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# **Discovery and development of a novel sustainable contact herbicide based on natural fatty acids**

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Dedicated to my Family



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## **Resumen**

La agricultura del siglo XXI se enfrenta a múltiples desafíos. Por un lado, debe proporcionar suficientes alimentos para satisfacer las necesidades de la población mundial en pleno crecimiento, haciendo un uso eficiente y sostenible de los recursos disponibles, y por otro lado debe hacer frente a una creciente demanda de productos con alta calidad impulsada por parte de los consumidores. Para ello debe apoyarse en avances tecnológicos. En la producción de cultivos, el frecuente uso de pesticidas y en particular de los herbicidas se encuentra bajo el foco de la atención pública. La normativa europea obliga al uso sostenible de los productos fitosanitarios, entre ellos los herbicidas. Si bien estos productos son necesarios en las estrategias de gestión y control de malas hierbas, para garantizar el máximo rendimiento de los cultivos, también causan efectos negativos en el medio ambiente y la salud humana. Sin embargo, su ausencia supondría pérdidas incalculables en la lucha contra las malas hierbas.

En los últimos años, muchos herbicidas han sido retirados del mercado, debido a que se buscan productos menos tóxicos para el medio ambiente, la salud humana y organismos no objetivo y menos persistentes. Esto ha provocado un aumento en la inversión para la investigación y el desarrollo de productos herbicidas más sostenibles. Sin embargo, hoy en día, hay pocas opciones comerciales que puedan reemplazar eficazmente a los herbicidas tradicionales. La comunidad agrícola ha posicionado al ácido pelargónico (PA) como una buena alternativa a los herbicidas de contacto convencionales, e incluso al glifosato en ciertas situaciones. El PA es un herbicida no selectivo de contacto, que presenta un buen control de las malezas sin dañar el medio ambiente. Sin embargo, su uso en la agricultura se encuentra limitado debido a algunos inconvenientes, como los problemas de su formulación, el olor rancio y desagradable después de su aplicación y principalmente las altas dosis de pulverización a las que debe ser aplicado para que sea efectivo, teniendo un coste elevado, comparado con otros herbicidas disponibles en el mercado.

Por estas razones, el objetivo de esta tesis fue primero desarrollar un nuevo compuesto no tóxico con actividad herbicida, que pudiera ser una alternativa a los herbicidas convencionales. A continuación, se estudiaron las condiciones óptimas de aplicación de la nueva sustancia: dosis de aplicación, ajustes de las barras de pulverización y condiciones climáticas fueron definidas para un mayor rendimiento de la nueva sustancia. Igualmente, se usaron coadyuvantes en el caldo, para incrementar la actividad del nuevo herbicida. Además, el modo de acción de la nueva sustancia fue investigado.

Los resultados de esta tesis doctoral reportan la actividad herbicida de trece compuestos a base de ésteres de ácidos grasos, que podrían ser alternativas sostenibles para el control de malas hierbas. Su efectividad herbicida fue evaluada sobre *Digitaria sanguinalis* (L.) Scop. y *Solanum nigrum* L. Todos los componentes mostraron una interesante actividad herbicida de contacto que no está relacionada con el ácido libre de los ácidos grasos, además de buenas propiedades fisicoquímicas. La mayor eficacia se obtuvo con el éster de ácido pelargónico de polietilenglicol metilado (PA-MPEG), con seis óxidos de etileno.

El PA-MPEG es un compuesto líquido, soluble en agua y sin olor rancio, debido a su nula volatilidad, a diferencia del PA. También tiene unas excelentes propiedades mojantes, pudiéndose diluir directamente en agua y aplicar sin la necesidad de una formulación, en contraste con el PA. PA-MPEG fue pulverizado a diferentes caudales, proporcionando un control de las malas hierbas estudiadas igual o mejor que el obtenido por los herbicidas comerciales a base de PA. La aplicación de PA-MPEG a una tasa de 12.8 kg de ácido equivalente de PA por hectárea con un caudal de 500 L por hectárea, fue la dosis más adecuada para lograr un excelente control (90 %) de las malas hierbas con un tamaño medio (18-20 cm; BBCH 16-22). Esta dosis de producto y el volumen de caldo son relativamente más bajos que los recomendados en la etiqueta del herbicida comercial a base de PA, formulado con una concentración de 273.4 g L<sup>-1</sup>. Como PA-MPEG y PA tienen actividad de contacto y su eficacia depende de la cobertura de rociado, en el estudio se reportó y se confirmó que las pulverizaciones realizadas con caudales inferiores a 200 litros por hectárea

presentaron un control deficiente sobre *D. sanguinalis* y *S. nigrum*, al ser la cobertura de rociado y la penetración en el follaje insuficiente.

La eficacia de PA-MPEG a una dosis subóptima fue mejorada cuando la aplicación se realizó con la barra de pulverización a una altura menor, lo que redujo la distancia al follaje de las malas hierbas. Condiciones climáticas cálidas (T: 33 °C; 30 % r.h.) durante la aplicación y los siguientes días también favorecieron el control de malas hierbas con PA-MPEG. Ambos aspectos de la aplicación podrían ser útiles para reducir las dosis de pulverización de PA-MPEG, manteniendo su eficacia. El uso de aditivos en el rociado también incrementó la efectividad de PA-MPEG. Aunque varios coadyuvantes adicionados al caldo de pulverización potenciaron la eficiencia de PA-MPEG sobre *D. sanguinalis* y *S. nigrum*, el coadyuvante a base de aceite de semilla etilado/metilado fue el preferido, debido a su nula fitotoxicidad por sí mismo y a su efecto en la penetración cuticular de PA-MPEG.

Además de reportar PA-MPEG como una alternativa a los herbicidas convencionales, la nula volatilidad de PA-MPEG sugiere que este grupo éster podría ser una solución interesante para evitar los problemas de volatilidad en nuevos pesticidas o corregirlos en los productos existentes, como los herbicidas auxínicos.



## Resum

L'agricultura del segle XXI s'enfronta a múltiples desafiaments. D'una banda, ha de proporcionar suficients aliments per a satisfer les necessitats de la població mundial en ple creixement, fent un ús eficient i sostenible dels recursos disponibles, i d'altra banda ha de fer front a una creixent demanda de productes amb alta qualitat impulsada per part dels consumidors. Per a això ha de secundar-se en avanços tecnològics. En la producció de cultius, el freqüent ús de pesticides i en particular dels herbicides es troba sota el focus de l'atenció pública. La normativa europea obliga a l'ús sostenible dels productes fitosanitaris, entre ells els herbicides. Si bé aquests productes són necessaris en les estratègies de gestió i control de males herbes, per a garantir el màxim rendiment dels cultius, també causen efectes negatius en el medi ambient i la salut humana. No obstant això, la seua absència suposaria pèrdues incalculables en la lluita contra les males herbes.

En els últims anys, molts herbicides han estat retirats del mercat, pel fet que es busquen productes menys tòxics per al medi ambient, la salut humana i organismes no objectiu i menys persistents. Això ha provocat un augment en la inversió per a la investigació i el desenvolupament de productes herbicides més sostenibles. No obstant això, hui dia, hi ha poques opcions comercials que puguen reemplaçar eficaçment als herbicides tradicionals. La comunitat agrícola ha posicionat a l'àcid pelargònic (PA) com una bona alternativa als herbicides de contacte convencionals, i fins i tot al glifosato en unes certes situacions. El PA és un herbicida no selectiu de contacte, que presenta un bon control de les males herbes sense danyar el medi ambient. No obstant això, el seu ús en l'agricultura es troba limitat a causa d'alguns inconvenients, com els problemes de la seua formulació, l'olor rànica i desagradable després de la seua aplicació i principalment les altes dosis de polvorització a les quals ha de ser aplicat perquè siga efectiu, tenint un cost elevat, comparat amb altres herbicides disponibles en el mercat.

Per aquestes raons, l'objectiu d'aquesta tesi va ser primer desenvolupar un nou compost no toxic amb activitat herbicida, que poguera ser una alternativa als herbicides convencionals. A continuació, es van estudiar les condicions òptimes d'aplicació de la nova substància: dosi d'aplicació, ajustos de les barres de polvorització i condicions climàtiques van ser definides per a un major rendiment de la nova substància. Igualment, es van usar coadjuvants en el caldo, per a incrementar l'activitat del nou herbicida. A més, la manera d'acció de la nova substància va ser investigat.

Els resultats d'aquesta tesi doctoral reporten l'activitat herbicida de tretze compostos a base d'èsters d'àcids grassos, que podrien ser alternatives sostenibles per al control de males herbes. La seua efectivitat herbicida va ser avaluada sobre *Digitaria sanguinalis* (L.) Scop. i *Solanum nigrum* L. Tots els components van mostrar una interessant activitat herbicida de contacte que no està relacionada amb l'àcid lliure dels àcids grassos, a més de bones propietats fisicoquímiques. L'eficàcia més gran es va obtenir amb l'èster d'àcid pelargònic de polietilenglicol metilado (PA-MPEG), amb sis òxids d'etilé.

El PA-MPEG és un compost líquid, soluble en aigua i sense olor rànica, a causa de la seua nul·la volatilitat, a diferència del PA. També té unes excel·lents propietats mojanter, podent-se diluir directament en aigua i aplicar sense la necessitat d'una formulació, en contrast amb el PA. PA-MPEG va ser polvoritzat a diferents cabals, proporcionant un control de les males herbes estudiades igual o millor que l'aconseguit ingut pels herbicides comercials a base de PA. L'aplicació de PA-MPEG a una taxa de 12.8 kg d'àcid equivalent de PA per hectàrea amb un cabal de 500 L per hectàrea, va ser la dosi més adequada per a aconseguir un excel·lent control (90%) de les males herbes amb una grandària mitjana (18-20 cm; BBCH 16-22). Aquesta dosi de producte i el volum de caldo són relativament més baixos que els recomanats en l'etiqueta de l'herbicida comercial a base de PA, formulat amb una concentració de 273.4 g L<sup>-1</sup>. Com a PA-MPEG i PA tenen activitat de contacte i la seua eficàcia depèn de la cobertura de ruixat, en l'estudi es va reportar i es va confirmar que les polvoritzacions realitzades amb cabals inferiors a 200 litres per hectàrea van presentar un

control deficient sobre *D. sanguinalis* i *S. nigrum*, a l'ésser la cobertura de ruixat i la penetració en el fullatge insuficient.

L'eficàcia de PA-MPEG a una dosi subòptima va ser millorada quan l'aplicació es va realitzar amb la barra de polvorització a una altura menor, la qual cosa va reduir la distància al fullatge de les males herbes. Condicions climàtiques càlides (T: 33 °C; 30% r.h.) durant l'aplicació i els següents dies també van afavorir el control de males herbes amb PA-MPEG. Tots dos aspectes de l'aplicació podrien ser útils per a reduir les dosis de polvorització de PA-MPEG, mantenint la seua eficàcia. L'ús d'additius en el tanc de mescla també va incrementar l'efectivitat de PA-MPEG. Encara que diversos coadjuvants addicionats al caldo de polvorització van potenciar l'eficiència de PA-MPEG sobre *D. sanguinalis* i *S. nigrum*, el coadjuvant a base d'oli de llavor etilado/metilado va ser el preferit, a causa de la seua nul·la fitotoxicitat per si mateix i al seu efecte en la penetració cuticular de PA-MPEG.

A més de reportar PA-MPEG com una alternativa als herbicides convencionals, la nul·la volatilitat de PA-MPEG suggereix que aquest grup èster podria ser una solució interessant per a evitar els problemes de volatilitat en nous pesticides o corregir-los en els productes existents, com els herbicides auxínics.





## Summary

Agriculture in the 21st century faces multiple challenges. On the one hand, it must provide enough food to meet the needs of the growing world population, making efficient and sustainable use of available resources, and on the other hand, it also must handle the increasing demand for high-quality and safe products driven by consumers. To do this, it must rely on technological advances. In crop production, a particular focus is given to the extensive use of pesticides and in particular herbicides. European regulations make mandatory the sustainable use of phytosanitary products, including herbicides. Although these products are essential in weed control and management strategies to guarantee the maximum crop yield, they also cause many negative impacts on the environment and human health. However, the non-use of herbicides would mean incalculable losses in the fight against weeds.

In the last years, many herbicides have been withdrawn from the market, due to the search for less toxic products for the environment, human health, and non-target organisms, and with lower persistence, increasing the investment for research and development of more sustainable herbicide products. However, today, there are few commercial options that can effectively replace traditional herbicides. The agricultural community has positioned pelargonic acid (PA) as a good alternative to conventional contact herbicides and even for glyphosate in specific situations. PA is a non-selective contact herbicide that achieves good weed control efficacy without harming the environment. However, its use is limited in agriculture due to some drawbacks, such as its formulation problems, the rancid and unpleasant odour after its application and mainly the high spray doses at which it must be applied to be effective, having a high cost, compared to other herbicides available on the market.

