# Effectiveness of Clodinafop-Propargyl, Haloxyfop-p-methyl and Difenzoquat-methyl-sulfate Plus Adigor<sup>®</sup> and Propel<sup>™</sup> Adjuvants in Controlling *Avena ludoviciana* Durieu.

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#### ABSTRACT

Various adjuvants carry out different functions depending on the herbicides types and the target species. Outdoor pot experiments were conducted to evaluate the effects of three post-emergence herbicides, namely, clodinafop-propargyl, haloxyfop-p-methyl, and difenzoquat-methyl-sulfate, as influenced by two adjuvants, on wild oat (Avena ludoviciana Durieu.) control. The study was carried out at the Ferdowsi University of Mashhad, Iran, during 2010. The applied adjuvants were Adigor<sup>®</sup> and Propel<sup>™</sup>, registered and sold for use with pinoxaden and tralkoxydim herbicides, respectively, at 0.1 and 0.2% (v/v). These two adjuvants in tank-mixture with the tested herbicides were completely compatible physically and resulted in improvement in controlling wild oats. When Propel<sup>™</sup> was added to all three herbicides, herbicidal activity was higher than when Adigor<sup>®</sup> was added. With increasing adjuvant concentrations, the performance of the tested herbicides increased significantly. In general, the benefit of the two adjuvants appeared greater for clodinafop-propargyl than for the other herbicides. The performance against wild oat of clodinafop-propargyl, haloxyfop-p-methyl, or difenzoquat-methyl-sulfate plus Propel<sup>TM</sup> at 0.2% was higher by 2.92, 1.42, and 1.67 times, respectively, compared with the use of those herbicides without adjuvants. This result may be related to differences in the physio-chemical characteristics of the tested herbicides. Overall, use of Propel<sup>™</sup> with clodinafop-propargyl is recommendable.

Keywords: Herbicide efficacy, Petroleum-based oil, Vegetable-based oil.

## INTRODUCTION

The proper usage of adjuvants with certain herbicides often enhances the active ingredient in biological activity (Hammami *et al.*, 2011), as indicated on the herbicide label (Pannacci *et al.*, 2010). However, it should be noted that presently, some adjuvants have been registered and released for use with certain herbicides. For instance, Adigor<sup>®</sup> and Propel<sup>TM</sup> are registered for use with pinoxaden and tralkoxydim herbicides, respectively. They are used for the selective control of grasses in wheat and barley fields (Rashed-Mohassel *et al.*, 2011). Propel<sup>TM</sup> is a crop oil concentrate that contains petroleum-based oils plus some

nonionic surfactant, while Adigor<sup>®</sup> is derived from vegetable-based oils plus some nonionic surfactant (Anonymous, 2005 and 2008).

In some experiments, vegetable-based oils were less effective than petroleum-based oils. This has been reported for propanil (Jordan *et al.*, 1997), clethodim (Jordan *et al.*, 1996) and quinclorac (Zawierucha and Penner, 2001). Occasionally, in some experiments, vegetable-based oils enhance herbicidal activity as much as petroleum-based oils. This has been reported for quizalofop, haloxyfop (Manthey *et al.*, 1989), sethoxydim (Mack *et al.*, 1995), and fenoxaprop-P (McMullan *et al.*, 1995). In other reports, vegetable-based oils were found to be more effective than petroleum-based oils.

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This was the case with sethoxydim (Matysiak and Nalewaja, 1999), diclofop, fluazifop-butyl (Manthey et al., 1989), dithiopyr (Keeley et al., 1997), phenmedipham (DeRuiter et al., 1997), isoxaflutole (Young and Hart, 1998), triflusulfuron (Starke et al., 1996), tralkoxydim (McMullan et al., 1995). clethodim (Jordan et al., 1996), nicosulfuron (Strahan et al., 2000; Nalewaja et al., 1995), et al., aciflurofen (Nalewaja 1995), primisulfuron (Nandula al., 1995), et rimsulfuron (Tonks and Eberlein, 2001) and atrazine (Robinson and Nelson, 1975).

