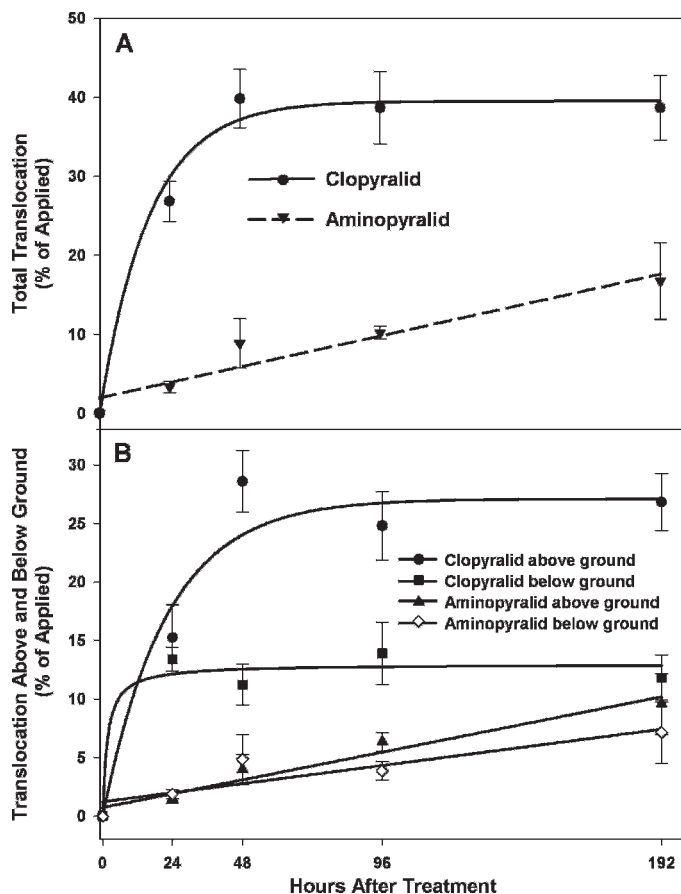


Figure 4. Translocation of ^{14}C -labeled clopyralid and aminopyralid out of treated leaves of Canada thistle. Data points are means and standard errors. (A) Total translocation as percentage of total applied radioactivity; clopyralid regression ($P < 0.0001$): $y = 39.5(1 - e^{-0.06x})$; aminopyralid regression ($R^2 = 0.71$, $P < 0.0001$): $y = 1.9 + 0.08x$. (B) Translocation above and below ground as percentage of total applied radioactivity; clopyralid aboveground regression ($P < 0.0001$): $y = 27.1(1 - e^{-0.05x})$; clopyralid belowground regression ($P < 0.0001$): $y = 12.9x/1.6+x$; aminopyralid aboveground regression ($R^2 = 0.75$, $P < 0.0001$): $y = 0.72 + 0.05x$; aminopyralid belowground regression ($R^2 = 0.57$, $P < 0.0001$): $y = 1.2 + 0.03x$.

receptors auxin-binding protein 1 (ABP1) and transport inhibitor response 1 (TIR1) are auxin specific, initiate gene expression, and may be target sites for auxinic herbicides (Kelley and Riechers 2007). Auxinic herbicides are classified on the basis of the type of aromatic ring and location of the carboxylic acid moiety in relation to the aromatic ring, but recent work indicates that the carboxyl group may not be required for auxin activity (Kelley and Riechers 2007). The only difference between aminopyralid and clopyralid is that aminopyralid has an amine group on the aromatic ring, which may be the critical portion for target site recognition. Auxin receptor homologues to ABP1 and TIR1 in Canada thistle may be more sensitive to aminopyralid than clopyralid. Taken together, aminopyralid could very well have greater biological activity at an auxin receptor, which would explain why aminopyralid has greater field-level biological activity with lower absorption and less translocation than clopyralid.

Our results showed that clopyralid was more readily absorbed and had greater translocation to both roots and shoots than aminopyralid. Clopyralid and aminopyralid have very similar $\log K_{ow}$ and pK_a values, which makes it difficult to explain the significant differences in translocation. According to the mathematical model unifying the weak acid