Therefore, the objectives of this thesis were first to develop a non-toxic compound with herbicidal activity, which could be an alternative to conventional herbicides. Next, the

optimal application conditions of the new substance were studied: application rates, spray bar settings and climatic conditions were defined for a higher performance of the new substance. Similarly, adjuvants were used to enhance the activity of the new herbicide. The results of this doctoral thesis report the herbicidal activity of thirteen sustainable alternative compounds based on fatty acid (FA) esters, which could be sustainable alternatives for weed control. Its herbicidal effectiveness in weed control was evaluated on *Digitaria sanguinalis* (L.) Scop. and *Solanum nigrum* L. All the components showed an interesting contact herbicidal activity that is not related to the free acid of fatty acids, in addition to good physicochemical properties. The highest efficacy was obtained with methylated polyethylene glycol pelargonic acid ester (PA-MPEG), with six ethylene oxides.

PA-MPEG is a liquid compound, soluble in water, non-volatile and consequently without rancid smell, unlike PA. Furthermore, it has excellent wetting properties, being able to be diluted directly in water and applied without further formulation efforts in contrast to PA. Additionally, it was suggested that PA-MPEG and other FA herbicides could cause desiccation symptoms due to the break of the water continuum at the site of evaporation in the intercellular spaces.

PA-MPEG applied at different spray volumes provided equal or better weed control than commercial PA herbicides. The application of PA-MPEG at a rate of 12.8 kg of PA acid equivalent per hectare in a spray volume of 500 L per hectare was the most suitable rate for achieving excellent weed control (above 90 %) on medium-sized weeds (18-22 cm height; BBCH 18-22). These product doses and spray volume are relatively lower than those recommended on the label of a commercial PA formulation (273.4 g L<sup>-1</sup>). Since PA-MPEG and PA have contact herbicidal activity and their weed control efficacy depends on the spray coverage, the study reported and confirmed that application performed with spray volumes below 200 L ha<sup>-1</sup> resulted in poor *D. sanguinalis* and *S. nigrum* control due to insufficient weed coverage and spray penetration into the weed canopy.

The efficacy of PA-MPEG at a suboptimal use rate was improved when the application was performed at a lower boom height, which reduced the distance to the weed canopy. Warm weather conditions (T: 33 °C; 30 % r.h.) during the application and the following days also increased weed control efficacy with PA-MPEG. Both application aspects could reduce PA-MPEG use rates while keeping its effectiveness. The use of adjuvants added into the spray tank also caused an enhancement of PA-MPEG performance. Although several tank-mix partners improved *D. sanguinalis* and *S. nigrum* control, an alkylated seed oil-based adjuvant was preferred because of its penetration-enhancing properties and non-phytotoxicity.

Besides PA-MPEG could be an alternative to conventional herbicides, the non-volatility of PA-MPEG suggests that this ester group could be an interesting solution for overcoming volatility-related problems in new pesticides or to correct or manage them in existing ones, like auxins.



## **Zusammenfassung**

Die heutige Agrarwirtschaft sieht sich mit vielen Herausforderungen konfrontiert. Auf der einen Seite muss sie genug Nahrung für eine wachsende Weltbevölkerung bereitstellen, auf der anderen Seite besteht von Konsumentenseite her ein immer größeres Bedürfnis nach qualitativ hochwertigen und sicheren Produkten. In der Nahrungsmittelproduktion ist die Verwendung von Herbiziden integraler Bestandteil. Während diese Produkte essenziell für die strategische Unkrautbekämpfung sind und ein Maximum an Ernteertrag garantieren, können sie vielfältige, negative Einflüsse auf die menschliche Gesundheit und die Umwelt haben. Das Nichtverwenden von Herbiziden kann zu einer kritischen Lage im Kampf gegen Unkräuter mit erheblichen Ertragseinbußen führen.

In den letzten Jahren wurden viele Herbizide vom Markt verbannt, was die Entwicklung von nachhaltigeren Produkten gefördert hat. Heutzutage können einige kommerziell verfügbare Herbizide einige traditionellen Wirkstoffe ersetzen. Bauernverbände äußern sich positiv zu Pelargonsäure (PA) als guten Ersatz für konventionelle Kontaktherbizide, in spezifischen Anwendungsfällen sogar als Ersatz für Glyphosat. PA ist ein nichtselektives Kontaktherbizid, welches eine gutes Wirkungsspektrum hat, mit geringem Einfluss auf die Natur und ohne die Umwelt zu zerstören. Aufgrund einiger Herausforderungen in der Anwendung und Handhabung, z.B. die hohe Applikationsrate pro Hektar, der unangenehme, ranzige Geruch noch lange nach der Anwendung und die Formulierungsstabilität, findet PA bislang nur sehr limitierten Einsatz in der Landwirtschaft.

Es war das Ziel dieser Arbeit, eine Alternative mit gutem Wirkungsspektrum zu konventionellen Herbiziden in Gewächshausversuchen zu entwickeln. Weiterhin wurde die neue Substanz applikationstechnisch weiterentwickelt, bezüglich ihrer Dosierungsrate, den Sprüh- und Düseneigenschaften und klimatischer Bedingungen. Auch wurde die Nutzung von Additiven mit einbezogen, um die Effizienz der Unkrautkontrolle zu steigern. Darüber hinaus ist der Mode of Action der neuen Substanz untersucht worden.

Es wurde die herbizide Wirkung von 13 Alternativen auf Basis von verschiedenen, erneuerbaren Fettsäureestern (FA) untersucht. Ausgewertet wurde die Kontrolle von *Digitaria sanguinalis* (L.) Scop. und *Solanum nigrum* L. Alle zeigten vielversprechende Kontaktwirkung und physiochemische Eigenschaften, unabhängig von der Bildung freier Säure. Die höchste Effizienz hat dabei Methyl-polyethylenglykol Pelargonsäureester (PA-MPEG) mit sechs Ethylenoxid-Einheiten. PA-MPEG ist flüssig, löslich in Wasser, nicht flüchtig und ohne jeglichen unangenehm ranzigen Geruch - im Gegensatz zur Pelargonsäure. Weiterhin ist es selbstemulgierend und kann direkt, ohne weitere Formulierhilfsmittel mit Wasser gemischt werden. Vermutlich unterbricht das PA-MPEG und andere Fettsäureherbizide die kontinuierliche Wasserversorgung in Kapillaren der interzellularen Zwischenräume und ruft so Vertrocknungssymptome hervor.

PA-MPEG zeigt gleiche oder bessere Unkrautkontrolle als PA-Herbizide. Die beste Rate für eine exzellente Kontrolle mittelgroßer Unkräuter liegt bei 12.8 kg PA-Säureäquivalent pro Hektar bei einer Aufwandmenge von 500 L/ha. Volumen und Applikationsrate sind im Vergleich zur empfohlenen Anwendungskonzentration kommerzieller Pelargonsäureformulierungen (273.4 g/L) niedriger. Wie schon erwähnt, sind PA und PA-MPEG Kontaktherbizide, deren Wirkung und Effizienz vom Bedeckungsgrad der Applikation abhängig ist. Diese Studie zeigt und bestätigt, dass Aufwandmengen unter 200 L/ha nur schwach den Wuchs von *D.sanguinalis* und *S.nigrum* kontrollieren können, da durch das dichte, obere Blattwerk eine ausreichende Benetzung der Pflanze nicht stattfindet.

Den Performanceverlust niedrigerer Aufwandmengen lässt sich durch geringeren Spritzabstand bis zu einem gewissen Grad kompensieren. Günstige, warme Wetterbedingungen nach der Applikation mit PA-MPEG führen ebenfalls zu gesteigerter Effizienz. Beide Maßnahmen können helfen, die Applikationsrate und Kosten bei gleicher Unkrautkontrolle zu senken. Weiterhin hat sich gezeigt, dass verschiedene Tankmixpartner die herbizide Wirkung von PA-MPEG verstärken können. Hierzu zählt besonders ein Additiv basierend auf alkyliertem Saatenöl, mit penetrationsfördernden, nicht phytotoxischen Eigenschaften.

Abschließend kann gesagt werden, dass PA-MPEG eine echte Alternative zu konventionellen Kontakt-Herbiziden darstellt. Die geringe Verdunstung des PA-MPEG lässt vermuten, dass die Estergruppe eine interessante Lösung für andere flüchtige Wirkstoffe sein könnte, wie z.B. Auxine.





Chapter I.

# **Introduction**



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## INTRODUCTION

### 1. Weeds.

#### *1.1. Definition.*

Weeds affect everyone in the world (Kraehmer and Baur 2013). They are defined as “plants growing in a place where they are not desired” (Buchholtz 1967). In broadacre and horticultural crops, weeds include local and invasive alien plants (IAP) competing with crops as well as neophytes challenging natural vegetation (Rejmánek 2000; Zimdahl 2018), and attracting pests or diseases to crops (Capinera 2005). Parasitic plant species like *Striga* spp. or *Orobanche* spp. are also reported as a problem in agricultural production, particularly for African farmers (Woomer et al. 2008). Considering the Buchholtz definition, a plant could be considered a weed in one situation and a desirable plant in another. For instance, *Digitaria sanguinalis* (L.) Scop. is used as a pasture grass in some areas of North America, but five plants per square meter of this monocotyledon plant can reduce sweetcorn yields by 33% (Hartley 1992). Whereas *Solanum nigrum* L. is an important wild vegetable in many African countries because of its high nutritional value (Edmonds and Chweya 1997), in crops from southern France or Italy, black nightshade could cause up to 73% yield reduction (Maillet and Abdel-Fata 1983; McGiffen et al. 1992). The term weed is also employed to refer plant species like *Urtica* spp. or *Delphinium* spp. that are sources of aeroallergens or poison for humans and domesticated animals (Pfister et al. 1999), or seedlings of *Pinus sylvestris* L., which may represent a safety risk on railways and motorways (Nyberg 2016).

#### *1.2. Challenges to agricultural production.*

In crop production, weeds are the most harmful threat. They are abundant, invasive, competitive, destructive and difficult to control. It is nearly impossible to evaluate yield loss due to a single weed because thousands of weed seeds coexist in soil and form a biocenosis (Carretero 1977). Weeds cause the highest potential yield loss (34 %) worldwide (Oerke

2006). They affect crop production by competing directly with the crop for light and mineral resources, sheltering crop pests, interfering with water management, reducing the yield and quality, and subsequently increasing the cost of processing (Zimdahl 2018). Thus, a key and significant part of crop production and cost factor is weed management, which aims to reduce weed populations by keeping them at low levels and reducing its dissemination to protect the crops. An example is that weeds usually cause a reduction of 12 % in yield in the US, representing an economic value of \$33 bn. in annual yield loss. In addition, another \$4 bn. is spent each year on herbicides to control these weeds and more than \$3 bn. on cultural and other control methods (Pimentel 2005).

## ***2. Weed control methods***

Since humans started to grow crops, a wider range of methods have been used to fight against undesirable plants (Davies et al. 1982). First, humans removed the weeds by hand; later, domesticated animals were used as an energy input for weed control; finally, feedstock was employed for combustion and mechanical methods, changing the world and soil cultivation (Alder et al. 1977). Most efficient was the introduction of chemistry and biotechnology to reduce weed control work (Zimdahl 2018). While no weed control technique has ever been abandoned, older methods became less important in further developed agriculture where time, cost-saving and technology are getting relative importance (Zimdahl 2018). A challenge that even in third world countries is preferentially solved chemically. However, the demand for a more sustainable agriculture has promoted the use of the methods described in the next sections for integrated weed management, as required in the European Directive 2009/128/EC of the European Parliament and the Council (Tataridas et al. 2022).

### ***2.1. Cultural methods.***

Refers to any crop management in which weeds are less likely to become established and/or increased in number. Crop rotation and cover crops often reduce the population of specific

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weeds which were able to flourish in the previous crop (Korres et al. 2019). The preparation of a false seedbed or changes in the planting times also prevents the dominance of weeds (Tu et al. 2001; Zimdahl, 2018). The selection of the best-looking plans and seeds (breeding) with the best features to grow in the following seasons also cause the competition of weeds with the crop to be diminished.

### ***2.2. Mechanical and physical methods.***

Farm equipment (hoes, rakes, cutters) powered by humans, animals, or machinery to destroy or remove weeds are classified as mechanical weed control. Tilling or burial soil and mowing are the most common methods. Fire or flaming is a form of thermal weeding, which causes the dehydration of the treated plant parts and is considered a physical method for weed control as well as the technique of mulching, soil solarization and flooding of the fields (Tu et al. 2001). While these methods effectively control annual plants, weed control is less effective on perennial weeds with stolon and long roots that can regrow quickly from these organs.

### ***2.3. Biological methods – biocontrol and allelopathy***

Since weeds have natural enemies that can destroy them, insects, fungi, animals, or other microbes which feed upon, parasitise, or meddle with an aimed pest species are used to control undesirable plants (Tu et al. 2001). Examples of successful biological control programs include sheep and goats in the pasture and the ragwort flea beetle (*Longitarsus jacobaeae* W.) controlling the *Senecio jacobaea* L. (McEvoy and Rudd 1993). Nonetheless, it is also documented that some biocontrol programs have culminated in critical and irreversible damage to non-target organisms (Louda 2000). Therefore, biological agents must be selectively managed; otherwise, they will be more harmful than the target plant.