Thus, it is noted that the impact of these types of adjuvants on herbicidal activity is complicated and depends on the interactions among the herbicide, adjuvant, and weed species (Aliverdi *et al.*, 2009). It is always said that "to choose the correct adjuvant for a specific agrochemical, first read the label". However, labels of many post-emergence herbicides only state a specific type of adjuvant (Hazen, 2000), but do not specify which brand of adjuvant to add. Indeed, following the general recommendation written on the label could bring about failure or success. Hence, Adigor<sup>®</sup> and Propel<sup>™</sup> adjuvants are commercially recommended for pinoxaden and tralkoxydim, respectively.

The level to which adjuvants increase the effectiveness of specific herbicides cannot be quantified without experimentation (Aliverdi *et al.*, 2009). From the farmer's point of view, this increased efficacy may result in decreased herbicide use and reduced costs (Sheibani and Ghadiri, 2012). The main objective of this research was to specify the compatibility of Adigor<sup>®</sup> and Propel<sup>TM</sup> adjuvants in order to increase the efficacy of clodinafop-propargyl, haloxyfop-p-methyl, and difenzoquat-methyl-sulfate against wild oat.

## MATERIALS AND METHODS

### **Plant Material**

The seeds of wild oat (Avena ludoviciana Durieu.) were collected from plants in the fields of the Mashhad Agricultural and Natural Resources Research Center, Iran and were stored in a refrigerator at  $4\pm1^{\circ}$ C, during 2010. To break the seed dormancy, the seeds were dehulled and placed in 11 cm diameter Petri dishes over the surface of a single layer of Whatman no. 1 filter paper. Then, 10 mL of 0.2% KNO<sub>3</sub> solution were added to each Petri dish and the seeds were incubated for 48 hours at 4-5°C in darkness (Rashed-Mohassel *et al.*, 2011). Then, the seeds were sown in potting trays (3×3×5 cm) filled with moistened peat.

One week after sowing, when the seedlings were at one leaf stage, ten seedlings were transplanted in each 2 L plastic pot filled with a mixture of sand, clay loam soil, and peat (1:1:1; v/v/v). The pots were placed outdoor and sub-irrigated every three days. At the two leaf stage, the seedlings were thinned from ten to five per pot and 40 mL of a watersoluble N:P:K (20:20:20) fertilizer, at a concentration of 3 g of fertilizer per liter of tap water, were applied to each pot. During the experiment, the temperature varied between  $24\pm6^{\circ}$ C during the day and between  $16\pm4^{\circ}$ C at night.

#### **Treatments and Chemicals**

Clodinafop-propargyl at 0 (control), 8, 16, 32, 48, and 64 g ai ha<sup>-1</sup> (Topik<sup>®</sup>, 8% EC, Syngenta, Switzerland), haloxyfop-p-methyl at 0 (control), 12.5, 25, 50, 75, and 100 g ai  $ha^{-1}$  (Gallant Super<sup>®</sup> Ultra, 10.8% EC, DowAgro, USA), and difenzoquat-methylsulfate at 0 (control), 125, 250, 500, 750, and 1000 g ai ha<sup>-1</sup> (Avenge<sup>®</sup>, 25% SL, BASF, Germany) were used separately against wild oat in three experiments. Each of these herbicides was applied without and with the adjuvants of: (i) Adigor<sup>®</sup> (a methylated seed oil, 44% methylated rapeseed oil, Syngenta, Switzerland) and (ii)  $Propel^{TM}$  (a petroleumbased oil, 432 g L<sup>-1</sup> mineral oil, Genfarm, Australia) at two concentrations of 0.1 and 0.2% (v/v). For each herbicide, the experiment was arranged in completely randomized design with factorial arrangement of treatments with four replications. The experiment was performed twice, but with both giving similar results, only one of the two was reported. The herbicides were applied at the four leaf stage by using an overhead trolley sprayer (Matabi 121030 Super Agro 20 L sprayer; Agratech Services-Crop Spraying Equipment, Rossendale, UK), equipped with an 8,002 flat fan nozzle tip delivering 200 L ha<sup>-1</sup> at 2 bar spray pressure. Four weeks after spraying, the biomass of the experimental units were harvested and weighed to estimate fresh matter. Then, biomass was oven-dried at 75°C for 48 hours and reweighed to estimate dry matter.

