The Herbicidal Potential of Different Pelargonic Acid Products and Essential Oils against Several Important Weed Species

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Abstract: There is growing consideration among farmers and researchers regarding the development of natural herbicides providing sufficient levels of weed control. The aim of the present study was to compare the efficacy of four different pelargonic acid products, three essential oils and two natural products’ mixtures against L. rigidum, A. sterilis and G. aparine. Regarding grass weeds, it was noticed at 7 days after treatment that PA3 treatment (pelargonic acid 3.102% w/v + maleic hydrazide 0.459% w/v) was the least efficient treatment against L. rigidum and A. sterilis. The mixture of lemongrass oil and pelargonic acid resulted in 77% lower dry weight for L. rigidum in comparison to the control. Biomass reduction reached the level of 90% as compared to the control in the case of manuka oil and the efficacy of manuka oil and pelargonic acid mixture was similar. For sterile oat, weed biomass was recorded between 31% and 33% of the control for lemongrass oil, pine oil, PA1 (pelargonic acid 18.67% + maleic hydrazide 3%) and PA4 (pelargonic acid 18.67%) treatments. In addition, the mixture of manuka oil and pelargonic acid reduced weed biomass by 96% as compared to the control. Regarding the broadleaf species G. aparine, PA4 and PA1 treatments provided a 96–97% dry weight reduction compared to the corresponding value recorded for the untreated plants. PA2 (pelargonic acid 50% w/v) treatment and the mixture of manuka oil and pelargonic acid completely eliminated cleaver plants. The observations made for weed dry weight on the species level were similar to those made regarding plant height values recorded for each species. Further research is needed to study more natural substances and optimize the use of natural herbicides as well as natural herbicides’ mixtures in weed management strategies under different soil and climatic conditions.

Keywords: bioherbicide; pelargonic acid; manuka oil; lemongrass oil; pine oil; grass weeds; broadleaf weeds

1. Introduction

Weeds are considered to be one of the major threats to agricultural production since they affect the crop production indirectly, by competing with the crop for natural resources, sheltering crop pests, reducing crop yields and quality, and subsequently increasing the cost of processing [1]. Chemical control remains the most common control practice for weed management. Unfortunately, this overreliance on herbicides has led to serious problems, such as the possible injury to non-target vegetation and crops, the existence of herbicide residues in the water and the soil and concerns for
human health and safety [2–5]. Another major issue associated with the use of synthetic herbicide is the growing problem of herbicide resistance since many harmful weed species including *Amaranthus*, *Conyza*, *Echinochloa*, and *Lolium* spp. are notorious for their ability to rapidly evolve resistance to a wide range of herbicide sites of action [6]. The development of natural herbicides based on either organic acids or essential oils could decrease these negative impacts. They are less persistent in comparison to synthetic herbicides, more environmentally friendly, and they also have different modes of action which can prevent the development of herbicide-resistant weed biotypes [7,8]. Organic acids, essential oils, crude botanical products and other natural substances derived from plant tissues can be used as bio-herbicides in terms of weed management in both organic and sustainable agriculture systems [9].

Such natural substances face several opponents among the European Commission members, since there are doubts regarding the registration processes of natural products due to the lack of relevant toxicological data for their use at commercial scale [10]. Although these concerns might exist, there is evidence that most essential oils and their main compounds are not necessarily genotoxic or harmful to human health [11]. Such natural herbicides are sometimes less hazardous for environmental and human health in comparison to the commercial synthetic herbicides. In the case of pelargonic acid, toxicity tests on non-target organisms, such as birds, fish, and honeybees, revealed little or no toxicity [12]. The chemical decomposes rapidly in both land and water environments, so it does not accumulate. To minimize drift and potential harm to non-target plants, users are required to take precautions such as avoiding windy days and using large spray droplets. However, product labels describe precautions that users should follow to prevent the products from getting in their eyes or on their skin since the acid is a skin and eye irritant [13].

Pelargonic acid (PA) \((\text{CH}_3\text{CH}_2\text{CO}_2\text{H}, \text{n-nonanoic acid})\) is a saturated, nine-carbon fatty acid (C9:0) naturally occurring as esters in the essential oil of *Pelargonium* spp. And can be derived from the tissues of various plant species [14–16]. Pelargonic acid along with its salts and formulated with emulsifiers is used in terms of weed management as a nonselective herbicide suitable either for garden or professional uses worldwide [8,14]. They are applied as contact burndown herbicides, which attack cell membranes and then as a result, cell leakage is caused and followed by membrane acyl lipids breakdown [16,17]. The phytotoxic effects due to the application of pelargonic acid are visible in a very short time after spraying and the symptoms involve phytotoxicity for the plants and their cells, which rapidly begin to oxidize, and necrotic lesions are observed on the aerial parts of plants [18]. The potential use of pelargonic acid as a bioherbicide poses an attractive non-chemical weed control option which can be effectively integrated with other eco-friendly weed management strategies in important crops such as soybean [19]. Several commercial pelargonic acid-based natural herbicides include also maleic hydrazide \((1,2\text{-dihydro-3,6-pyrazidinedione})\) which is a systemic plant growth regulator that has also been used as a herbicide since its introduction [20]. Maleic hydrazide \((1, 2\text{-dihydropyridazine-3, 6-dione}),\) a hormone-like substance synthesized and first introduced to USA in 1949, with crystal structure and structural similarity to the pyrimidine base uracil [20–22]. After application to foliage, maleic hydrazide is translocated in the meristematic tissues, with mobility in both phloem and xylem [23]. Although its mode of action is not clear, it can be used effectively for sprout suppression on vegetable crops such as onions and carrots as well as for the control of troublesome parasitic weed species where synthetic herbicides are limited [24–26].

Essential oils derived from a variety of aromatic, biomass, invasive or food crop plants are also known to have potential as natural non-selective herbicides [9,27–29]. Similarly, with the case of pelargonic acid, the foliage of weeds burns down in a very short time after application, which is more effective against young plants than older ones [30]. Manuka oil is isolated from the leaves of *Leptospermum scoparium* J. R. Forst. and G. Forst. and is considered to be an acceptable product in terms of organic standards [9]. The active ingredient in this essential oil is leptospermone, a natural b-triketone, which targets the enzyme p-hydroxyphenylpyruvate dioxygenase (HPPD) such as the conventional synthetic herbicides mesotrione and sulcotrione [31–33]. Lemongrass essential oil, derived from either *Cymbopogon citratus* Stapf. or *C. flexuosus* D.C. containing up to 80% citral is also commercialized as an organic herbicide whose mode of action involves the disruption of
polymerization of plant microtubules [34]. Lemongrass oil acts as a contact herbicide, and since the active ingredient does not translocate, only the portions of plants receiving the spray solution are affected [9]. Pine essential oil is also commercialized as a 10% aqueous emulsion for weed control as a natural herbicide [9]. It is derived from steam distillation of needles, twigs and cones of *Pinus sylvestris* L. and a wide range of other species belonging to *Pinus* spp. and includes terpene alcohols and saponified fatty acids. Monoterpenes such as a- and b-pinene can increase the concentration of malondialdehyde, proline and hydrogen peroxide, indicating lipid peroxidation and induction of oxidative stress in weeds [35,36].