Plants also cause a negative impact on the growth and development of other plants through the release of secondary metabolites into the soil rhizosphere (allelopathy) by volatilization, leaching, root exudation and decomposition of plant residues (Mushtaq et al.

2020). These secondary products are called allelochemicals and can inhibit seed germination (Natarajan et al. 2014) or suppress weed activity (Dhima et al. 2006), among other effects. Herbicides like mesotrione or tembotrione have been discovered from allelopathic substances (Mushtaq et al. 2020). Therefore, today, allelochemicals show a huge potential to develop natural and nontoxic herbicides (Weston and Duke 2010; Mushtaq et al. 2020).

#### ***2.4. New technologies – biotechnology and precision farming.***

Although agriculture is falling behind the other scientific branches, farming progress and weed management is moving fast into the new technologies and precision techniques (Young et al. 2017) with ecological concepts (Liebman and Gallandt 1997). Modified crop breeding, commonly known as GMO crops, could be the oldest new method used to fight against weeds. Biotechnology and plant genome tools have generated crops with mutation or modified genes to be herbicide resistant, e.g., glyphosate-resistant crops such as soybean, corn and sugarbeet, among others (Duke and Powles 2008). Today, CRISPR (Clustered Regularly Interspaced Short Palindromic Repeat), ZFN (Zinc Finger Nucleases), or TALENS (Transcription Activator-Like Effector Nucleases) are the new plant genome tools. They are used in some countries but still need to be accepted worldwide. The progress is promoted to improve the adaptability-resilience of the crop to the new climate conditions, but it could also be used to manage weed problems (Neve 2018; Korres et al. 2019).

Agriculture is fast moving to big data and digital farming too. Companies have data warehouses to be more precise in resolving problems through digitalisation, e.g., Xarvio™ – BASF. In the following years, image processing and remote sensing with robotics will be expected to perform automated herbicide applications by drones or robots (Korres et al. 2019; Hafeez et al. 2022).

#### ***2.5. Agrochemical methods.***

Nowadays, agrochemicals are the preferred method for weed control worldwide by farmers (Pannel et al. 2016; Zimdahl 2018). The input of weed control to yield is immediate. This

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method has been used for a very long time (sea salt and oils), but since 1945 with the discovery of the selective compounds, agrochemicals' use has increased dramatically (Troyer 2001; Kraehmer 2012). The herbicides rapidly resulted in revolutionary changes in weed control strategies in industrialised countries, and their sale and use have become increasingly subject to government regulations (Schroeder et al. 1993). While herbicides increased the efficiency of farming being part of the “Green revolution” (Pingali 2012), and become safer and more effective, they have also generated many concerns about their side effects on human health and the environment (Sondhia 2014; Pannel et al. 2016; Carvalho 2017).

### **3. Herbicides.**

Herbicide comes from the Latin *herba*, meaning “plant,” and *caedere*, meaning “to kill”. The Weed Science Society of America (WSSA) defined herbicide as “a chemical substance used to kill or reduce undesirable plant population.” (Vencill 2002). An herbicide disrupts the plant physiology of a plant over a period to kill it or severely limit its growth.

#### **3.1. History.**

Since World War II, there has been a significant development in chemical products for agricultural uses to optimise crop yields. Synthetic herbicides started in 1945 with the idea of spraying a group of plants with a compound to control the herbs without damaging the crop. One year later, the first systemic and selective phenoxide herbicide, 2,4-dichlorophenoxyacetic acid (2,4-D), was launched to manage undesirable dicotyledonous plants (Troyer 2001), followed in the next 30 years by dinitroanilines, triazines, chloroacetamides and others which are still in use today. For the first time, a good combination of these compounds allowed to control a broad spectrum of plants at an acceptable and effective cost (Kraehmer 2012). It was possible to kill undesirable plants without damaging crops and in a wide timing application (Macías 1995). With this generation of compounds in the market, it became clear that plant biochemistry (biological pathways)

must be known for understanding the functioning and optimising of new molecules (Baker et al. 1987). These pathways were the first targets in the design of the actual agrochemicals (Hedin et al. 1985; Baker et al. 1987; Kraehmer 2012). In 1974, the commercial introduction of the molecule N-(phosphonomethyl) glycine (Glyphosate) was the first quantum leap. This highly effective and broad-spectrum herbicide will become the most important herbicide (Duke and Powles 2008; Kraehmer 2012) and the dominant product thanks to the introduction of glyphosate-tolerant transgenic crops in 1995 (Duke and Powles 2008; Kraehmer et al. 2014a, 2014b). Sulfonylureas herbicides discovery in the 80s (Levitt 1991; Drobny et al. 2012) marked the start-line of today's herbicides, characterised by very selective herbicides at shallow doses (Macías 1995; Drobny et al. 2012).

### 3.2. *Herbicide use and its concerns.*

Herbicide expenditures steadily accounted for the most significant share of total costs in crop production (about 43%) over the last years, followed by insecticides, fungicides, and other pesticides (Figure 1).

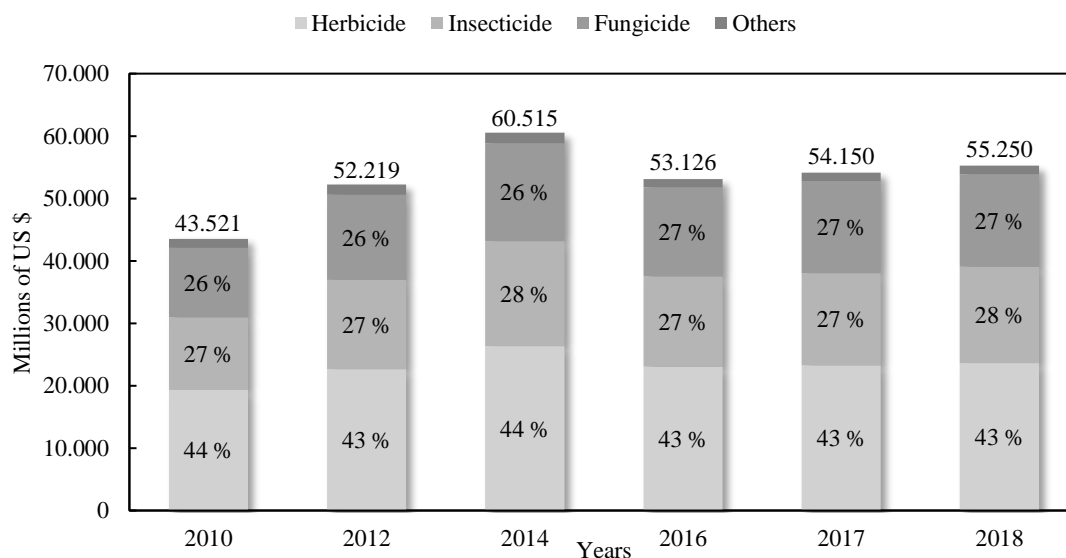


Figure 1 – World pesticide expenditures by farmers. Source: Kleffmann Group 2019.



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Glyphosate, with an economic value of \$5576.68 m., is the dominating active ingredient in both the herbicide and total pesticide market (Duke and Powles 2008; Fogliatto et al. 2020). However, WSSA and Herbicide Resistance Action Committee (HRAC) reported 326 and 357 active ingredients, respectively, for weed control (WSSA 2020; HRAC 2020). In Germany, farmers can use 96 compounds representing a total of 763 commercial herbicides with widely different ways of application. They can be applied before sowing, prior to or after the emergence of the crop or weeds (Hatcher and Froud-Williams 2017; Kraehmer et al. 2021). Some herbicides are incorporated into the soil, whereas others are applied with shields between rows. Therefore, designing an effective weed management strategy relies on a good knowledge of the different herbicide classifications. Herbicides can be categorised according to the mode of action, chemical family, systemicity, selectivity, application timing or site of absorption, among others (Hatcher and Froud-Williams 2017; Jeschke et al. 2019). Thus, understanding their effects and limitations and how they are classified could minimise the side effects and the concerns driven by agronomists, final-food consumers, environmental associations and administrations.

### ***3.3. Weed resistance.***

The occurrence of herbicide (cross) resistance is a key problem for farmers, which is fast increasing (Pannel et al. 2016). While resistant weed biotypes are mainly linked to the inappropriate use and overuse of herbicides, changes in agricultural practices and climate also affect the weed mutations (Pannel et al. 2016; Zimdahl 2018). These have led to the evolution of resistant weed flora to multiple herbicide sites of action, being selected the weeds with the ability to survive and reproduce after exposure to the herbicide's lethal dose.

### ***3.4. Novel weed control in dicot crops.***

Besides the resistant weeds, genetically modified crops have generated an extra problem in Europe and countries in other regions that do not tolerate transgenic crops. The use of non-selective herbicides in GM crops has caused a lack of innovation on selective herbicides for crops like sugar beet, which are getting limited in the fight against weeds (Kraehmer et al.

2014b). Today there are many collaborations between agrochemical and breeding companies to create effective solutions.

### ***3.5. Volatility and drift.***

Off-target herbicide movement can cause severe problems like damage to neighbouring crops and communal areas, exposure of humans and animals to herbicides, and contamination of soils and water sources. Spray drift injuries occur when droplets are moved away from the target site and placed on non-target sites due to environmental conditions (wind velocity) and mistaken boom sprayer parameters that cause more fine droplets (Branham and Hanson 1987; Dexter 1993). These are issues that could be better managed following more stringent principles of good agricultural practices by farmers (Pringnitz 1999). Unlike spray drift, volatility, also known as vapour drift, relies on herbicide physicochemical properties. It appears when the herbicide changes to a gas phase and drifts to the atmosphere or susceptible plants due to an airborne movement (Branham and Hanson 1987). Soil herbicide incorporation and avoiding unfavourable climate conditions like temperature inversions are recommendations for applying herbicides with volatility risk (Mueller and Steckel 2019).

### ***3.6. Environment and human health.***

Some active ingredients have physicochemical properties that can interact with the ecosystem, driving higher mobility and/or persistence of the herbicide. The herbicides' degradation depends not solely on the chemistry but also on the climate conditions, soil structure, and application technology (Buchholtz 1965). The extensive chemical pollution of ecosystems has been caused by the increasing herbicide application over the last years (Van Bruggen et al. 2018; Silva et al. 2019). Many studies have reported side effects in the environment such as soil residue accumulation, the inhibition of helpful soil organisms, fish mortality or water sources contamination (Sondhia 2014; Brühl and Zaller 2019). Aside from this, traces of active ingredients have been found in final food products, opening multiple controversial headlines against herbicides (Van Bruggen et al. 2018). Studies have also described the likely acute and chronic effects on humans, such as eye and skin irritation,

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cancers, or immune disorders. While these impacts and safety recommendations are given on labels, herbicides are still widely applied without safety measurements.

### ***3.7. Regulatory concerns.***

Weed control practically relies on herbicide use. However, the handles for registrations are high, and the number of available products for weed control decreases, and even more the number of new compounds. Today, the use and commercialisation of pesticides in Europe are regulated by the Regulation (EC) No. 1107/2009 and the Directive 2009/128/EC to reduce the pesticide risks and protect human health and the environment by achieving sustainable use of pesticides (Tataridas et al. 2022). The situation may worsen in the future due to stricter national restrictions and action plans for pesticide reduction, causing a lack of products for weed management.

### ***3.8. Current situation.***

The withdrawal and restrictions on herbicides and the ongoing concerns on herbicide use (Carvalho 2017; Tataridas et al. 2022; Van Bruggen et al. 2018) have led to a growing interest in the research of natural compounds with herbicidal activity as well as further investigation on the current bioherbicides to minimise the shortcomings of existing conventional herbicides (Marrone 2019; Tataridas et al. 2022). However, new commercial alternatives to current synthetic products are bare. The market is still dominated by big players with cheap and profitable products. Rigid and stricter legislation and efforts to keep the environment safe have greatly increased development costs and lengthened the time scale for introducing and registering new products (Kraehmer et al. 2014a). The search for new molecules employs a large team of chemists, biologists and agronomists, and the effective use of these molecules requires stable formulations to facilitate its handling, storage and application with low risk for users and the environment (Knowles 1998). This all has caused a delay in the return on investment, being unable to afford by small-medium companies and reducing the launch of new products.

Today, bioherbicides or organic herbicides like essential oils, acetic acid or fatty acid (FA) herbicides, particularly pelargonic acid (PA), have become the best alternatives to conventional herbicides (Fogliatto et al. 2020). They are suggested to be incorporated in weed management programmes. However, they continue to represent a tiny share of the agrochemical market value (Figure 2).