#### Statistical Analyses

The response of fresh and dry matter (U) on dose (z) was assumed by a log-logistic model as described by Nielsen *et al.* (2004):

$$U_{ij} = C_i + \frac{D - C_i}{1 + \exp[b_i(\log(z_{ij}) - \log(ED_{50i}))]}$$
(1)

Where,  $U_{ij}$  denotes the fresh or dry matter at the  $j^{\text{th}}$  dose of the  $i^{\text{th}}$  herbicide preparation; D and  $C_i$  denote the upper and lower limit of the fresh or dry weight at zero and at infinite doses;  $ED_{50i}$  denotes the required dose of herbicide, i, to give 50% wild oat control; and bi is proportional to the slope of the curve around the  $ED_{50i}$ . The  $ED_{50}$  parameter can be replaced by any *ED* level (e.g. the  $ED_{90}$ ). The  $ED_{90}$  denotes the required dose of herbicide, *i*, to give 90% wild oat control. The logistic response-dose model was fitted to the experimental data by the Slide Write software (Advanced Graphics Software, Carlsbad, CA, USA).

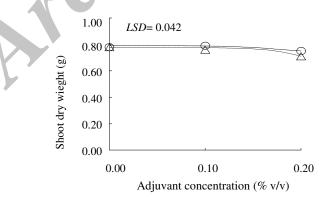
Theoretically, whether the response curves are parallel or not, the horizontal displacement between the curves describes the relative potency of the two herbicides (Ritz *et al.*, 2006). If a is the commercial herbicide alone and b is the commercial herbicide accompanied by adjuvant, then the relative potency is defined as the ratio of the doses for commercial herbicide alone and commercial herbicide accompanied by adjuvant that give the same effect:

$$r_b = ED_{50a} / ED_{50b} \tag{2}$$

If  $r_b < 1$ , the commercial herbicide a is more potent than the commercial herbicide accompanied by adjuvant, b, and if  $r_b > 1$ , the reverse is correct. If  $r_b = 1$ , then the two are equally potent.

#### **RESULTS AND DISCUSSION**

The results indicated that the two adjuvants, Adigor<sup>®</sup> and Propel<sup>TM</sup>, did not affect the growth of oat plants when applied alone in the range from 0.1 to 0.2% (Figure 1).

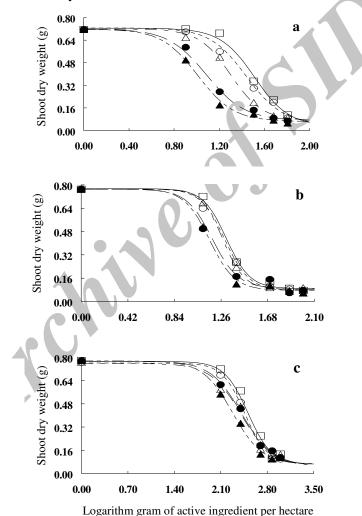


**Figure 1.** Dose-response curves of the shoot dry weight of wild oat on  $\operatorname{Adigor}^{\otimes}(O)$  and  $\operatorname{Propel}^{\mathbb{M}}(\Delta)$ . The lines were fitted on data and belong to shoot dry weight using logistic dose-response model of Equation (1). The data points of each treatment were averaged over five plants per pot.

Therefore, in this study, the herbicides were responsible for all the recorded reductions in biomass. This agrees with previous studies by Rashed-Mohassel *et al.* (2011) and Kudsk (1997) who reported that adjuvants were inactive biologically at the recommended concentrations. However, when the logistic dose-response model was fitted to the experimental data, it was observed that the addition of Adigor<sup>®</sup> or Propel<sup>TM</sup> in tank-mixture with clodinafop-propargyl, haloxyfop-p-methyl, or difenzoquat-methyl-sulfate improved wild oat control efficacy. Since fresh

weight and dry weight data showed similar trend, only dose-response curves on the basis of dry weight data are reported (Figure 2). The addition of either adjuvant increased the efficacy of all three herbicides in reducing wild oat biomass.