The aim of the present study was to evaluate and compare the efficacy of four different pelargonic acid products, three essential oils and two mixtures (of a pelargonic acid product and two essential oils) against three target weed species, i.e., rigid ryegrass (*Lolium rigidum* Gaud.), sterile oat (*Avena sterilis* L.) and cleaver (*Galium aparine* L.).

2. Materials and Methods

2.1. Plant Material Collection and Seed Pretreatment

Seeds of rigid ryegrass (*L. rigidum*), sterile oat (*A. sterilis*) and cleaver (*G. aparine*) were collected from winter wheat fields of the origins of Fthiotida, Viotia and Larisa, respectively, during June 2019 (Table 1). In each field, panicles and seeds were collected from 20 plants and transferred to the Laboratory of Agronomy (Agricultural University of Athens).

| Common Name       | Scientific Name     | Origin       | Position           |
|-------------------|---------------------|--------------|--------------------|
| Rigid ryegrass    | *Lolium rigidum* Gaud. | Fthiotida   | 39°08′07″ N, 22°24′56″ E |
| Sterile oat       | *Avena sterilis* L.  | Viotia      | 38°24′41″ N, 23°00′40″ E |
| Cleaver           | *Galium aparine* L. | Larisa      | 39°25′51″ N, 22°45′47″ E |

Two experiments were conducted and repeated twice to evaluate and compare the efficacy of the different pelargonic acid products, essential oils and mixtures of natural herbicides against the three target weed species. The collected seeds were air-dried, threshed, placed in paper bags, and stored at room temperature to be used in the subsequent experimental runs. Different were the seed pretreatment processes carried out to release dormancy in the seeds of the grasses and in the seeds of cleaver. To release dormancy in the seeds of rigid ryegrass and sterile oat, the seeds were individually nicked with 2 teeth tweezers and placed in Petri dishes on two sheets of Whatman No.1 paper filter disk (Whatman Ltd., Maidstone, England) saturated with 6 mL distilled water, in 10 November. The Petri dishes were kept at 2–4 °C (refrigerator) for a period of 7 days. After that, the non-dormant seeds were used for sowing during the first experimental run, carried out during 2019. About half of the total collected grass weed seeds had been stored at room temperature to be used in the second experimental run, carried out during 2020. For cleaver, the seeds were sown in rectangular pots (28 × 30 × 70 cm³) and buried into the soil at approximately 3–4 cm depth, in 17 June. The pots were kept outside under natural conditions for 3 months to break the dormancy in the cleaver seeds. The seeds were carefully removed from the pots in 19 September. Afterwards, they were air-dried, placed and stored in paper bags at room temperature until use either for the first or the second experimental run.

Approximately fifteen seeds of rigid ryegrass and sterile oat, and twenty seeds of cleaver were sown in separate pots (12 × 13 × 15 cm³) in 18 November 2019, during the experiments of the first run. Rigid ryegrass and sterile oat seeds were sown at 1 cm depth. Cleaver seeds were also sown at 1 cm depth to achieve maximum seedling emergence. Pots had been filled with a mix of herbicide-free soil from the experimental field of the Agricultural University of Athens and peat at the ratio of 1:1 (v/v). The soil of the experimental field is clay loam (CL) with pH value of 7.29, whereas the contents of CaCO₃ and organic matter were 15.99% and 2.37%, respectively. Moreover, the concentrations of NO₃⁻ P (Olsen) and Na⁺ were 104.3, 9.95 and 110 ppm, respectively. When the weed seedlings of all
the weed species reached the appropriate phenological stage for spraying, they were carefully thinned to twelve plants per pot. All pots were watered as needed and placed outdoors. The pots were randomized every 5 days in order to achieve uniform growth conditions for all the plants. Regarding the duration of the first experiment, it was conducted between 18 November and 28 December 2019. Regarding the second experimental run, the pot experiments were established in 14 January 2020 and were conducted until 25 February 2020. For the second experimental run, the same courses of action were carried out regarding seed pretreatment and experiment establishment as compared to the corresponding ones carried out for the run. Typical climatic conditions for Greece were observed during the experimental periods. Maximum month temperatures for November, December, January and February were 21.3, 15.6, 9.2 and 11.3 °C, respectively. Minimum month temperatures for the same months were 14.2, 9.2, 2.1 and 1.8°C, respectively, whereas total heights of precipitation for these months were 120.4, 90.6, 16.4 and 12.0 mm, respectively.

2.2. Experimental Treatments

Several pelargonic acid products along with essential oils with a potential herbicidal action have been used. In particular, PA1 (3Stunden Bio-Unkrautfrei, Bayer Garten, Germany) and PA2 (Beloukha Garden, Belchim Crop Protection NV/SA, Technologlaan 7, 1840 Londerzeel, Belgium) contained only pelargonic acid at concentrations shown in Table 2, while PA3 and PA4 (Finalsan Ultima, W. Neudorff GmbH KG, Emmerthal, Germany) contained pelargonic acid along with maleic hydrazide (Table 2). For PA1, PA2, PA3 and PA4 treatments, pelargonic acid was applied as a single treatment without being mixed. Regarding the treatments containing essential oil application, EO1 (Manuka oil, *Leptospermum scoparium*, Salvia, India), EO2 (Lemon grass oil, *Cymbopogon citratus*, Sheer Essence, India) and EO3 (Pine oil, *Pinus sylvestris*, Sheer Essence, India) were used at 5% concentration. All of the essential oils were diluted with water before treatment to achieve a 5% concentration. In fact, commercial essential oils must be applied at high concentrations, often 10% or more per volume [30]. In the present study, an intermediate concentration of 5% was selected to reduce the cost of essential oil application in order to evaluate whether sufficient weed control can be achieved with the application of such natural herbicides at lower concentrations, acceptable also by an economic aspect. All herbicide applications were carried out with a handy pressure sprayer equipped with a variable conical nozzle. Spraying was carried out at 0.3 MPa pressure and the spraying angle was 80°. The height between the conical nozzle and the soil level was 40 cm for all the experimental treatments. The spray head was set to move over the plants at 1.5 km h⁻¹ and the apparatus was calibrated to deliver the equivalent of 200 L ha⁻¹.