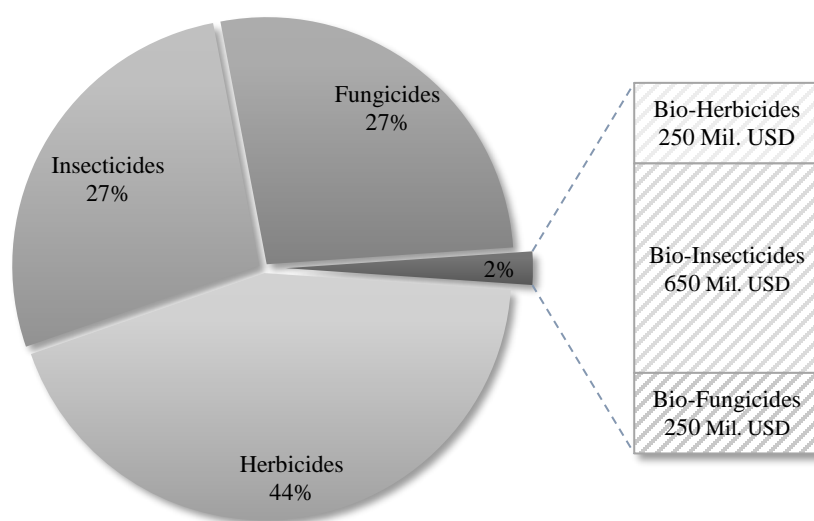


Figure 2 – Representation of the global pesticide and biopesticide market size during the year 2016; Source: Market and Markets study, 2017.

#### 4. Pelargonic acid.

Commercial formulations of short-chain fatty acids (FA) and their salts have been applied for weed control since the early 90s (EPA 2020). Caprylic and Capric acid (C<sub>8</sub>/C<sub>10</sub>) blends and PA have been used for such nontoxic contact herbicidal products.

PA is a naturally occurring fatty acid with nine carbon atoms, also called nonanoic acid. It was first obtained from the oil of geranium (*Pelargonium* spp.) (Windholz 1983; Ciriminna

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et al. 2019). Since there is no economical natural source, PA can be synthesised by various oxidative cleavage processes, using unsaturated fatty acids such as oleic acid from vegetable oil sources (Sabarino et al. 1994) or aldehydes from petrochemical feedstock as starting raw material (Springer 2003), getting a purity from 95 to 99 % wt., which depends on the production process.

The first PA herbicide was registered in 1992 (EPA 2020). In November of 1999, there were four products registered as weed killers. Other applications such as nematicide (Davis et al. 1997); adjuvant (Pline et al. 1999); inhibitor of seed germination (Le Poidevin 1965); and thinning agent (Byers 1999) were also studied for this active ingredient. Today, there are several registered PA products with different active content. They are sold worldwide under distinct trade names such as Scythe in the US, Vorox Unkrautfrei in Germany, Slasher Organic Weed Killer in Australia, or Ouchinokusakorori in Japan. These PA herbicides cause a rapid wilting of the tissues, followed by the complete desiccation and necrosis of the treated organs (Ciriminna et al. 2019). PA is not translocated to untreated aerial parts of the plant and root system, allowing the weed regrowth, and thus, a second application is sometimes needed (Ciriminna et al. 2019). While PA mode of action is categorised as unknown by the HRAC (Webber 2009), it is generally suggested a membrane degradation, an increase in leaf transpiration, and a disintegration of biomembranes, and as a result, reduced photosynthesis (Fukuda et al. 2004; Lederer et al. 2004; Ciriminna et al. 2019).

Recently PA herbicides have become popular for weed control in farming (Fogliatto et al. 2020). Besides the excellent efficacy in small weeds, it has also been reported the no occurrence of resistant weed biotypes and a low toxicity profile (EPA 2020). PA decomposes rapidly in the environment (EPA 2020), and it is not expected to have adverse effects on non-target organisms or the environment (EPA 2020). In addition, U.S. Food and Drug Administration (FDA) has approved this substance for use in food as an additive (FDA 2019). While PA herbicides should be applied according to the standard safety measurements, they do not have bad labelling, just skin and eye irritant pictograms.

On the other hand, PA has shortcomings, limiting its use in agriculture. PA is not soluble in water; therefore, the formulation is essential and not trivial for FA (Campos et al. 2021). Basic formulation concepts are available through patent literature, but they also have one or more issues, providing just a few commercial formulations to the farmers. The high PA volatility, and consequently the disagreeable smell after the application during days, is another drawback which has not been addressed yet. Still, the high rate and large spray volume used in the applications is undoubtedly the most crucial inconvenience why PA remains unutilised by farmers (Crmaric et al. 2018).

## **5. The need for a sustainable food supply.**

Earth's population is expected to rise by 2 bn. in the next 30 years. This means the World's population will reach 9.7 bn. in 2050, according to World Population Prospects 2019 (UN 2019). That is a large number of people to feed, especially given the significant famine issues the world faces today; 827 million are estimated to be suffering from chronic hunger (FAO 2013), and nearly 2 billion suffer from malnutrition (WHO 2013).

An enlarged global population leads to increasing demand for farming products, which puts soil, water and biodiversity under increasing pressure. This entails that agriculture will play a key role in many countries in the following years. It is a call for ending hunger and accelerating overall economic growth, but notwithstanding, it is also a call for being in line with nature and facing environmental challenges. In crop production, even with limitations to pesticides and locally poor conditions, particularly in the recent few years, there have been several record yields by extending arable land area. The challenge of efficient distribution and staple foods so far prevents enough supply of people with food. This aspect might become even more important as consumers are starting to request more sustainable agriculture and food production with less or without pesticides. Authorities have supported this trend by limiting or banning pesticides such as chlorpyrifos, glufosinate, imidacloprid

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and many more. At the same time, farmers also demand new solutions against pests such as *Psylliodes chrysocephala* L. (cabbage-stem flea beetle) in oilseed rape or *D. sanguinalis* in sweetcorn fields. How can the increase in agricultural production be sustainable? What are the scenarios for farmers and farming investments? Can foodstuff provide to almost 10 bn. people without counting on conventional methods?

On the road to succeeding in this challenge, all involved parties must work together. Farmers, industry, and institutions must seek the most suitable options to fulfil the expectations and demands because today, it is impossible without pesticides to protect the crop and feed 10 bn. people. It is an inconvenient fact ignored by the public that the major threats to crop yield and quality is the competition by weeds, followed by diseases mainly due to fungi and many insects and mite pests. While shifts in species and population peak times can be expected in the forthcoming century of global warming, the number of weeds and pests will increase drastically at elevated temperatures. Thus, the pressure on agricultural productivity will increase. Land use will not expand due to a couple of reasons such as increasing natural reserves, poor soil quality, limitations due to lack of precipitation, and mainly ground use by civilisation, therefore, integrated crop protection with sustainable chemicals remains an indispensable asset to secure yields.

In this work an alternative tool to classical synthetic chemicals for weed control without residues on crops and grains is explored. Such a contact product has paramount significance in fighting weeds in agriculture, industrial areas and home gardens.

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Chapter II.

# **Objectives**



## OBJECTIVES

The main objective of this doctoral research was to discover a non-toxic, non-selective contact herbicide based on natural fatty acid as an alternative to conventional herbicides and current fatty acid herbicides, without limitations by bad residue levels.

The specific objectives of this work were determined as follows:

1. To establish a new lead compound based on short fatty acids without the drawbacks of fatty acid herbicides and with enough phytotoxic activity against undesirable plants and a low or non-residue level.
2. To determine the optimum dose rate and spray volume of the new lead substance to achieve maximum efficacy on the target plants.
3. To study different parameters of the sprayer and assess the potential role of the climate conditions on the efficacy of the herbicide to define its recommended use for increasing weed control.
4. To evaluate the potential of formulation auxiliaries' ingredients into the spray tank to increase the herbicidal activity of the new compound on monocot and dicot weed species at suboptimal application rates.



Chapter III.

# **Results**



Publication I

# **Capped polyethylene glycol esters of fatty acids as novel active principles for weed control**

Chapter published as an original article in *Pest Management Science* (Journal indexed in Journal citation reports, JCR).

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## **Capped polyethylene glycol esters of fatty acids as novel active principles for weed control**

### **Abstract**

Ever since the beginning of agriculture, yields have been threatened by weeds. Chemical control is far more effective and economical than other weed control methods. The frequent use of herbicides has led to environmental and human health concerns, causing the ban of several herbicides and challenges for the future of important actives like glyphosate. The herbicidal activity of sustainable alternatives based on certain esters of fatty acids (FA), the action of which is unrelated to the free acid, on common weeds is assessed and reported. The 13 derivatives of FA showed better physicochemical properties than pelargonic acid-based herbicides. All the reported compounds have phytotoxic activity, the highest efficacy being displayed by the methyl end-capped polyethylene glycol (mPEG) ester of pelargonic acid having 6EO (ethylene oxide). This mPEG ester showed equal or better phytotoxicity than the pelargonic acid benchmark at reduced application rate and spray volume. The active compound is a liquid at ambient temperatures, has no bad smell and is not volatile, in contrast to pelargonic acid. Notably, this active compound can be the final product, can be sprayed without adjuvants and is relatively easy to co-formulate. A new lead substance is presented that is a sustainable alternative to current contact herbicides. In particular, it has potential application on railways, in precision agriculture and as a harvest aid. Its good performance and technical properties suggest this mPEG ester group may also overcome the volatility-related problems of other organic acids such as auxins.

### **Keywords**

Pelargonic acid, fatty acid derivatives, natural herbicides, non-toxic herbicide, novel herbicide, contact herbicide.



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## 1. Introduction

Weeds are responsible for up to 40 % of yield loss globally and are the most harmful biological threat to agricultural production (FAO 2019). In 1977, Holm *et al.* reported more than 200 plant species that are major weeds (Holm et al. 1991). Kraehmer and Baur described 32 of the most frequent terrestrial weeds, among these several grasses like *Digitaria sanguinalis* L. Scop. (large crabgrass) (Kraehmer 2016). Inappropriate use of herbicides and changes in agricultural practices have led to modifications in the weed flora, increasing the number of problematic weeds (Kraehmer 2016). For example, *Solanum nigrum* L. (black nightshade) has become more difficult to control due to the development of herbicide-resistant biotypes (Harrington KC; <https://resistance.nzpps.org>). Weed control is of major importance in agricultural production and is a significant cost. To date, weeds have been managed mainly using synthetic herbicides rather than other methods such as cultural, biological or mechanical removal (Qasem 2011). However, the use of herbicides has raised many concerns because of related problems such as weed-resistance (Qasem 2011; Pannell et al. 2016), the lack of novel chemistry for weed control in dicot crops (Kraehmer et al. 2014), poor agricultural practices (Pringnitz 1999; Mueller and Steckel 2019), environmental impacts (Sondhia 2014), food residues (WHO 2018) and regulatory concerns (Kraehmer et al. 2014).

In 2009, the European Union adopted Directive 2009/128/EC on the sustainable use of pesticides, which obligated professional users to implement the principles of integrated pest management by 2014 (EU 2009). Industry and research institutions have intensified their search for solutions that minimize the shortcomings of existing conventional herbicides (Chandler et al. 2011; Marrone 2019). In recent years, efforts have included research into natural products with herbicidal effects, such as plant extracts or secondary metabolites from plants or microorganisms (Marrone 2019). Some new active compounds have been used directly in weed control or as leads for new herbicides, being degradable, non-toxic and produced by or aligned with nature (Chandler et al. 2011; Marrone 2019). Many substances derived from natural products like triketones or essential oils have proven herbicidal potential although only a few have been commercialized (Chandler et

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al. 2011; Travlos et al. 2020). Especially needed are fast-acting and resistance-breaking contact herbicides, particularly since the loss of previous products such as paraquat.

Currently, some of the most popular products for sustainable weed control are fatty acids (FA) with a carboxylic chain length of between eight and ten carbons, for example pelargonic (nonanoic) acid (PA) or a mixture of caprylic and capric acids (Crmaric et al. 2018; Ciriminna et al. 2019; Marrone 2019; Krauss et al. 2020). For many years, the rancid odour of short-chain FA has restricted its use in gardens, industry or crop production greenhouses, despite its popularity as a natural herbicide (EPA 2000; Ciriminna et al. 2019). Currently, PA is the main proposed alternative for natural weed control in agriculture, being the most studied FA herbicide (EPA 2000; Ciriminna et al. 2019). Notwithstanding its lack of toxicity (FDA 2019), environmental advantages (EPA 2000) and fast and good efficacy (Webber and Shrefler 2006), there are some features limiting the use and combination of FA-based compounds in agriculture. For example, at *Bundesamt für Verbraucherschutz und Lebensmittelsicherheit* (BVL; <https://www.bvl.bund.de>), some PA herbicides need to be sprayed at very high rates in a large volume of water, which is not viable economically (Crmaric et al. 2018); the newest PA formulation is applied at a lower spray volume, but gives a weaker weed control (Crmaric et al. 2018; Krauss et al. 2020). In addition, the rapid symptoms caused by PA are not favourable for co-formulation or tank mixing with other systemic compounds (Chuah et al. 2008; Wehtje et al. 2009). Also, FAs are not soluble in water, and the demands of the formulation are considerable and not trivial. There is also a loss of weed control efficacy due to non-stable and heterogenous spray preparations (oil droplet formation followed by phase separation). The literature describes basic formulation concepts for FA (Puritch et al. 1990; Beste et al. 2001; Schweinsberg and Ziegler 2011), but all of these formulations have one or more issues, such as the need to handle concentrated alkaline substances like ammonia (EPA 1992), limited active ingredient content, use of solvents, limited biological efficacy due to a lack of suitable adjuvants that boost performance, and the requirement for eye and skin irritation labelling (EPA 2000; Wahlberg and Lindberg 2003; ECHA 2019). In addition, these formulations do not address the high volatility of PA, and consequently its unpleasant smell, and likely reduction in efficacy (Mueller and Steckel 2019). Thereby, several unmet needs in current

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FA herbicides remain unresolved if performance equivalent to that of conventional contact herbicides is to be achieved. However, FA herbicides are perfectly suitable for use as a cornerstone of research into new active substances (Araniti et al. 2020) because they are recently discovered new compounds (Baur et al. 2019).