The  $ED_{50}$  values of clodinafop-propargyl plus the two adjuvants were significantly less than that of the  $ED_{50}$  values of clodinafop-propargyl without adjuvants (Table 1). Also, an almost similar result was

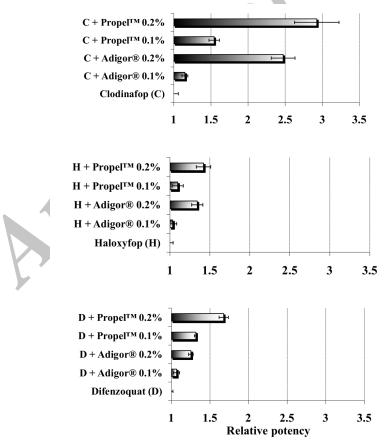


**Figure 2.** Dose-response curves of the shoot dry weight of wild oat on: (a) Clodinafoppropargyl; (b) Haloxyfop-p-methyl; (c) Difenzoquat-methyl-sulfate alone ( $\Box$ ), Clodinafoppropargyl, haloxyfop-p-methyl, or difenzoquat-methyl-sulfate plus adjuvants of Adigor<sup>®</sup> 0.1% ( $\circ$ ) and 0.2% ( $\bullet$ ), Propel<sup>TM</sup> 0.1% ( $\Delta$ ) and 0.2% ( $\blacktriangle$ ). The lines were fitted on data and belong to shoot dry weight using logistic dose-response model of Equation (1). The data points of each treatment were averaged over five plants per pot.

Treatment <sup>a</sup>	Shoot fresh weight		Shoot dry weight	
	$ED_{50}$	$ED_{90}$	$ED_{50}$	$ED_{90}$
	(g a.i. ha <sup>-1</sup> ) ± SD	$(g a.i. ha^{-1}) \pm SD$	$(g a.i. ha^{-1}) \pm SD$	$(g a.i. ha^{-1}) \pm SD$
Clodinafop alone	$22.91 \pm 2.05$	$49.88 \pm 1.78$	$30.36 \pm 2.09$	$52.68 \pm 2.09$
Clodinafop + Adigor <sup>®</sup> 0.1%	$21.49 \pm 1.61$	$39.92 \pm 1.56$	$26.43 \pm 1.50$	$51.11 \pm 1.49$
Clodinafop + Adigor <sup>®</sup> 0.2%	$12.02 \pm 2.34$	$31.12 \pm 0.31$	$12.28 \pm 0.82$	$29.48 \pm 0.79$
Clodinafop + Propel <sup>™</sup> 0.1%	$16.05 \pm 1.22$	$37.37 \pm 0.22$	$19.67 \pm 0.85$	$37.14 \pm 2.38$
Clodinafop + Propel <sup>TM</sup> $0.2\%$	$07.79 \pm 1.45$	$22.22 \pm 0.40$	$10.38 \pm 2.10$	$24.62 \pm 2.58$
Haloxyfop alone	$19.25 \pm 0.85$	$44.01 \pm 1.88$	$20.56 \pm 1.01$	$36.23 \pm 1.69$
Haloxyfop + Adigor <sup>®</sup> 0.1%	$16.48 \pm 1.01$	$37.78 \pm 1.48$	$19.88 \pm 0.71$	$34.73 \pm 0.77$
Haloxyfop + Adigor <sup>®</sup> 0.2%	$12.73 \pm 0.88$	$31.58 \pm 1.14$	$15.32 \pm 1.44$	$29.10 \pm 2.48$
Haloxyfop + Propel <sup>™</sup> 0.1%	$15.10 \pm 1.09$	$34.05 \pm 2.04$	$18.74 \pm 0.74$	$30.75 \pm 1.70$
Haloxyfop + Propel <sup>™</sup> 0.2%	$12.39 \pm 0.77$	$29.00 \pm 0.48$	$14.48 \pm 1.46$	$27.40 \pm 0.64$
Difenzoquat alone	$404.49 \pm 4.65$	$694.14 \pm 8.61$	$296.24 \pm 5.60$	$584.13 \pm 6.70$
Difenzoquat + Adigor <sup>®</sup> 0.1%	$333.09 \pm 6.88$	$638.13 \pm 6.81$	277.79 ± 4.79	$577.35 \pm 4.70$
Difenzoquat + Adigor <sup>®</sup> 0.2%	$165.28 \pm 4.36$	$363.32 \pm 4.33$	$236.62 \pm 4.89$	$508.72 \pm 5.82$
Difenzoquat + Propel <sup>™</sup> 0.1%	$151.96 \pm 7.63$	$327.17 \pm 7.65$	$224.96 \pm 5.61$	$536.93 \pm 7.67$
Difenzoquat + Propel <sup>™</sup> 0.2%	$115.94 \pm 7.93$	$200.73 \pm 7.89$	$176.62 \pm 4.88$	$445.66 \pm 7.89$
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**Table 1**. Estimated  $ED_{50}$  and  $ED_{90}$  doses of clodinafop-propargyl or haloxyfop-p-methyl or difenzoquat-methyl-sulfate alone and in the presence of adjuvants in the control of wild oat.