The treatments were applied in 20 December, 2019, for the two runs of the first year (in 16 February 2020, for the two runs of the second year) when plants had reached the phenological stage of 2–3 true leaves, corresponding to stage 12–13 of the BBCH scale for rigid ryegrass and sterile oat, and the phenological stage of 3–4 true leaves, corresponding to stage 13–14 of the BBCH scale for cleaver. The pots were placed outdoors, and the leaves of the weed plants were vertically oriented at the time of spraying. The experimental treatments were carried out at a sunny day and air temperature during spraying was 16.1 °C, for the first year (13.4 °C for the second year).
Table 2. The experimental treatments (e.g., natural herbicides) applied in the current study.

| Treatment                      | Active Ingredient Content in (g/L) or (ml/L) | Dose Rate (L/ha) | Active Ingredient per Unit Area in (g/ha) or (ml/ha) | Abbreviation |
|--------------------------------|-----------------------------------------------|------------------|-------------------------------------------------------|--------------|
| Control                        | -                                             | -                | -                                                     | -            |
| Pelargonic acid 18.67%         | 18.67 \(^1\)                                 | 200              | 3734 \(^3\)                                          | PA1          |
| Pelargonic acid 50%            | 50 \(^1\)                                    | 200              | 10000 \(^3\)                                         | PA2          |
| Pelargonic acid 3.102% + maleic hydrazide 0.459% | 3.102 \(^1\)                             | 200              | 620.4 \(^3\)                                         | PA3          |
| Pelargonic acid 18.67% + maleic hydrazide 3% | 18.67 \(^1\) + 3 \(^1\)                  | 200              | 3734 \(^3\) + 600 \(^3\)                            | PA4          |
| Manuka oil 5%                 | 5 \(^2\)                                      | 200              | 1000 \(^4\)                                          | EO1          |
| Lemongrass oil 5%             | 5 \(^2\)                                      | 200              | 1000 \(^4\)                                          | EO2          |
| Pine oil 5%                   | 5 \(^2\)                                      | 200              | 1000 \(^4\)                                          | EO3          |
| Pelargonic acid 18.67% + maleic hydrazide 3% + Manuka oil 5% | 18.67 \(^1\) + 3 \(^1\) + 5 \(^2\)      | 200              | 3734 \(^3\) + 600 \(^3\) + 1000 \(^4\)              | M1           |
| Pelargonic acid 18.67% + maleic hydrazide 3% + Lemongrass oil 5% | 18.67 \(^1\) + 3 \(^1\) + 5 \(^2\)      | 200              | 3734 \(^3\) + 600 \(^3\) + 1000 \(^4\)              | M2           |

\(^1\) Data refer to the active ingredient contents of the four different pelargonic acid formulations. The active ingredients are expressed in g/L. \(^2\) Data refer to the active ingredient contents of the three different essential oil formulations. The active ingredients are expressed in mL/L. \(^3\) Data refer to the amount of the active ingredient of the four different pelargonic acid formulations per unit area. The amounts are expressed in g/ha. \(^4\) Data refer to the amount of the active ingredient of the three different essential oil formulations. The amounts are expressed in mL/ha.

2.3. Evaluation of the Efficacy of Each Natural Herbicide against Targeted Weeds

To evaluate the efficacy of each natural herbicide against the targeted weed species, dry weight and plant height of four plants per pot were measured for each weed species at 1, 3 and 7 days after treatment (DAT). For measuring dry weight, the selected plants were dried at 60 °C for 48 h and then the measurements of dry weight were carried out. The scale to measure dry weight had an accuracy of three decimal places and plant height was measured to nearest cm. Each one of the experiments started with twelve plants in each pot and four plants were removed from each pot at 1, 3 and 7 DAT. The assessment period was not longer than 7 DAT because the current experiment was focused on evaluating the knockdown effect of the natural herbicides on each one of the studied weed species. No observations regarding necrosis levels or NDVI values were made since these will be the objects of future experimentation.

2.4. Statistical Analysis

Both of the experiments were repeated twice per year. All the experiments were conducted in a completely randomized design with four replicates and nine experimental treatments (PA1, PA2, PA3, PA4, EO1, EO2, EO3, M1 and M2). Four replicate pots were used for the evaluation of the effects of the experimental treatments on each weed species. For all the experiments, the weed dry weight as well as the plant height values which corresponded to each treatment were measured, for each weed species separately. These values were recorded at 1, 3 and 7 DAT, and expressed as percentages of the corresponding values recorded for the untreated control plants. An analysis of variance (ANOVA) combined over years and runs was conducted for all data and differences between means were compared at the 5% level of significance using the Fisher’s Protected LSD test. The ANOVA indicated no significant treatment x year interactions, across the two experimental runs, for each one of the weed species studied. Thus, the means of plant dry weight and height, for each weed species, were averaged over the two years and the two experimental runs. Afterwards, the pooled data were analyzed by ANOVA at a ≤ 5% probability level using Statgraphics® Centurion XVI. Fisher’s Protected LSD test was used to separate means regarding the effects of the application of the experimental treatments on plant dry weight and height for each one of the weed species studied.
3. Results

3.1. Effects of the Experimental Treatments on L. rigidum Dry Weight and Height

In the first measurement carried out at 1 DAT, it was noticed that PA3 reduced dry weight of rigid ryegrass by 41% as compared to the control whereas biomass reduction was by 13% higher in the case of PA1. The efficacy of manuka, lemongrass and pine essential oils was similar. The mixture of manuka oil and pelargonic acid resulted in 63% lower rigid ryegrass dry weight than the value recorded for the untreated plants whereas similar was the efficacy of the mixture of lemongrass essential oil and pelargonic acid. In the second measurement, carried out at 3 DAT, it was revealed that PA3 resulted in 48% lower fresh weight compared to the untreated control. Rigid ryegrass dry weight was recorded at 34% and 37% of control when PA4 and EO3 treatments were applied, respectively. Manuka oil provided the highest efficacy of all the experimental treatments against rigid ryegrass. In the final measurement, carried out at 7 DAT, a 47% biomass reduction was recorded for PA3 as compared to the control. Increased was the efficacy of PA2 and pine oil application since rigid ryegrass dry weight was recorded at 30% and 33% of control. The mixture of lemongrass oil and pelargonic acid resulted in 77% lower dry weight in comparison to the value recorded for the control. Biomass reduction reached the level of 90% as compared to the control in the case of manuka oil and similar was the efficacy of manuka oil and pelargonic acid mixture (Table 3).