In this study, we aimed to synthesize new substances based on short FAs, although not acting as a pre-drug, and evaluate their biological performance against noxious weeds in greenhouse experiments to identify promising non-toxic herbicides. The resulting molecules should offer similar or better biological performance than the best PA-based herbicide, when applied at lower rates and spray volumes. In addition, these active compounds should overcome the above-mentioned drawbacks such as the troublesome formulation and volatility, avoiding loss of efficacy and the unpleasant smell.

## 2. Materials and methods

### *Chemicals*

Pelargonic acid at 99 % purity was acquired from Matrica (Porto Torres, Italy). It was used for the synthesis of some test compounds as well as one of the two references in the biological assays. Other FA were purchased from Sigma-Aldrich Chemie GmbH (Merck KGaA, Darmstadt, Germany). Ethylene oxide (EO), propylene oxide (PO) and their respective mixtures produced by Clariant (Gendorf, Germany) were used as gases or oligomeric glycols. The catalysts used for synthesizing the test compounds were purchased from Merck Chemicals GmbH (Merck KGaA, Darmstadt, Germany).

### *Synthesis of fatty acid derivatives*

FA derivatives were prepared based on literature (Baur et al. 2019). They were provided by the Group Technology & Innovation of Clariant, following standard procedures (Wrigley et al. 1959; Smith 2019). A simplified formula is given in Figure 1, wherein R<sup>1</sup> was a linear aliphatic group, and R<sup>2</sup> was a hydrogen, an aliphatic or acyl group. Index values “m”, “n” and “p” had numbers from 0 to 8 (Table 1). The synthesis routes were

esterification of open polyglycerin and/or polyethyleneglycols (PEG) or with alkyl-end-capped PEG or ethoxylation insertion in methyl esters of FA (Baur et al 2019).

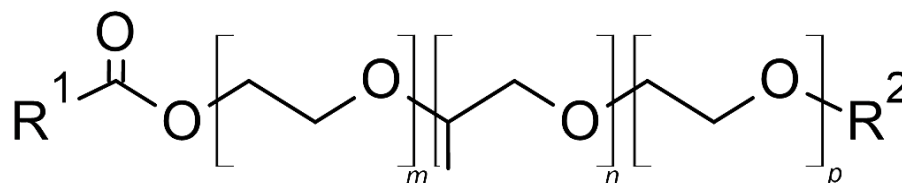


Figure 1. Simplified formula of fatty acid derivatives. Figure modified from Baur et al. (2019).

The obtained compounds were esters of certain FA with alkylene glycol and/or glycerol mono-, oligo- or polymers (Baur et al. 2019). Here, we report 13 of a large number of compounds, as shown in Table 1.

Test compounds A1 – A3, A6 - A9 and A11 - A13 were prepared by reacting the particular FA and the respective alcohol alkoxyate in a bottle with a Dean-Stark head. To achieve a reaction between the two compounds, sulfuric acid was used as an acid catalyst at reaction temperature of 200 °C with constant agitation under a constant nitrogen flow to maintain an inert atmosphere. The reaction sub-products (water or methanol) were removed from the reactor until the final product was obtained (Wrigley et al. 1959; Smith 2019). A10 was synthesized using the same procedure, except that the reaction was carried out with a PA-alkoxyate and PA in a stoichiometric ratio of 1:1 to obtain the FA diester (Smith 2019).

For test compound A4, PA was reacted with potassium hydroxide in a 1-L stainless steel autoclave. The reaction process was dried at 100 °C for 2 h while a vacuum was applied to evacuate water stream. The corresponding alkylene oxide was then added slowly to the reactor. This synthesis route resulted in a mixture of free PEG monoester, PEG diester and free PEG as described in the literature (Wrigley et al. 1959). Test compound A5 was prepared by reacting PA ester with one or more alkylene oxides in the presence of a suitable calcium-based embedding catalyst at 170°C.

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The structures of the synthesized products were confirmed by  $^1\text{H}$  NMR spectroscopy. Spectral descriptions for the test compounds are provided in Figures S1–S13.

#### ***Formulation quality test***

The quality of the formulation was first examined by testing the dilution stability of the test compounds at 10 % v/v. Collaborative International Pesticides Analytical Council (CIPAC) guideline MT 41.1 (Dilution Stability of Aqueous Solutions) was followed (Dobrat and Martijn 1994). Test compounds that did not form homogenous solution were formulated with castor oil ethoxylates (Emulsogen EL 400, Clariant) or fatty alcohol alkoxyate (Emulsogen MTP 070, Clariant). The amount of emulsifier did not exceed 20 % v/v in the test compound. After addition of emulsifier, an emulsion test was undertaken following CIPAC guideline MT 36.6 (Emulsion Characteristics and Re-emulsion Properties) (Dobrat and Martijn 1994). The pH value was also recorded for each test preparation as an indicator of stability.

#### ***Volatility measurement***

A volatility test was performed by adding 10  $\mu\text{l}$  of a spray solution of a known mass of active ingredient (a.i.) or the candidate to a weighed isolated cuticle of *Hedera helix* L. (ivy) (Cronfeld et al. 2001). The droplet was exposed to controlled conditions of 25 °C and 45 % relative humidity (RH). The container was weighed again at 2, 24 and 48 h after droplet application to record the amount of evaporated product (Strachan et al. 2010). The result was calculated as the per cent mean weight recovery. Test compound (50 g L<sup>-1</sup>) and straight PA (31 g a.i. L<sup>-1</sup>) without emulsifiers were dissolved in a mixture of acetone/deionized water (1:1) and placed in an ultrasonic bath to obtain a homogenised solution suitable for application. The influence of pH adjustments on volatilization was also measured. To do this, different pH buffers were used for the preparations. A preparation at pH 5 was obtained by diluting acetone with a buffer solution of pH 4 (citric acid/sodium hydroxide/hydrogen chloride) at a 1:1 ratio. For pH 8, a 1:1 dilution of acetone was carried out using a buffer solution of potassium dihydrogen phosphate/disodium hydrogen phosphate (pH 7).

**Table 1** – Fatty acid derivatives selected and synthesis route.

<b>Test Compound</b>	<b>Description</b>	<b>R<sup>1</sup></b>	<b>m</b>	<b>n</b>	<b>p</b>	<b>R<sup>2</sup></b>	<b>Synthesis</b>
<b>A1</b>	Heptanoic acid 6 EO ester methyl ether	C <sub>6</sub>	6	0	0	CH <sub>3</sub>	E <sup>a</sup>
<b>A2</b>	C <sub>8</sub> /C <sub>10</sub> fatty acid 6 EO ester methyl ether	C <sub>7</sub> /C <sub>9</sub>	6	0	0	CH <sub>3</sub>	E
<b>A3</b>	Pelargonic acid 6 EO ester methyl ether	C <sub>8</sub>	6	0	0	CH <sub>3</sub>	E
<b>A4</b>	Pelargonic acid 6 EO mono- / diester	C <sub>8</sub>	6	0	0	CH <sub>3</sub> / C <sub>9</sub> H <sub>17</sub> O	DE <sup>b</sup>
<b>A5</b>	Pelargonic acid 6 EO ester methyl ether	C <sub>8</sub>	6	0	0	CH <sub>3</sub>	IE <sup>c</sup>
<b>A6</b>	Dodecanoic acid 6 EO ester methyl ether	C <sub>11</sub>	6	0	0	CH <sub>3</sub>	E
<b>A7</b>	Pelargonic acid 2 EO ester methyl ether	C <sub>8</sub>	2	0	0	CH <sub>3</sub>	E
<b>A8</b>	Pelargonic acid 8 EO ester methyl ether	C <sub>8</sub>	8	0	0	CH <sub>3</sub>	E
<b>A9</b>	Pelargonic acid 5 EO 1PO ester methyl ether	C <sub>8</sub>	3	1	2	CH <sub>3</sub>	E
<b>A10</b>	Pelargonic acid 6 EO diester	C <sub>8</sub>	6	0	0	C <sub>9</sub> H <sub>17</sub> O	E
<b>A11</b>	Pelargonic acid 5 EO ester hexyl ether	C <sub>8</sub>	5	0	0	C <sub>6</sub> H <sub>13</sub>	E
<b>A12</b>	Pelargonic acid 6 EO ester allyl ether	C <sub>8</sub>	6	0	0	C <sub>3</sub> H <sub>5</sub>	E
<b>A13</b>	Pelargonic acid 6 EO ester benzyl ether	C <sub>8</sub>	6	0	0	C <sub>6</sub> H <sub>5</sub>	E

<sup>a</sup>Esterification<sup>b</sup>Direct ethoxylation<sup>c</sup>Ethoxylation-Insertion



### ***Greenhouse assays***

A completely randomized design with four replications for each weed species was used to evaluate the effects of the test compounds in accordance with European and Mediterranean Plant Protection Organization (EPPO) guidelines. A commercial formulation of PA (RV1, Vorox Unkrautfrei Express, 237.59 g a.i. L<sup>-1</sup>, EW, Compo) at the recommended rate, and straight PA (31 g a.i. L<sup>-1</sup>) formulated with a castor oil ethoxylate (RPA) were used as positive controls.

*Digitaria sanguinalis* and *S. nigrum* were used as representative monocotyledon and dicotyledon weed species, respectively. Seeds were planted in artificial substrate (Typ B Hawita Fruhstorfer. Hawita Gruppe) in 9 × 9 cm plastic pots. Seeds were grown in a greenhouse (phytotron) under a 16:8 h light/dark photoperiod with natural light, including UV, and supplemental sodium vapour lights to fulfil the plant's light requirements. The climate system was set up to give a daytime temperature of 23 ± 1 °C and night-time temperature of 18 ± 1 °C. RH was fixed at 55 ± 5 %. Plants were watered from the bottom as needed to maintain adequate moisture until the end of the trial.

Test preparations and positive controls, as described in Table 2, were applied to medium sized (18 to 20 cm) plants of *D. sanguinalis* and *S. nigrum*. The plants were in development stage BBCH 22 and 16, respectively (*Biologische Bundesanstalt, Bundessortenamt und Chemische Industrie*). Treatments were applied at a spray volume of 500 L ha<sup>-1</sup> at 300 kPa, using a spray chamber with a single flat fan nozzle (LU-120-06, Lechler). Visual estimates of per cent weed control were recorded 1, 2 and 7 days after application (DAA) on a scale of 0 to 100 %, where 0 % is no weed control and 100 % is complete weed control. Desiccated and necrotic tissues were the main symptoms observed. Table 3 gives the rating scale for weed control. In case of regrowth, weed control values were decreased.

**Table 3** – Rating Score used to interpreted the weed control efficacy.

<b>Weed control efficacy (%)</b>	<b>Description</b>
0 - 19	No control. Plants completely tolerant (weeds alive).
20 - 39	Poor control. Plants moderately tolerant. Transient desiccated symptoms.
40 - 59	Moderate control. Plants moderately susceptible. Desiccated tissues
60 - 79	Good control. Plants susceptible. Necrotic tissues
80 - 100	Excellent control. Plants Highly susceptible (weeds killed).

### *Statistical analysis*

Data were subjected to analysis of variance (ANOVA) using ARM software (Gylling Data Management Inc., Brookings, US). Means were compared using Student-Newman-Keuls least significant difference (LSD) test ( $P < 0.05$ ) for separations of the means. Prior to analysis, the normality and homoscedasticity of the data were verified using functionalities of the software, and corrective actions like automatic arcsine square root percentage were undertaken if required.

## **3. Results**

### *Formulation quality test*

Some of the test compounds were stable in the dilution assessment without formulation (Table 2). For compounds that were not stable, castor oil ethoxylation or fatty alcohol alkoxylation were needed to give a homogenous and stable spray solution. Adjustments were made in the application rate of the formulated test compounds in order to apply the same amount of product as shown in Table 2. There were no striking differences in pH values among the 13 preparations indicating a direct influence on herbicidal efficacy. The preparations were slightly acidic in comparison with the positive control spray liquids. pH values ranged between 5.0 and 7.0, except for test preparation A12 which had the lowest pH value, 3.60.