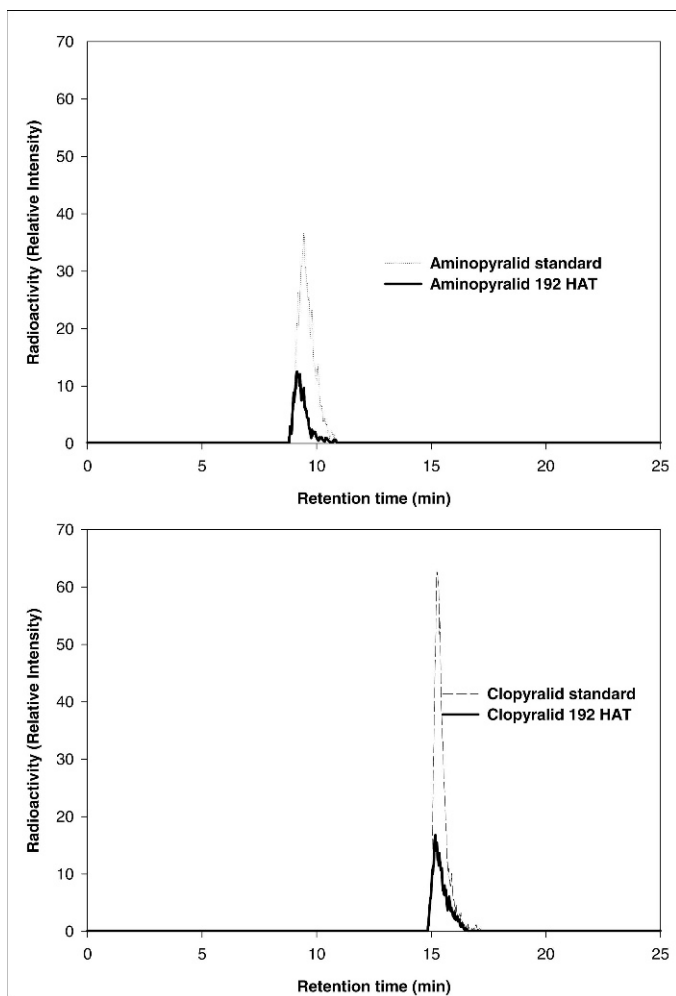


Figure 5. Chromatograms from reverse-phase high-performance liquid chromatography (HPLC) on analytical standards and acetone extract from Canada thistle plants 192 h after treatment with ^{14}C -labeled aminopyralid (upper panel) and clopyralid (lower panel).

and intermediate permeability theories (Kleier 1988), both molecules should have limited translocation. Kleier's model would suggest that the $\log K_{ow}$ values for these herbicides are too low and the pK_a too acidic to compensate for low membrane permeability. In this context, clopyralid's level of absorption and translocation is probably unusually high on the basis of $\log K_{ow}$ and pK_a values. Despite clopyralid's greater translocation, aminopyralid has better herbicidal activity at lower rates on Canada thistle. Aminopyralid probably has higher biological activity at the site of action than clopyralid, since less aminopyralid is required to achieve better control than clopyralid and much less aminopyralid actually translocates out of treated leaves. Future research into the biological activity of aminopyralid may help explain these differences, including identifying the site of action for aminopyralid and clopyralid and determining the binding kinetics of these two herbicides.

Sources of Materials

¹ Conviron Controlled Environments Limited (Model 15), Winnipeg, MB, Canada.

² Deepot cones, Stuewe and Sons, Inc., Corvallis, OR 97333.

³ Osmocote®, Scotts Miracle-Gro Company, Marysville, OH 43041.

⁴ Loveland Industries, Inc., Greeley, CO 80537.

⁵ Dow AgroSciences LLC, Indianapolis, IN 46268.

⁶ Milestone™, Dow AgroSciences LLC, Indianapolis, IN 46268.

⁷ Packard Tri-Carb (Model 2500 TR), Packard Instrument Co., Meriden, CT 06450.

⁸ Ultima Gold LLT (6013371), PerkinElmer Life and Analytical Sciences, Inc., Waltham, MA 02451.

⁹ Transline™, Dow AgroSciences LLC, Indianapolis, IN 46268.

¹⁰ DeVries Manufacturing Corp., Hollandale, MN 56045.

¹¹ Dow AgroSciences LLC, Indianapolis, IN 46268.

¹² OX500, R.J. Harvey Instrument Co., Tappan, NY 10983.

¹³ OX-161, R.J. Harvey Instrument Co., Tappan, NY 10983.

¹⁴ Tempest homogenizer, Virtis Company, Gardiner, NY 12525.

¹⁵ Hitachi Instruments, Inc., San Jose, CA 95134.

¹⁶ Zorbax C8 column, 2.1 mm by 150 mm, Agilent Technologies, Santa Clara, CA 95051.

¹⁷ βRAM Detector, IN/US Systems, Inc., Tampa, FL 33610.

¹⁸ Systat Software, Inc., San Jose, CA 95110.

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