Table 3. Dry weight and height of L. rigidum plants as affected by the application of the natural herbicides at 1, 3 and 7 days after treatment (DAT). Dry weight and height values of L. rigidum plants was expressed as % of control.

| Treatment | 1 DAT | 3 DAT | 7 DAT | 1 DAT | 3 DAT | 7 DAT |
|-----------|-------|-------|-------|-------|-------|-------|
| PA1       | 46 b  | 42 ab | 41 b  | 44 cb | 43 b  | 40 ab |
| PA2       | 34 d  | 29 cde| 30 cd | 38 bcd| 27 def| 28 cd |
| PA3       | 59 a  | 52 a  | 53 a  | 63 a  | 54 a  | 51 a  |
| PA4       | 41 bcd| 37 bcd| 37 b  | 42 bcd| 33 cde| 35 bc |
| EO1       | 41 bcd| 27 de | 10 e  | 45 b  | 28 cde| 8 e   |
| EO2       | 42 bc | 39 bc | 40 b  | 40 bcd| 36 bc | 38 bc |
| EO3       | 38 cd | 34 bcd| 33 cd | 37 de | 35 bcd| 36 bc |
| M1        | 37 cd | 22 e  | 6 e   | 36 e  | 24 f  | 7 e   |
| M2        | 36 cd | 29 cde| 23 d  | 40 bcd| 26 ef | 21 d  |

LSD (0.05) 8 10 11 7 8 11

*p value ** ** *** *** *** **

Different letters in the same column for L. rigidum dry weight and height, separately, indicate the significant differences between the means for each treatment at *p* = 5% significance level. ***, ** = significant at 0.05, 0.01 and 0.001, respectively.

At 1 DAT, height of rigid ryegrass was recorded at 63% of the untreated control when PA3 was applied. Lemongrass essential oil (EO2), PA2 and PA4 treatments resulted in 58–62% lower height as compared to the control. The efficacy of the manuka oil and pelargonic acid mixture as well as the efficacy of pine oil was similar and slightly increased in comparison to the three treatments mentioned above. In the second measurement carried out at 3 DAT, rigid ryegrass height was recorded at 43% of control in the case of PA1 whereas the adoption of PA2, PA4 and EO1 resulted in 67–73% in comparison to the control. Similar was the efficacy of the two mixtures used since height reduction reached the level of 74–76% as compared to the value recorded for the untreated plants and these two treatments were the most efficient against rigid ryegrass. In the final measurement carried out at 7 DAT, the efficacy of PA3 was similar to the two previous measurements whereas the application of lemongrass and pine oil resulted in 62–64% lower plant height as compared to the control. In addition, PA2 was even more effective since plant height was recorded at 28% of control in the case of this treatment. Manuka oil, as well as its mixture with pelargonic acid, were by far the most effective treatments since rigid ryegrass plant height was reduced by 92–93% (Table 3).
3.2. Effects of the Experimental Treatments on A. sterilis Dry Weight and Height

Regarding sterile oat, at 1 DAT it was observed that PA3 reduced dry weight by 52% as compared to the control. The efficacy of PA2 treatment was significantly higher than PA3. Essential oils derived from manuka, lemongrass and pine showed similar efficacy. The mixture of manuka oil and pelargonic acid (M1) was by approximately 6% more effective than the mixture of lemongrass oil and pelargonic acid (M2). At 3 DAT, it was noticed that sterile oat dry weight was recorded at 44% of control when PA3 treatment was applied while the corresponding value recorded under pine oil application was recorded at 35% of control. PA1 and PA4 treatments were more effective than PA3 treatment whereas lemongrass and manuka oils were characterized by similar efficacy. The most effective treatment was the mixture of manuka oil and pelargonic acid given that its application reduced dry weight by 82% as compared to the control. The results of the measurement carried out at 7 DAT clarified that PA3 was the least efficient treatment against sterile oat since weed biomass was recorded at 41% of control whereas the corresponding values recorded for PA4, PA1, EO2 and EO3 treatments ranged between 31 and 33% of control. The efficacy of the lemongrass oil and pelargonic acid mixture was significantly higher. Manuka oil resulted in a biomass reduction higher than 90% whereas the manuka oil and pelargonic acid mixture reduced weed biomass by 96% as compared to the value recorded for the untreated plants (Table 4).

Table 4. Dry weight and height of A. sterilis plants as affected by the application of the natural herbicides at 1, 3 and 7 days after treatment (DAT). Dry weight and height values of A. sterilis plants was expressed as % of control.

| Treatment | Dry weight (%) of Control | Height (%) of Control |
|-----------|---------------------------|-----------------------|
|           | 1 DAT | 3 DAT | 1 DAT | 3 DAT | 1 DAT | 3 DAT |
| PA1       | 36    | 33    | ab    | 33    | bc    | 38    | bc    | 36    | 36    | 35    | ab    |
| PA2       | 27    | e     | 24    | de    | 23    | bc    | 29    | c     | 27    | cde   | 24    | cd    |
| PA3       | 48    | a     | 44    | a     | 41    | a     | 53    | a     | 46    | a     | 42    | a     |
| PA4       | 33    | cde   | 30    | bcd   | 31    | ab    | 36    | bc    | 33    | bc    | 32    | bc    |
| EO1       | 42    | ab    | 28    | bcd   | 7     | de    | 44    | ab    | 31    | bcd   | 12    | e     |
| EO2       | 36    | bcd   | 31    | bcd   | 32    | ab    | 37    | bc    | 34    | bc    | 34    | ab    |
| EO3       | 39    | bc    | 35    | b     | 32    | ab    | 42    | b     | 37    | b     | 35    | ab    |
| M1        | 28    | de    | 18    | e     | 4     | e     | 30    | c     | 20    | e     | 8     | f     |
| M2        | 34    | bcde  | 25    | cde   | 17    | cd    | 36    | bc    | 25    | de    | 19    | de    |

LSD (0.05) 9 8 11 9 7 9

*p value*  
*** Significant at a = 0.05, 0.01 and 0.001, respectively.