**Table 2** – Results of formulation quality and rate adjustment for greenhouse trials.

Test compound	Straight dilution test results <sup>a</sup>	Emulsion results <sup>b</sup>	Greenhouse
		Rate (% v/v)	Application rate (L ha <sup>-1</sup> )
A1	Clear – Stable	n/a <sup>c</sup>	50
A2	Clear – Stable	n/a	50
A3	Clear – Stable	n/a	50
A4	Turbid - No soluble	10 <sup>d</sup>	55.5
A5	Clear – Stable	n/a	50
A6	Turbid - Phase separation	10 <sup>d</sup>	55.5
A7	2 Phases - Phase separation	10 <sup>e</sup>	55.5
A8	Clear – Stable	n/a	50
A9	Clear – Stable	n/a	50
A10	Cloudy - Phase separation	10 <sup>d</sup>	55.5
A11	Cloudy - Not soluble	20 <sup>e</sup>	62.5
A12	Turbid - Phase separation	10 <sup>e</sup>	55.5
A13	Milky - No soluble	10 <sup>d</sup>	55.5
RPA <sup>f</sup>	2 Phases - Phase separation	10 <sup>d</sup>	18
RV1 <sup>g</sup>	Milky emulsion	n/a	130

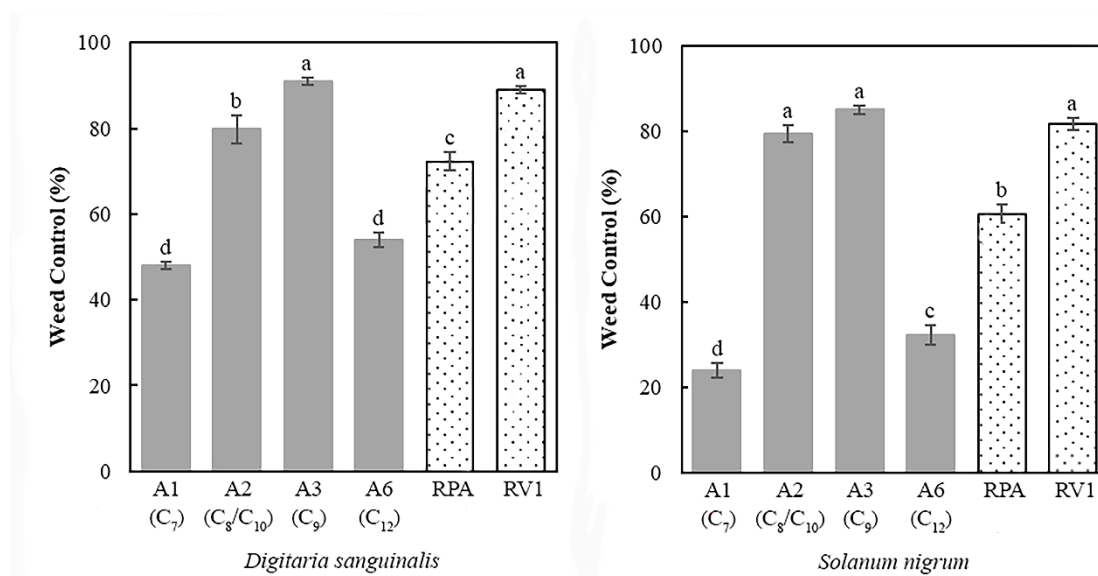
<sup>a</sup> CIPAC MT 41.1<sup>b</sup> CIPAC MT 36.6<sup>c</sup> not applicable<sup>d</sup> Emulsogen EL 400<sup>e</sup> Emulsogen MTP 070.<sup>f</sup> Straight pelargonic acid.<sup>g</sup> Commercial formulation of pelargonic acid.***Herbicidal activity in greenhouse assay***

The weed control efficacy of the selected FA derivatives against benchmarks is shown in Figures 2-5. These are compared according to structural variations in the formula given in Figure 1 in each figure. Only performance at 2 DAA is shown because the maximum knockdown effect was reached by this point. Weed control at 7 DAA is shown only for

A3 in Figures 6 and 7. Values are the mean of four replicates, and error bars represent standard errors.

### ***Impact of fatty acid chain length on weed control***

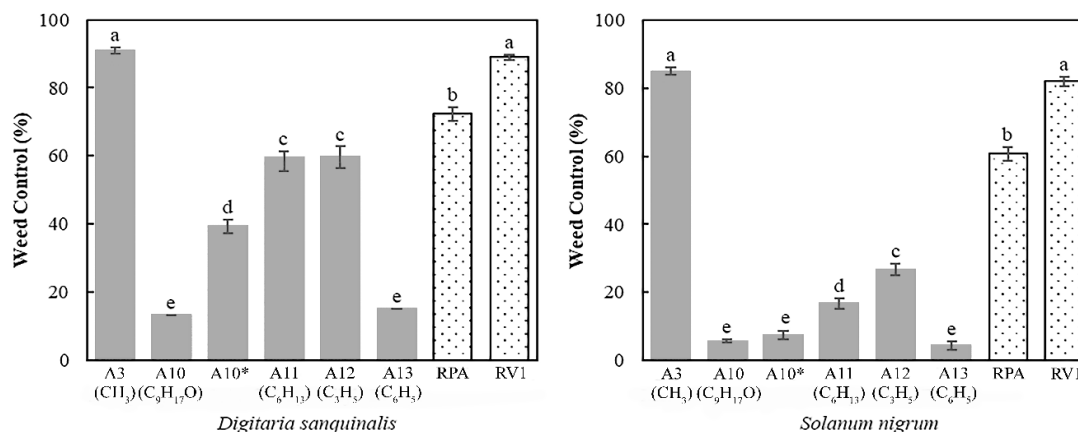
Maximum phytotoxicity was found with A3 (C<sub>9</sub> fatty acid), as shown in Figure 2. Both plant species were highly susceptible to treatment with A2 (C<sub>8</sub>/C<sub>10</sub> fatty acid), which showed excellent control in *D. sanguinalis* and good control against *S. nigrum*. The other FA compounds had a lesser effect than A3 and A2. No significant differences were observed between A3 and RV1.



**Figure 2.** Effect of fatty acid chain length (C<sub>6</sub>–C<sub>12</sub>) in the fatty acid EO ester methyl ether on weed control at 2 days after application. A1–A3, A6: test compounds. RPA, RV1: Generic and commercial pelargonic acid formulation. Different letters above bars indicate significant differences ( $P < 0.05$ , Student–Newman–Keuls test).

### ***Herbicidal activity of FA diesters and type of end-capping of PEG monoesters***

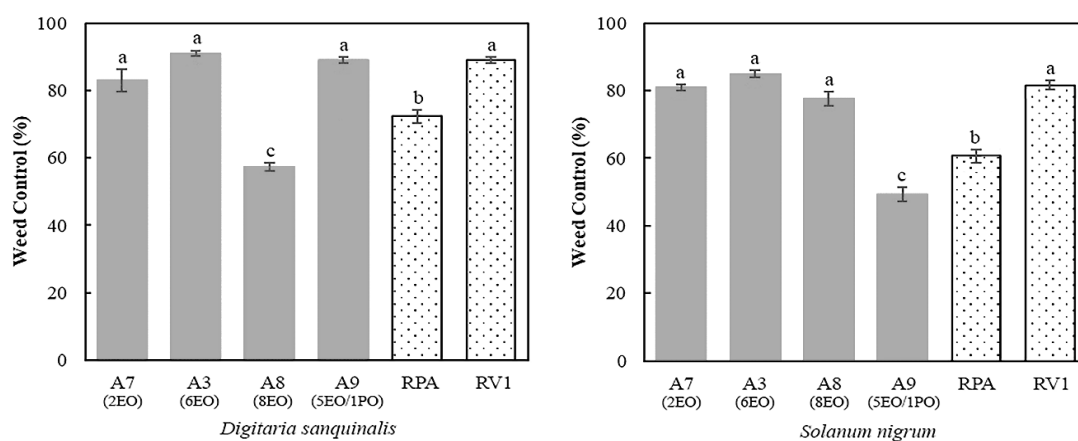
The most effective treatment in both weeds was the FA with methyl end-capping (A3). *D. sanguinalis* was moderately susceptible to A11 (-C<sub>6</sub>H<sub>13</sub>O) and A12 (-C<sub>3</sub>H<sub>5</sub>), whereas *S. nigrum* was tolerant to both. Other end-capping variations showed weaker weed control than RPA for both plant species, for example benzyl end-capping (A13), or even at higher rates like the FA diester (A10) as shown in Figure 3.



**Figure 3.** Influence of herbicidal activity of fatty acid diesters and type of end-capping of polyethylene glycols (PEG) monoesters on weed control at 2 days after application. A3, A10–A13: test compounds. RPA, RV1: generic and commercial pelargonic acid formulation. Different letters above bars indicate significant differences ( $P < 0.05$ , Student–Newman–Keuls test). The rate of A10\* is the A10 rate increased four times.

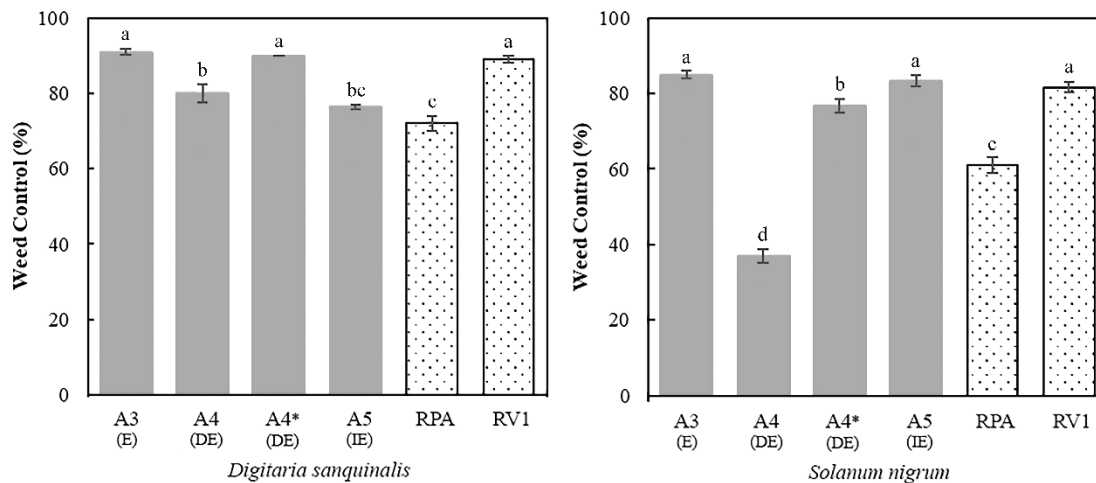
#### *Impact of ethoxylation of the test compound on weed control*

A7 (2EO) was able to control *D. sanguinalis* and *S. nigrum*, as did A3 (6EO) and RV1. A8 (8EO) was less effective, but the level of control reached was acceptable for both weeds. Surprisingly, the copolymer A9 (5EO/1PO) did not show equal performance for the model plants, giving an excellent weed control for *D. sanguinalis*, but only fair control for *S. nigrum* (Figure 4).



**Figure 4.** Effect of the ethoxylation degree of methyl-capped pelargonic acid ester ethoxylates on weed control at 2 days after application. A3, A7–A9: test compounds. RPA, RV1: generic and commercial pelargonic acid formulation. Different letters above bars indicate significant differences ( $P < 0.05$ , Student–Newman–Keuls test).

### Synthesis route on the herbicide efficacy

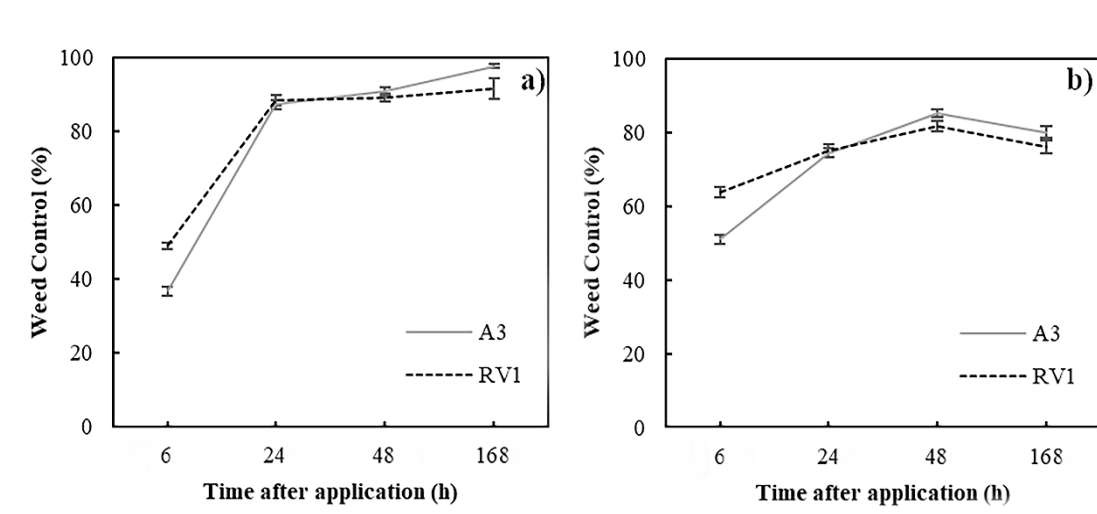


**Figure 5.** Impact of the synthesis route of pelargonic acid 6EO ester methyl ether on the weed control at 2 days after application. Synthesis: esterification (E), direct ethoxylation (DE), insertion ethoxylation (IE). A3–A5: test compounds. RPA, RV1: generic and commercial pelargonic acid formulation. Different letters above bars indicate significant differences ( $P < 0.05$ , Student–Newman–Keuls test). The rate of A4\* is the A4 rate increased two times.