<sup>*a*</sup> Clodinafop-propargyl, haloxyfop-p-methyl and difenzoquat-methyl-sulfate are shortened to clodinafop, haloxyfop and difenzoquat, respectively. The parameters were calculated using Equation (2).



**Figure 3.** Relative potency values of clodinafop-propargyl (C), haloxyfop-p-methyl (H) or difenzoquat-methylsulfate (D) when combined with the adjuvants Adigor<sup>®</sup> and Propel<sup>TM</sup> at two concentrations on wild oat. The values were calculated using Equation (2). Horizontal bars are confidence intervals at P < 0.01.

found for the ED<sub>90</sub>s. With increasing adjuvant concentrations, the  $ED_{50}$  and ED<sub>90</sub> values decreased, indicating an effectiveness increase in the of clodinafop-propargyl (Table 1). Compared with the activity of clodinafop-propargyl applied without adjuvants, the increase in the activity of clodinafop-propargyl in the presence of the Adigor<sup>®</sup> at 0.1 and 0.2% (v/v) was higher by 1.15, 2.47 times, and for Propel<sup>™</sup>, 1.54, and 2.92 times, respectively (Figure 3). Thus, the effect of clodinafop-propargyl plus Propel<sup>™</sup> at 0.2% against wild oat was about three times higher than that of clodinafoppropargyl without adjuvants. Between the evaluated adjuvants, the addition of Adigor<sup>®</sup> to clodinafop-propargyl resulted in a lower increase in herbicidal activity than when the same rate of  $Propel^{TM}$  was added ( $r_b$ = 1.15 vs.  $r_b$ = 1.54 at 0.1% (v/v);  $r_b = 2.47 vs. r_b = 2.92 at 0.2\% (v/v)$ ) (Figure 3).

For haloxyfop-p-methyl, the additions of Adigor<sup>®</sup> or Propel<sup> $^{M}$ </sup> at 0.2% (v/v) was required for wild oat control to be significantly improved in comparison with haloxyfop-p-methyl (1.34 and 1.42 times higher, respectively) alone (Table 1, Figure 3). Although the performance of haloxyfop-p-methyl increased significantly with increasing adjuvant concentrations, there were no significant differences between the two adjuvants at similar concentrations.

The  $ED_{50}$  and  $ED_{90}$  values of difenzoquatmethyl-sulfate decreased in the presence of the adjuvants of Adigor<sup>®</sup> and Propel<sup>TM</sup> and the relative potency values were significantly higher than difenzoquat-methyl-sulfate alone (Table 1), indicating a significant increase in performance. Thus, in this experiment, the performance of 1 kg ha<sup>-1</sup> difenzoquat-methylsulfate plus the adjuvant of Adigor<sup>®</sup> and Propel<sup>TM</sup> at 0.1 and 0.2% (v/v) equaled the performance of 1.07, 1.25, 1.32, and 1.67 kg ha<sup>-1</sup> difenzoquat-methyl-sulfate alone, respectively. Moreover, with increase in the concentration of each adjuvant from 0.1 to 0.2% (v/v), the effectiveness of difenzoquatmethyl-sulfate was significantly increased. Both concentrations of Propel<sup>TM</sup> had a greater influence on difenzoquat-methyl-sulfate' performance against wild oat compared with Adigor<sup>®</sup>.