Sterile oat height was recorded at 53% of control when PA3 was applied as it was observed at 1 DAT. Sterile oat height ranged between 36% and 38% of control for PA4 and PA1 while almost the same plant height reduction was attributed to lemongrass essential oil application. Height reduction was estimated at 30% as compared to the value recorded for the untreated plants in the case of manuka oil and pelargonic acid mixture. This mixture was also approximately 6% more effective than the lemongrass oil and pelargonic acid mixture. At 3 DAT, PA3 remained the least effective of all the studied treatments given that its efficacy was lower than the corresponding of EO3, PA1 and PA4 treatments. The plant height values observed when manuka and lemongrass essential oils were applied were similar. PA2 application resulted in 73% lower sterile oat height as compared to the control. The efficacy of lemongrass oil and pelargonic acid mixture was similar, whereas mixing manuka oil and pelargonic acid was the most effective treatment of all against sterile oat. The final measurement carried out at 7 DAT confirmed that PA3 was the least effective treatment of all, while lemongrass and pine essential oils were more efficient than PA3 treatment. Mixing lemongrass oil with pelargonic acid was more effective than the treatments mentioned above. Manuka oil
application was even more effective whereas its mixture with pelargonic acid resulted in the greatest plant height reduction which was recorded at 92% as compared to the control (Table 4).

3.3. Effects of the Experimental Treatments on G. aparine Dry Weight and Height

In general, all the experimental treatments were more effective against cleaver than against the grass weeds studied. In particular, manuka and lemongrass essential oils provided a 67–70% biomass reduction in comparison to the control whereas biomass reduction for the two mixtures ranged between 76% and 78% in comparison to the control as observed in the measurement carried out 24 h after treatment. The efficacy of all the pelargonic acid formulations was remarkable. At 3 DAT, it was observed that pine oil was 7% and 11% more effective than manuka and lemongrass essential oils, respectively, and the efficacy of the two mixtures was similar. PA3 treatment reduced weed biomass by 90%, whereas the application of PA2 treatment almost eliminated cleaver plants. At 7 DAT, the efficacy of lemongrass and pine oils was similar, whereas manuka oil was characterized by increased efficacy (up to 92%). PA4 and PA1 treatments resulted in a 96–97% dry weight reduction than the corresponding value recorded for the untreated plants. Weed dry weight was recorded at 6% of control in the case of lemongrass oil and pelargonic acid mixture whereas PA2 and M1 treatments completely eliminated cleaver plants (Table 5).

Table 5. Dry weight and height of G. aparine plants as affected by the application of the natural herbicides at 1, 3 and 7 days after treatment (DAT). Dry weight and height values of G. aparine plants is expressed as % of control.

| Treatment | 1 DAT | 3 DAT | 1 DAT | 3 DAT | 1 DAT | 3 DAT |
|-----------|-------|-------|-------|-------|-------|-------|
| PA1       | 12 def| 5 cd  | 4 d   | 14 def| 6 cd  | 6 cd  |
| PA2       | 5 f   | 2 d   | 0 d   | 8 f   | 4 d   | 0 d   |
| PA3       | 17 cde| 10 bc | 8 bc  | 20 cde| 12 bc | 11 bc |
| PA4       | 10 ef | 5 cd  | 3 d   | 13 ef | 6 cd  | 5 cd  |
| EO1       | 33 a  | 23 a  | 8 bc  | 36 a  | 27 a  | 11 bc |
| EO2       | 30 ab | 27 a  | 25 a  | 33 ab | 29 a  | 27 a  |
| EO3       | 19 cd | 16 b  | 14 b  | 21 cd | 19 b  | 18 b  |
| M1        | 22 c  | 12 b  | 0 d   | 25 c  | 13 bc | 0 d   |
| M2        | 24 bc | 15 b  | 6 bc  | 26 bc | 16 b  | 8 cd  |
| LSD (0.05) | 8     | 6     | 9     | 8     | 7     | 9     |
| p value   | ***   | ***   | **    | ***   | ***   | **    |

Different letters in the same column for G. aparine dry weight and height, separately, indicate the significant differences between the means for each treatment at a = 5% significance level. **, *** = significant at 0.05, 0.01 and 0.001, respectively.

Cleaver height was by 64 and 67% lower compared to the control when manuka and lemongrass oils were applied, respectively, as noticed at 1 DAT. The efficacy of manuka oil and pelargonic acid were by 11% higher than the corresponding value of manuka oil alone and even higher was the efficacy of PA4 and PA1. PA2 treatment was the most effective of all the treatments studied, since its application reduced weed height by approximately 92% as compared to the control. The results of the second measurement revealed that cleaver height was recorded at 27% and 29% of control when manuka and lemongrass essential oils were applied, respectively. The mixture of lemongrass oil and pelargonic acid was characterized by similar efficacy to pine oil whereas PA3 treatment reduced plant height by almost 88% as compared to the control. At 7 DAT, it was noticed that lemongrass oil application was the least effective treatment against cleaver whereas pine oil was by 9% more effective. Cleaver height was only recorded at 5%, 6% and 8% of control when PA4, PA1 and M2 treatments were applied, while either manuka oil and pelargonic acid mixture or PA2 treatment completely eliminated cleaver plants (Table 5).
4. Discussion

The results of the current study revealed the different efficacy of the four pelargonic acid products against the different weed species. In most cases, broadleaf weeds like cleaver were more susceptible than grass species, while the formulations of increased pelargonic acid concentration (e.g., PA2) were significantly more effective. Our findings are in contrast with the corresponding of Muñoz et al. [8] who noticed that all the pelargonic acid-based herbicides managed to completely eliminate *Avena fatua (L.)* plants at 3 DAT whereas there were no significant differences regarding the efficacy of the different pelargonic acid formulations. The insufficient control of rigid ryegrass and sterile oat when the low-concentration formulation of pelargonic acid was applied is in agreement with the findings of a previous study in which the application of pelargonic acid at the concentration of 2% (v/v) provided only 20% total weed control [14]. However, the same authors noticed that the same treatment controlled broadleaf weeds such as velvetleaf (*Abutilon theophrasti* Medic.) by only 31%. In our study, cleaver was adequately controlled by the majority of the pelargonic acid-based treatments even 24 h after treatment. Moreover, it was noticed that at 7 DAT, all the treatments did reduce cleaver dry biomass and plant height sufficiently.