The products obtained using the different synthesis routes, direct esterification ethoxylation and ethoxylation insertion, were able to control *D. sanguinalis*, showing good to excellent efficacy. However, *S. nigrum* was highly susceptible only to A3 (esterification) and A5 (ethoxylation insertion). The efficacy of A4 (ethoxylation route) against *S. nigrum* was poor, increasing to good only at double application rates (Figure 5).

#### Detailed comparison between A3 and pelargonic acid (RV1)

Owing to its higher phytotoxicity, A3 was selected and subjected to further study to compare its activity against the commercial formulation RV1. In general, RV1 was slightly faster, but A3 achieved better results for both model plants. Significant differences were not found before the last assessment at 7 DAA. *Digitaria sanguinalis* was more susceptible than *S. nigrum* to both products, with A3 giving an excellent level of control in *D. sanguinalis* and a good level of control in *S. nigrum* (Figure 6).



**Figure 6.** Time dependence of weed control of *Digitaria sanguinalis* (a) and *Solanum nigrum* (b).

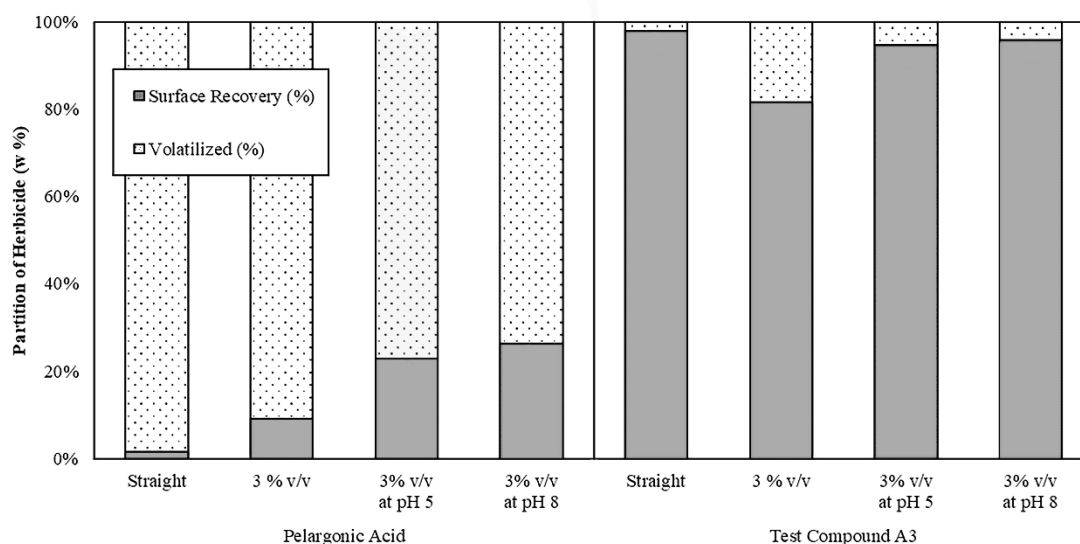
Weed control over a period of 7 days is shown in Figure 6, thereafter phytotoxicity symptoms did not develop further. Faster development of phytotoxicity was observed in weeds treated with RV1 after 6 h (Figures 6 and 7). However, at 1 DAA, both products achieved similar efficacy, with A3 giving the best weed control results at the end of the trial.



**Figure 7.** Example for differential weed control of pelargonic acid 6EO ester methyl ether (A3) and commercial pelargonic acid formulation (RV1). (Left) Weed treated with A3. (Right) Weed with RV1 applied. (a) Symptoms at 6 h after application. (b) Symptoms at 7 days after application.

### ***Volatility of the test compound A3***

The volatility study indicated zero volatility for the A3 derivative with the applied amount of straight A3 being recovered completely after 2 days. By contrast, straight PA was volatilized totally to ambient air after 2 days (Figure 8). The recovered amount of product was influenced by the pH conditions in the tested preparations, with buffered tap water giving less recovery than buffer systems. However, A3 still showed 80% or more recovery and much lower volatility from the leaf cuticle than RPA. A higher pH slightly reduced the volatility of both products, A3 and RPA.



**Figure 8.** Fractions of surface recovery and volatilized product (weight %) after 2 days (mean of ten repetitions). Test conducted with low permeable cuticle of *Hedera helix* L.

## **4. Discussion**

FAs and FA derivatives have multiple applications in agriculture, for example as herbicides, fungistatic agents, insecticides, emulsifiers and wetting agents (Siegler and Popenoe 1925; Maag 1984; Chadeganipour and Haims 2001). More than 50 derivatives of the formula shown in Figure 1 and others like amides have been synthesized and evaluated for their herbicidal activity (Baur et al. 2019). In this work, new compounds based on short-chain FA esters and benchmarks were evaluated to identify a lead structure for new contact (bio)herbicides. In addition to their potential as contact herbicides, other



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benefits have been found that are not discussed here. For example, FA amides, alkyl and PEG esters with long chains are interesting for other applications, such as drift retardancy and solvent or carrier agent function without any herbicidal activity (Mouloungui and Gauvrit 1998; Shao et al. 2013).

The performance of PA herbicides depends on the concentration used and requires maximum coverage of the treated plant organs (Webber and Shrefler 2006; Krauss et al. 2020). Climate conditions also interfere substantially their phytotoxic activity (Crmaric et al. 2018; Ciriminna et al. 2019; Krauss 2020). Thus, to prevent external factors from affecting the efficacy of the test preparations, prior trials on climate conditions, weed size and application rate were performed (data not shown). Overall, the findings were consonant with published studies (Crmaric et al. 2018; Ciriminna et al. 2019; Krauss 2020; Travlos et al. 2020). Accordingly, the trials were done under moderate climate conditions (approximately 23/18 °C day/night), and on medium sized (18–20 cm) weeds. We confirm that *D. sanguinalis* and *S. nigrum* are representative monocot and dicot weeds for such contact products (Holm et al. 1991; Kraehmer 2016). Rate application and spray volume were reduced to more appropriate agricultural levels, one of the requirements of this study, but also as a result of the excellent performance of nearly all the test compounds when applied at the label recommendation of the commercial positive control (130 L ha<sup>-1</sup> of product in a water volume of 870 L ha<sup>-1</sup>).

All 13 FA PEG esters showed phytotoxic activity, with significant differences among them. Base materials (PEG) led to enhanced performance, but did not own herbicidal activity (Mitchell and Hammer 1944). Furthermore, they are approved by the U.S. Environmental Protection Agency as inert ingredients in pesticide formulations (EPA 2021) and are considered safe for humans in other industries such as personal care or pharmaceuticals, being used for example as purgatives.

A3 was the most effective of the obtained products, showing excellent control on the weeds tested. Comparing the effect of alkyl chain length (Figure 2) of the esters on a constant number of 6 EO groups and methyl end-capping, optimum chain length was found to be C<sub>9</sub>. This chain length is also reported in the literature as being superior to straight FA (Fukuda et al. 2004; Coleman and Penner 2006). A2 with about 60 % C<sub>8</sub> and

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40 % C<sub>10</sub> linear FA is slightly less effective, indicating that C<sub>9</sub> is better than C<sub>8</sub>. By contrast, branched C<sub>8</sub>, C<sub>9</sub> or C<sub>10</sub> is not effective (data not shown). The C<sub>12</sub> chain length (A6) performed distinctly less well than other derivatives of this chain length or longer (data not shown). The methyl substituent for end-capping was very beneficial for performance when compared with the open derivative with 6 EO (A10) and other substituents such as benzyl, allyl or hexyl groups, all of which reduced efficacy significantly (Figure 3). At constant C<sub>9</sub> chain length and methyl end-capped, an EO number of 6 was superior to EO numbers of 2, and particularly 8 (Figure 4). Adding one propylene oxide group in the chain (A9) resulted in comparable good performance in *D. sanguinalis* control, but efficacy decreased significantly for the dicot, *S. nigrum* (Figure 4). It appears from these results that A3 is the most effective derivative and the highest active substance content in A3 was found when esterification was used for synthesis. Products with ethoxylation insertion contained some impurities or diesters (Janni et al. 2014), which reduced efficacy at least in one of the two weeds studied (Figure 5). This is also known for polyglycerols in other applications (Janni et al. 2014).

A new approach to the synthesis of molecules is presented. No literature is available on the action/effect of the substituents (Figure 1) on herbicidal outcome. Further studies are needed to discuss differences in herbicide efficacy. However, the foliar penetration hypothesis and penetration studies (data not shown) give some indication of the different effectiveness of these compounds. Foliar penetration across the cuticle depends on molar volume or molecular weight, and solutes above 450 g mol<sup>-1</sup> penetrate very slowly if they do not swell the cuticle or have a linear structure, which increases penetration severalfold (Baur 1998). PA esters are interesting in this respect because they are almost linear with one ester group, and partly act as swelling agents (Cronfeld et al. 2001). The C<sub>12</sub> ethoxylate (A6), for example, has a molecular weight just above 480 g mol<sup>-1</sup> and this is one of two unfavourable properties of this derivative. The other key property is lipophilicity, which impacts both movement of actives or solutes to the site of action and binding there. Passive translocation in the aqueous phase of cell walls and xylem is best at octanol/water partition coefficients or log $P$  values of 1.5 to 3.5 (Briggs et al. 1982). For PA, log $P$  is 3.4 and together with a pK<sub>a</sub> of approximately 5 this is within the suitable range.<sup>18</sup> The calculated log $P$  for A3 is 2.2, which also fits well. By contrast, the C12

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derivative (A6) has an estimated  $\log P$  of 3.7 with incremental 0.5 lipophilicity added to  $\log P$  per methylene group. This further limits its translocation to the limitation of movement due to higher molecular weight. Higher degrees of ethoxylation lower  $\log P$ , and for both pure and technically polydisperse alcohol ethoxylates 4.5EO reduces  $\log P$  by one unit with a corresponding impact on cuticle absorption and efficacy (Baur 1998, 1999). Other derivatives than A3 apparently deviate too much from the ideal combination of molecular weight and lipophilicity.

All derivatives, A1–13, are liquid at ambient temperatures. Many are water soluble or form reasonably stable micellar solutions, addressing PA formulation issues without addition of any non-ionic emulsifier (Table 2). For others, simple addition of an emulsifier is sufficient to achieve stable and homogenous dilutions, which are microemulsions or emulsions in contrast to commercial products like RV1, where PA is formulated in a tedious and expensive adjuvant system. No biological influence of the emulsifiers selected for the test compound was observed here, but both castor oil ethoxylate emulsifiers and fatty alcohol alkoxyates are able to increase the efficacy of systemic agrochemicals (Cronfeld et al. 2001). The presence of EO in the molecules adds more hydrophilic character (Maag 1981), which makes the new compounds self-emulsifiers or readily emulsifiers, unlike the straight PA. The number of 6 EO appears to be optimum compared with lower numbers of EO for example A2 (2 EO). A higher amount of EO like A8 (8 EO) or an average of 6 EO like the copolymer in A9 (5 EO/1 PO) leads to stable test preparations, although biological performance is affected (Figure 4). As mentioned above, the synthesis route is important and ethoxylation insertion causes a mixture of PEG monoester, PEG diesters and free PEG, all of which are inactive or even antagonistic, leading to higher rates of application for the same efficacy (Figure 5) (Janni et al. 2014). Gas chromatography–mass spectrometry confirmed that A3 contains some percentage of free acid but no meaningful non-active impurities. In addition to previous findings, the test compounds can act as wetting agents at the high used concentration with values for the dynamic surface tension below  $45 \text{ mN m}^{-1}$  and thus are excellent for spray adherence (Baur and Pontzen 2007). As a result, the active substances are often also the final product (Table 2), which can be applied straight away using drones or autonomous robots for precision agriculture.