The improvement in the tested herbicides by the two adjuvants may be related to a theory that explains the solubilizing, softening, or disrupting nature of cuticular waxes by the methylated seed oils or the petroleum-based oils (Hazen, 2000) despite the reduction in surface tension of the spray solution (Sharma and Singh, 2000). These processes can improve retention and diffusion of active ingredient of herbicide to the more hydrophilic structures under cuticular waxes (Kammler et al., 2010). Consequently, there is more active ingredient in the site of action and a subsequent increase in the effectiveness of the herbicides. The solubilizing, softening, or disrupting of the cuticular waxes is a more effective factor than a decrease in the surface tension of sprays droplets to improve the effectiveness of the herbicide by adjuvants (Sharma and Singh, 2000; Rashed-Mohassel et al., 2011). This is probably the reason why, although oil adjuvants cause a lower reduction in surface tension of herbicides solution, they lead to better control with quinclorac (Zawierucha and Penner, 2001), glyphosate (Collins and Helling, 2002) and sethoxydim and fenoxaprop-p-ethyl (Rashed-Mohassel et al., 2011) than surfactants.

Comparing the results of the three experiments, the benefit of the two adjuvants appears greater for clodinafop-propargyl than for haloxyfop-p-methyl or difenzoquatmethyl-sulfate. These results may be related to differences in the physio-chemical characteristics of the tested herbicides.

## CONCLUSIONS

Selecting the proper adjuvant is a key factor to an efficacious weed management via reducing herbicide rate, which is a main research priority (Rashed-Mohhasel *et al.* 2009). This research demonstrated that when Adigor<sup>®</sup> and Propel<sup>TM</sup> adjuvants were tank mixed with the tested herbicides, particularly clodinafop-propargyl, the herbicidal efficacy on wild oat species significantly improved. Besides, for the three tested herbicides, Propel<sup>TM</sup> was found to be more effective than Adigor<sup>®</sup>.

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## کارایی علف کش های کلودینافوپ پروپارژیل، هالو کسی فوپ پی متیل و دایفنزو کوات متیل سولفات به همراه مواد افزودنی آدیگور و پروپل در کنترل یولاف وحشی (.Avena ludoviciana Durieu)

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چکیدہ

مواد افزودنی مختلف دارای عملکرد متفاوتی با علف کش های مختلف بر روی گونه های هدف متفاوت هستند. به منظور ارزیابی اثرات سه علف کش پس رویشی کلودینافوپ پروپارژیل، هالوکسی فوپ پی متیل و دیفنزوکوات متیل سولفات به همراه دو ماده افزودنی در کنترل یولاف وحشی (Avena ludoviciana Durieu)، آزمایش هایی گلدانی در هوای آزاد در سال ۱۳۸۹ در دانشگاه فردوسی مشهد به انجام رسید. مواد افزودنی بکار رفته شامل آدیگور و پروپل بودند که در دو غلظت ۱/۰ و ۲/۰ درصد حجمی مورد استفاده قرار گرفتند. این دو ماده افزودنی در اختلاط با علف کش های مورد بررسی کاملا بطور فیزیکی سازگار بودند و موجب بهبود کنترل یولاف وحشی های پروپل به هر سه علف کش اضافه شد، فعالیت علف کشی بالاتر بود نسبت به زمانی که آدیگور اضافه شد. با افزایش غلظت ماده افزودنی، نمود علف کش های مورد آزمایش بطور معنی داری افزایش یافت. بطور کلی، اثر سودمند هر دو ماده افزودنی برای علف کش کال ویزافوپ پروپارژیل بیشتر از دو علف مند. با افزایش نظن ماده افزودنی، نمود علف کش های مورد آزمایش بطور معنی داری افزایش یافت. بطور کلی، اثر سودمند هر دو ماده افزودنی برای علف کش کالودینافوپ پروپارژیل بیشتر از دو علف منیل سولفات به همراه ماده افزودنی بروی در ای علف کش کالودینافوپ پروپارژیل بیشتر از دو علف مین دیگر بود. نمود علف کش های کلودینافوپ پروپارژیل، هالوکسی فوپ پی متیل و دیفنزو کوات مین ولفات به همراه ماده افزودنی بروی در غلظت ۲/۰ درصد حجمی به تر تیب به میزان ۲/۱۰۲، ۲/۱۲ مین اولات مایی در ویژگی های فیزیکوشیمیایی بین علف کش ها بود. این نتیجه ممکن است به دلیل مهراه علی در ویژگی های فیزیکوشیمیایی بین علف کش های مورد بررسی باشد. کاربرد پرویل به مهراه علی کش کلودینافوپ پروپارژیل قابل توصیه می باشد.