The possible effects of climatic conditions on the efficacy and the overall results is something that should be further studied. In our case, although weather conditions before and at spraying seemed favorable for the pot experiments, pelargonic acid products did not show remarkable efficacy against the two grass weed species. This outcome might be attributed to the air temperature at spraying time. The hypothesis of Krauss et al. [37] regarding the impact of weather conditions on the efficacy of pelargonic acid products was similar. In any case, this is an objective that should be systematically evaluated in future studies. In addition, there is evidence that various weed species can develop new shoots and recover after pelargonic acid application [38]. Hence, another objective for a future experiment would be to find out the level of weed regrowth that emerges over a longer term than 7 DAT for a wider range of weed species. In fact, the natural substances are not translocated systemically in the plants and they cannot provide long-term weed control for most species. However, it has already been reported that sufficient weed control might be achieved with repeated treatments [39]. Moreover, it was obvious that the different weed species’ responses to the application of the natural herbicides showed variability. This emphasizes the importance of further multifactor experiments towards the comparison of the effects of such experimental treatments between numerous weed species.

The efficacy of pelargonic acid-based herbicides under real field conditions is an unexplored area of great interest. There are not many studies evaluating the level of weed control in the field and defining the crops that can be favored by the adoption of such weed control practices. However, there were interesting results in a more recent study carried out in Greece by Kanatas et al. [19] in which pelargonic acid along with maleic hydrazide was applied for non-selective weed control before sowing soybean crop in a stale seedbed. In particular, it was revealed that stale seedbed combined with pelargonic acid application reduced annual weeds’ density by 95% as compared to normal seedbed, indicating that such pelargonic acid-based herbicides can be equally effective to glyphosate against annual weeds in a stale seedbed where a crop is about to be established and reap the benefits of pre-sowing weed elimination [19]. On one hand, it seems that integrated weed management strategies, including cultural practices such as the stale seedbed preparation, could maximize the herbicidal potential of pelargonic acid under real field conditions. Consequently, the level of weed control as assured by pelargonic acid-based herbicides could be sufficient if a vigorous and competitive crop is about to be sown. It has been reported recently in Greece that the competitiveness of barley (*Hordeum vulgare* L.) against troublesome weeds such as rigid ryegrass of sterile oat can be promoted if such organic weed control practices are applied before crop sowing [40]. On the other hand, after the nonanoic acid application, there was no weed cover reduction at one and two days after treatment in both experimental sites as well as repetitions in the field experiments of Martelloni et al. [41], where a treatment similar to PA-4 treatment was applied for weed control. The explanation suggested for this outcome was that weeds were in unsuitable growth stage for the natural herbicide to have an effect [41]. Previous research has reported that nonanoic acid needs to be applied to very
young or small plants for acceptable weed control [42], and repeated applications are suggested [39]. However, in the current experiment, it was observed that increasing pelargonic acid concentration in a natural herbicide product can result in more efficient control for grasses and barely elimination of broadleaves. This finding is in agreement with the ones reported by Rowley et al. [43], who observed an intermediate reduction in weed ground coverage, density, and dry weed biomass due to the higher rate of nonanoic acid used (39 L a.i. ha⁻¹). Other authors found an intermediate reduction in Japanese stiltgrass (Microstegium vimineum Trin.) ground coverage as compared to their control treatment due to the pelargonic acid application at a rate of 11.8 kg a.i. ha⁻¹ and 5% (v/v) concentration [44].

Concerning the potential role of maleic hydrazide, this was not statistically significant in the present study, probably due to the measurements being only for 7 days and not on a long-term basis. However, the use of products containing pelargonic acid along with maleic hydrazide is a promising tactic. An explanation might be given by the fact that maleic hydrazide has systemic activity and can be translocated in the meristematic tissues, with mobility in both phloem and xylem [23]. Although its mode of action is not totally clear, it can be used effectively for the control of troublesome parasitic weed species belonging to Orobanche spp. [24–26]. This is quite important, given that a factor restricting the herbicidal potential of pelargonic acid is the absence of systemic activity, with maleic hydrazide reducing weed regrowth and ensuring a long-term control [39].

The findings of the present study also revealed that manuka oil is a possible solution for dealing with the challenge of increasing the systemic activity of natural herbicides. Even without being mixed with pelargonic acid, manuka oil showed increased efficacy against all the weeds as compared to the other essential oils and pelargonic acid treatments. In the study of Dayan et al. [32], it was noticed that manuka oil and its main active ingredient, leptospermerone, were stable in soil for up to 7 d and had half-lives of 18 and 15 days after treatment, respectively. Such findings indicate the systemic activity of manuka oil and also that it can be a useful tool addressing many of the restricting factors related to the use of natural herbicides. Dayan et al. [32] also recorded 68%, 57%, 93%, 88%, 73% and 50% lower biomass for pigweed (Amaranthus retroflexus L.), velvetleaf, field bindweed (Convolvulus arvensis L.), hemp sesbania (Sesbania exaltata (Raf.) Rydb. ex A.W. Hill], large crabgrass (Digitaria sanguinalis L.) and barnyardgrass (Echinochloa crus-galli L. P.Beauv.) as compared to the control, respectively, when a mixture with lemongrass essential oil was mixed with manuka oil and applied to the targeted weed species mentioned above. Pine and lemongrass essential oils provided a biomass reduction for rigid ryegrass and sterile oat ranging between 60% and 70% whereas they were more effective against the broad leaf species G. aparine. In the study of Young [45], pine oil controlled hairy vetch (Vicia villosa Roth), broadleaf filaree (Erodium botrys (Cav.) Bertol.), and hare barley (Hordeum murinum L.) at least 83%, but yellow starthistle (Centaura solstitialis L.), soft brome (Bromus hordeaceus L.), control never surpassed the level of 85%. In the greenhouse experiment of Poonpaiboonpipat et al. [46], it was noted that lemongrass essential oil at concentrations of 1.25%, 2.5%, 5% and 10% (v/v) was phytotoxic against barnyard grass, since leaf wilt symptoms were observed at just 6 h after treatment. The same authors also noticed that chlorophyll a, b and carotenoid content decreased under increased concentrations of the essential oil, indicating that lemongrass essential oil interferes with the weeds’ photosynthetic metabolism [46]. Although the herbicidal potential of such essential oils does exist, many studies have concluded that there are limitations since the essential oils act as contact herbicides with no systemic activity [9,30,32,45,46]. They generally disrupt the cuticular layer of the foliage, which results in the rapid desiccation or burn-down of young tissues [9]. However, lateral meristems tend to recover, and additional applications of essential oils are necessary to control regrowth [45]. Essential oils must be applied at high concentrations to convey 50 to 500 L of active ingredient per hectare [30]. The limitations of applying either lemongrass or pine essential oils for weed control are similar to those mainly observed in the case of pelargonic acid-based herbicides. Manuka oil differs from other essential oils in that it contains large amounts of several natural b-triketones, including leptospermerone, which enable this oil to have systemic activity [47]. One of the most important findings of the present study was the satisfactory control of all the targeted weed species in the case where the mixture of manuka oil and pelargonic acid was applied. This synergy
resulted in improvement of overall weed control, compared to the cases in which pelargonic acid formulations, lemongrass and pine essential oils were used alone. This is one of the key findings of this study, and provides vital information for improving weed control in terms of either organic or sustainable agriculture. The findings of Coleman and Penner [14] were similar, finding that the addition of diammonium succinate and succinic acid improved the efficacy of a pelargonic acid formulation up to 200%, whereas l-Lactic acid and glycolic acid enhanced the efficacy of pelargonic acid formulations on velvetleaf and common lambsquarters (Chenopodium album L.) up to 138% even under real field conditions.

5. Conclusions

To date, no studies have evaluated the herbicidal potential of several pelargonic acid products, essential oils and mixtures of natural herbicides against major weed species in Greece. The findings of the present study revealed that selecting natural products with high concentrations of pelargonic acids can increase the control levels of grass weeds. However, in the case of broadleaf weeds, it seems that the application of natural products might lead to sufficient weed control even when products of lower pelargonic acid concentration are applied. The results of the current study also validated that lemongrass and pine oil act as contact burn-down herbicides, whereas manuka oil showed a systemic activity. The synergy between manuka oil and pelargonic acid is reported for the first time and is one of the key findings of the present study. This unique essential oil might deal with the lack of systemic activity associated with pelargonic acid and further experiments are in progress by our team. Further research is needed to evaluate more natural substances and combinations in order to optimize the use of natural herbicides as well as natural herbicides’ mixtures in weed management strategies in both organic and sustainable agriculture systems and also under different soil and climatic conditions.

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References

1. Zimdahl, R.L. Fundamentals of Weed Science, 5th ed.; Academic Press: Cambridge, MA, USA, 2018.
2. Li, Y.; Sun, Z.; Zhuang, X.; Xu, L.; Chen, S.; Li, M. Research progress on microbial herbicides. Crop Prot. 2003, 22, 247–252.
3. Cox, C. Ten reasons not to use pesticides. J. Pest. Ref. 2006, 26, 10–12.
4. Meksawat, S.; Pornprom, T. Allelopathic effect of itchgrass (Rottboellia cochinichinensis) on seed germination and plant growth. Weed Biol. Manag. 2010, 10, 16–24.
5. Pot, V.; Benoit, P.; Le Menn, M.; Eklo, O.M.; Sveistrup, T.; Kvaerner, J. Metribuzin transport in undisturbed soil cores under controlled water potential conditions: Experiments and modeling to evaluate the risk of leaching in a sandy loam soil profile. Pest Manag. Sci. 2011, 67, 397–407.
6. Heap, I. Herbicide resistant weeds. In Integrated Pest Manag.; Pimentel, D., Peshin, R., Eds.; Springer: Dordrecht, The Netherlands, 2014; Volume 3, pp. 281–301.
7. Ibáñez, M.D.; Blázquez, M.A. Phytotoxic effects of commercial Eucalyptus citriodora, Lavandula angustifolia, and Pinus sylvestris essential oils on weeds, crops, and invasive species. Molecules 2019, 24, 2847.
8. Muñoz, M.; Torres-Pagán, N.; Peiró, R.; Guijarro, R.; Sánchez-Moreiras, A.M.; Verdeguer, M. Phytotoxic effects of three natural compounds: Pelargonic acid, carvacrol, and cinnamic aldehyde, against problematic weeds in Mediterranean crops. Agronomy 2020, 10, 791.
9. Dayan, F.E.; Cantrell, C.L.; Duke, S.O. Natural products in crop protection. Bioorg. Med. Chem. 2009, 17, 4022–4034.
10. Pavela, R.; Benelli, G. Essential oils as ecofriendly biopesticides? Challenges and constraints. Trends Plant Sci. 2016, 21, 1000–1007.
11. Bakkali, F.; Averbeck, S.; Averbeck, D.; Idaomar, M. Biological effects of essential oils—A review. Food Chem. Toxicol. 2008, 46, 446–475.

12. European Food Safety Authority. Conclusion on the peer review of the pesticide risk assessment of the active substance Fatty acids C7 to C18 (approved under Regulation (EC) No 1107/2009 as Fatty acids C7 to C20). EFSA J. 2013, 11, 3023.

13. Wahlberg, J.E.; Lindberg, M. Nonanoic acid—an experimental irritant. Contact Derm. 2003, 49, 117–123.

14. Coleman, R.; Penner, D. Organic acid enhancement of pelargonic acid. Weed Technol. 2008, 22, 38–41.

15. Crmaric, I.; Keller, M.; Krauss, J.; Delabays, N. Efficacy of natural fatty acid based herbicides on mixed weed stands. Jul. Kühn Arch. 2018, 458, 327–332.

16. Ciriminna, R.; Fidalgo, A.; Ilharco, L.M.; Pagliaro, M. Herbicides based on pelargonic acid: Herbicides of the bioeconomy. Biofuels Bioprod. Biorefining 2019, 13, 1476–1482.

17. Dayan, F.E.; Duke, S.O. Natural compounds as next-generation herbicides. Plant Physiol. 2014, 166, 1090–1105.

18. Lebecque, S.; Lins, L.; Dayan, F.E.; Fauconnier, M.L.; Deleu, M. Interactions between natural herbicides and lipid bilayers mimicking the plant plasma membrane. Front. Plant Sci. 2019, 10, 329–340.

19. Kanatas, P.; Travlos, I.; Papastylianou, P.; Gazoulis, I.; Kakabouki, I.; Tsekoura, A. Yield, quality and weed control in soybean crop as affected by several cultural and weed management practices. Not. Bot. Hort. Agrobot. 2020, 48, 329–341.

20. Schoene, D.L.; Hoffmann, O.L. Maleic hydrazide, a unique growth regulant. Science 1949, 109, 588–590.

21. Naylor, A.W.; Davis, E.A. Maleic hydrazide as a plant growth inhibitor. Bot. Gaz. 1950, 112, 112–126.

22. Cradwick, P.D. Crystal structure of the growth inhibitor, “maleic hydrazide (1, 2-dihydroxypyridazine-3, 6-dione).” J. Chem. Soc. Perkin Trans. 1976, 2, 1386–1389.

23. Meyer, S.A.; Sheets, T.J.; Seltmann, H. Maleic hydrazide residues in tobacco and their toxicological implications. In Review of Environmental Contamination and Toxicology; Ware, G.W., Ed.; Springer-Verlag: New York, NY, USA, 1987; Volume 98, pp. 43–61.

24. Covarelli, L. Studies on the control of broomrape (Orobanche ramosa L.) in Virginia tobacco (Nicotiana tabacum L.). Beiträge Tabelle Int. 2002, 20, 77–81.

25. Boyd, D.R. The Food We Eat: An International Comparison of Pesticide Regulations; David Suzuki Foundation: Vancouver, BC, Canada, 2006.

26. Venezian, A.; Dor, E.; Achdari, G.; Plakhine, D.; Smirnov, E.; Hershenhorn, J. The influence of the plant growth regulator maleic hydrazide on Egyptian broomrape early developmental stages and its control efficacy in tomato under greenhouse and field conditions. Front. Plant Sci. 2017, 8, 691.

27. Dhanapal, G.N.; Struijk, P.C.; Timmermans, P.C.J.M.; Borg, S.J. Post-emergence control of broomrape with natural plant oils. J. Sustain. Agric. 1998, 11, 5–12.

28. Vasilakoglou, I. Herbicidal potential of essential oil of oregano or marjoram (Origanum spp.) and basil (Ocimum basilicum) on Echinocloa crus-galli (L.) P. Beauv. and Chenopodium album L. weeds. Allelopath. J. 2007, 20, 297–306.

29. Rassaeifar, M.; Hosseini, N.; Asl, N.H.H.; Zandi, P.; Aghdam, A.M. Allelopathic effect of Eucalyptus globulus’ essential oil on seed germination and seedling establishment of Amaranthus blitoides and Cynodon dactylon. Trakia J. Sci. 2013, 11, 73–81.

30. Dayan, F.E.; Duke, S.O. Natural products for weed management in organic farming in the USA. Outlooks Pest Manag. 2010, 21, 156–160.

31. Dayan, F.E.; Duke, S.O.; Sauldubois, A.; Singh, N.; McCurdy, C.; Cantrell, C.L. P-Hydroxyphenylpyruvate dioxygenase is a herbicidal target site for b-triketones from Leptospermum scoparium. Phytochemistry 2007, 68, 2004–2014.

32. Dayan, F.E.; Howell, J.; Marais, J.P.; Ferreira, D.; Koivunen, M. Manuka oil, a natural herbicide with preemergence activity. Weed Sci. 2011, 59, 464–469.

33. Owens, D.K.; Nanayakkara, N.P.D.; Dayan, F.E. In planta mechanism of action of leptospermone: Impact of its physico-chemical properties on uptake, translocation, and metabolism. J. Chem. Ecol. 2013, 39, 262–270.

34. Chaimovitsch, D.; Abu-Abied, M.; Belausov, E.; Rubin, B.; Dudai, N.; Sadot, E. Microtubules are an intracellular target of the plant terpene citral. Plant. J. 2010, 61, 399–408.

35. De Martino, L.; Mancini, E.; Almeida, L.F.R.D.; Feo, V.D. The antigerminative activity of twenty-seven monoterpenes. Molecules 2010, 15, 6630–6637.
36. Witzke, S.; Duelund, L.; Kongsted, J.; Petersen, M.; Mouritsen, O.G.; Khandelia, H. Inclusion of terpenoid plant extracts in lipid bilayers investigated by molecular dynamics simulations. J. Phys. Chem. 2010, 114, 15825–15831.

37. Krauss, J.; Eigenmann, M.; Keller, M. Pelargonic acid for weed control in onions: Factors affecting selectivity. J. Kühn Arch. 2020, 464, 415–419.

38. Andert, S.; Gerowitt, B. Controlling arable weeds with natural substances as bio-based herbicides. J. Kühn Arch. 2020, 464, 407–414.

39. Webber, C.L.; Taylor, M.J.; Shreffler, J.W. Weed control in yellow squash using sequential postdirected applications of pelargonic acid. Hort Technol. 2014, 24, 25–29.

40. Kanatas, P.J.; Travlos, I.S.; Gazoulis, J.; Antonopoulos, N.; Tsekoura, A.; Tataridas, A.; Zannopoulos, S. The combined effects of false seedbed technique, post-emergence chemical control and cultivar on weed management and yield of barley in Greece. Phytoparasitica 2020, 48, 131–143.

41. Martelloni, L.; Frasconi, C.; Sportelli, M.; Fontanelli, M.; Raffaelli, M.; Peruzzi, A. Flaming, glyphosate, hot foam and nonanoic acid for weed control: A comparison. Agronomy 2020, 10, 129.

42. Webber, C.L.; Shreffler, J.W.; Brandenberger, L.P.; Davis, A.R. AXXE® (Pelargonic Acid) and Racer® (Ammonium Nonanoate): Weed Control Comparisons; Vegetable Weed Control Studies; Oklahoma State University, Division of Agricultural Sciences and Natural Resources, Department of Horticulture & Landscape Architecture: Stillwater, OK, USA, 2012; pp. 1–4.

43. Rowley, M.A.; Ransom, C.V.; Reeves, J.R.; Black, B.L. Mulch and organic herbicide combinations for in-row orchard weed suppression. Int. J. Fruit Sci. 2011, 11, 316–331.

44. Ward, J.S.; Todd, L.M. Nonchemical and herbicide treatments for management of Japanese stiltgrass (Microstegium vimineum). Invasive Plant Sci. Manag. 2012, 5, 9–19.

45. Young, S.L. Natural product herbicides for control of annual vegetation along roadsides. Weed Technol. 2004, 18, 580–587.

46. Poonpaiboonpipat, T.; Pangnakorn, U.; Suvunnamek, U.; Teerarak, M.; Charoeying, P.; Laosinwattana, C. Phytotoxic effects of essential oil from Cymbopogon citratus and its physiological mechanisms on barnyardgrass (Echinochloa crus-galli). Ind. Crops Prod. 2013, 41, 403–407.

47. Douglas, M.H.; van Klink, J.W.; Smallfield, B.M.; Perry, N.B.; Anderson, R.E.; Johnstone, P.; Weavers, R.T. Essential oils from New Zealand manuka: Triketone and other chemotypes of Leptospermum scoparium. Phytochemistry 2004, 65, 1255–1264.

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