A3 clearly stands out among the other test compounds. It showed the best weed control (Figures 2-5) and does not need any formulation (Table 2), being relatively easy to co-formulate with other herbicidal substances (Baur et al. 2020). Co-formulation should be further studied, for example A3 and the triketone leptospermone, which showed good efficacy in combination with PA in the spray tank (Travlos et al. 2020). The biological outcome for A3 is equal, or even superior, to the PA herbicide applied (Figure 6), but this outstanding efficacy was achieved with 50 L of product and a water volume of 450 L ha<sup>-1</sup>, a reduction of 80 L ha<sup>-1</sup> of product and 420 L ha<sup>-1</sup> of water in comparison with the benchmark label recommendations. Thus, it appears that A3 could represent a substantial reduction in cost for farmers due to the reduced amount of product and water used in its application, and the absence of formulation.

Injuries on treated weeds suggest that A3 acts in the same way as the positive controls by destroying meristematic and differentiating cells (Tso et al 1965; Fukuda et al. 2004, Coleman and Penner 2006). Because PA constitutes the core of A3, they share many characteristics such as rapid wilting in treated plants, followed by necrotic tissues. Although the mode of action of PA is not fully understood, the consensus is that both active compounds (PA and A3) suppress the weed through membrane degradation, as claimed for PA in previous studies. The other major effect suggested was increased cuticular transpiration, thereby causing rapid wilting of plants (Ciriminna et al. 2019). Despite having similar modes of action, the herbicidal activity of A3 showed a reduced effect at 6 hours after application (Figures 6 and 7), offering some advantages, such as possible greater control of larger plants or the possibility of co-formulation with other systemic actives, like sulfonylureas (Baur et al. 2020), which could be better translocated in the first hours after application (Chuah et al. 2008).

A peculiar feature of PA is its strong malodour combined with high volatility (vapour pressure at 20 °C of 1.0 × 10<sup>5</sup> mPA) (EPA 2000). The rancid aroma of PA, which is released after a few hours and lasts for days, limits its use in homes and gardens, as well as on plantations or in railway applications. In addition, the high volatility of PA results in some loss of biological activity and problems known from other volatile herbicides like

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dicamba or clomazone (Sondhia 2014). A3 is practically not volatile (Figure 8) and has no bad odour, giving it a further advantage over PA products.

Looking at the results (Figures 2-6), it is striking that control of *D. sanguinalis* was better than control of *S. nigrum* throughout. Although it is tempting to conclude a difference in biological sensitivity to PA esters, this is unlikely. *D. sanguinalis*, like most weed grasses, is difficult to wet due to the high density of crystalline waxes on both leaf surfaces, whereas *S. nigrum* does not have wax crystals and is easy to wet (Kraehmer 2016). The wettability with water is therefore dramatically different, with *D. sanguinalis* retaining no water, whereas *S. nigrum* is completely wetted by spray droplets, even with plain water. The situation changes completely with surfactants. A dynamic surface tension below  $45 \text{ mN m}^{-1}$  at 200 ms and a static (equilibrium) surface tension just below  $40 \text{ mN m}^{-1}$  cause spray droplets to be captured almost quantitatively, and also spread over the whole leaf surface due to capillary wetting (Baur and Pontzen 2007). By contrast, on a wettable dicot like *S. nigrum*, droplets stick well but do not spread and the coverage is much lower than on monocot leaves. For contact herbicides that are not distributed within the plant and only slightly in the contacted tissue, maximum coverage affects herbicide action directly. Therefore, good dynamic wetting will ensure control with contact herbicides, particularly of monocots and difficult to wet dicots like *Chenopodium album* L. (Lamb's quarters). For others, maximum coverage is typically achieved by using high water volumes, because oil spreaders like mineral oils, typically also used in high concentrations, often counteract the penetration of lipophilic actives.

The two precursors, PA and PEG, used in the chemical reaction for the test substances are non-toxic (EPA 2000; EU 2008; FDA 2019; EPA2021) and as far as is currently known, A3 and its analogues are accordingly putative candidates to be generally recognized as safe substances. For this reason and because A3 can be synthesized easily from a renewable resource like PA and obtained on a large scale, this compound could be a good and sustainable alternative for weed control.

## **5. Conclusion**

Methyl-capped pelargonic acid 6 EO ester demonstrated equal or better herbicidal contact activity than commercial benchmarks of PA at a lower spray volume and without the negative properties that limit wider use of such FA. This new substance provides a slightly slower (yet still fast) contact action after application, which may offer better synergism in co-formulations or tank mixtures with systemic herbicides that need adequate translocation. Formulation of the solo product is easy and the liquid active compound is both self-dispersing and a wetting agent on its own. This contrasts with PA, where the formulation effort for effectiveness is high. Application in precision agriculture to control site-resistant weeds seems particularly interesting, either pure or in small quantities. Furthermore, the 6 EO ester has no unpleasant smell and is practically non-volatile. Although the aforementioned drawbacks of FA products have been addressed, further research is needed to resolve other problems with contact herbicides like regrowth or increasing efficacy at lower spray volumes, which could be improved with suitable growth-regulator herbicides. Additional research to enhance the product is ongoing, for example through as yet unidentified adjuvants or synergists.

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## **CONFLICT OF INTEREST DECLARATION**

The authors declare no competing financial interest.

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**SUPPORTING INFORMATION**

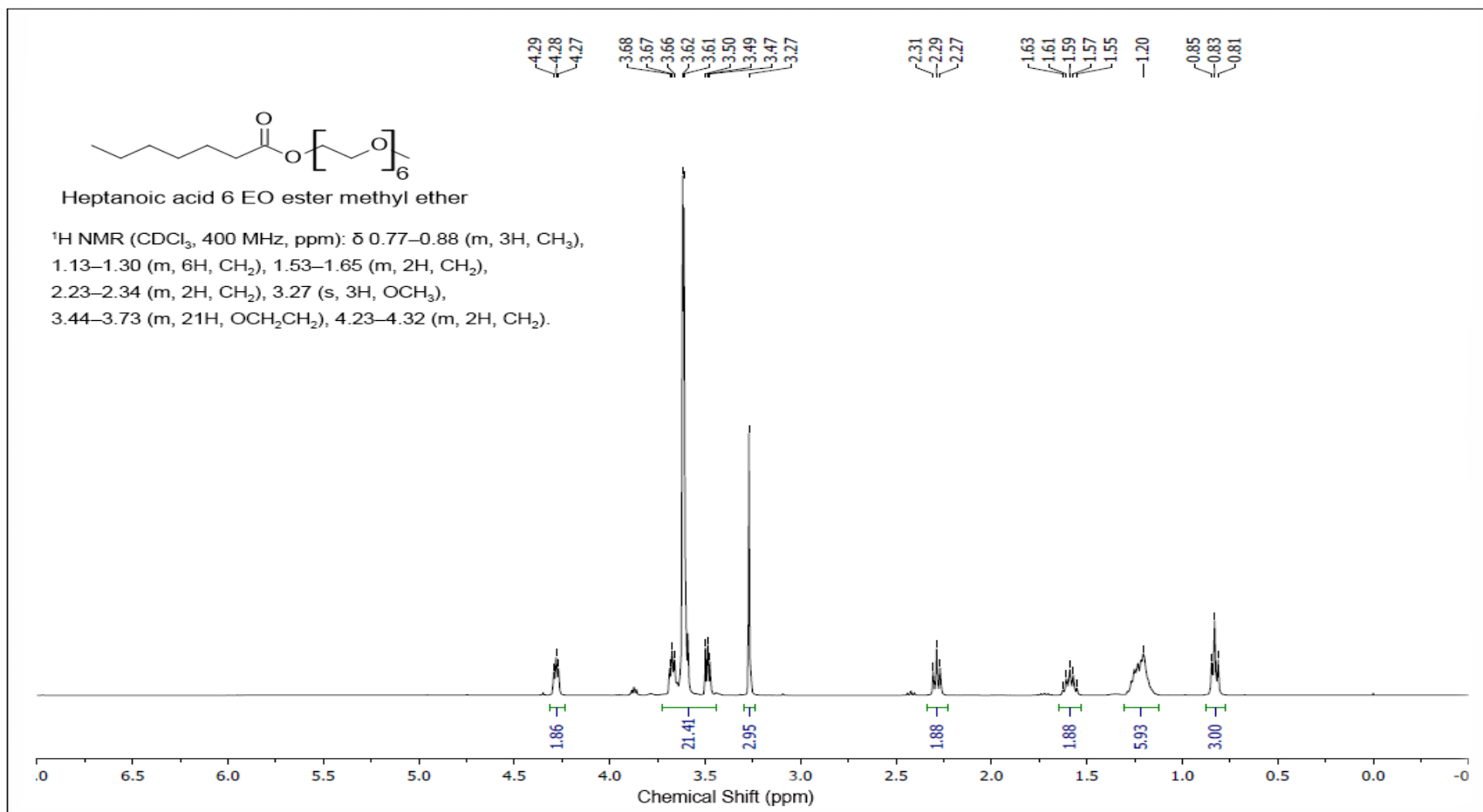
The following abbreviations were used to explain multiplicities in nuclear magnetic resonance (NMR) spectra:

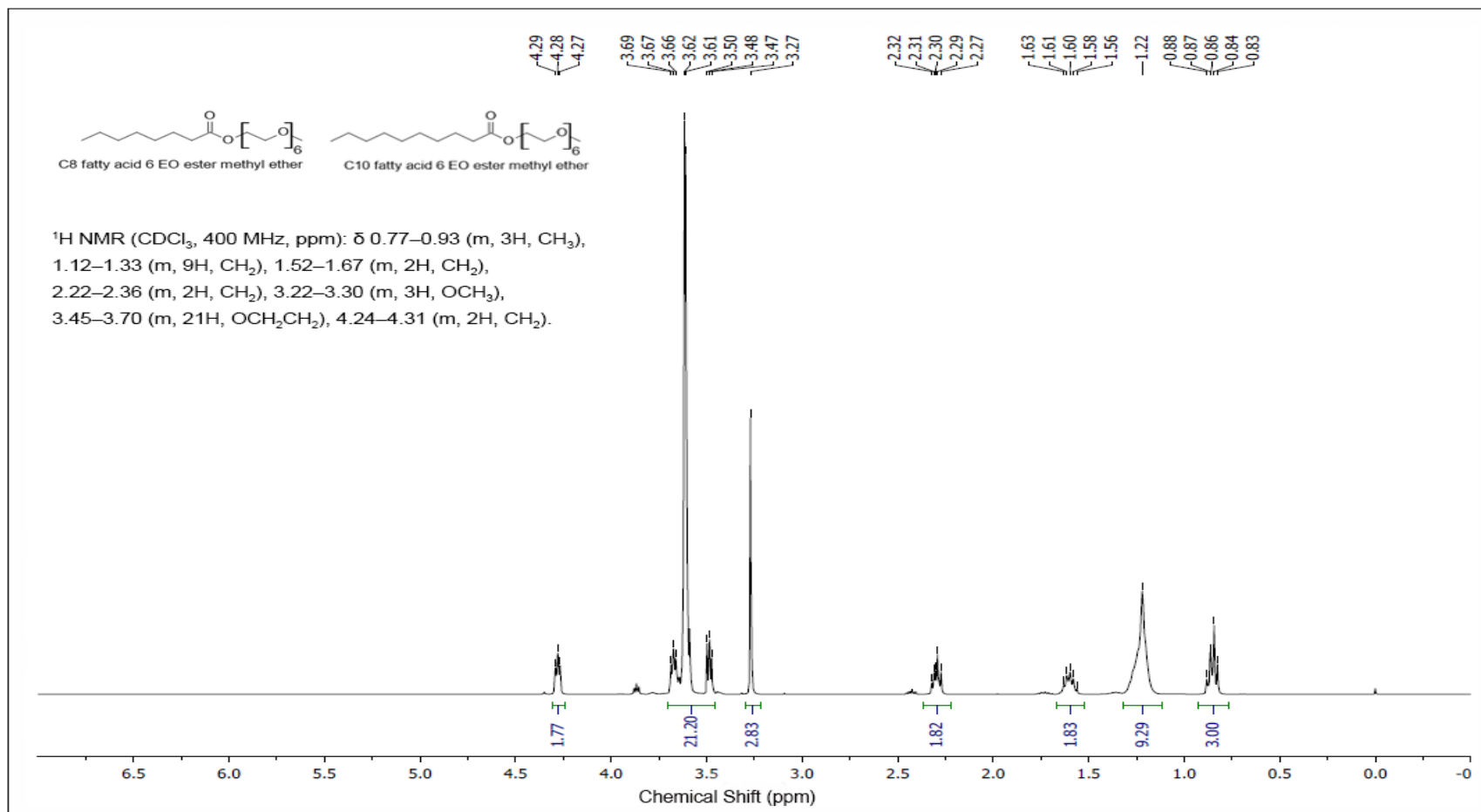
s: singlet;

d: doublet

t: triplet

m: multiplet

**Figure S1** -  $^1\text{H}$  NMR spectrum of test compound A1 (Heptanoic acid 6 EO methyl ether; Esterification synthesis route).

**Figure S2** -  $^1\text{H}$  NMR spectrum of test compound A2 ( $\text{C}_8/\text{C}_{10}$  fatty acid 6 EO ester methyl ether; Esterification synthesis route).

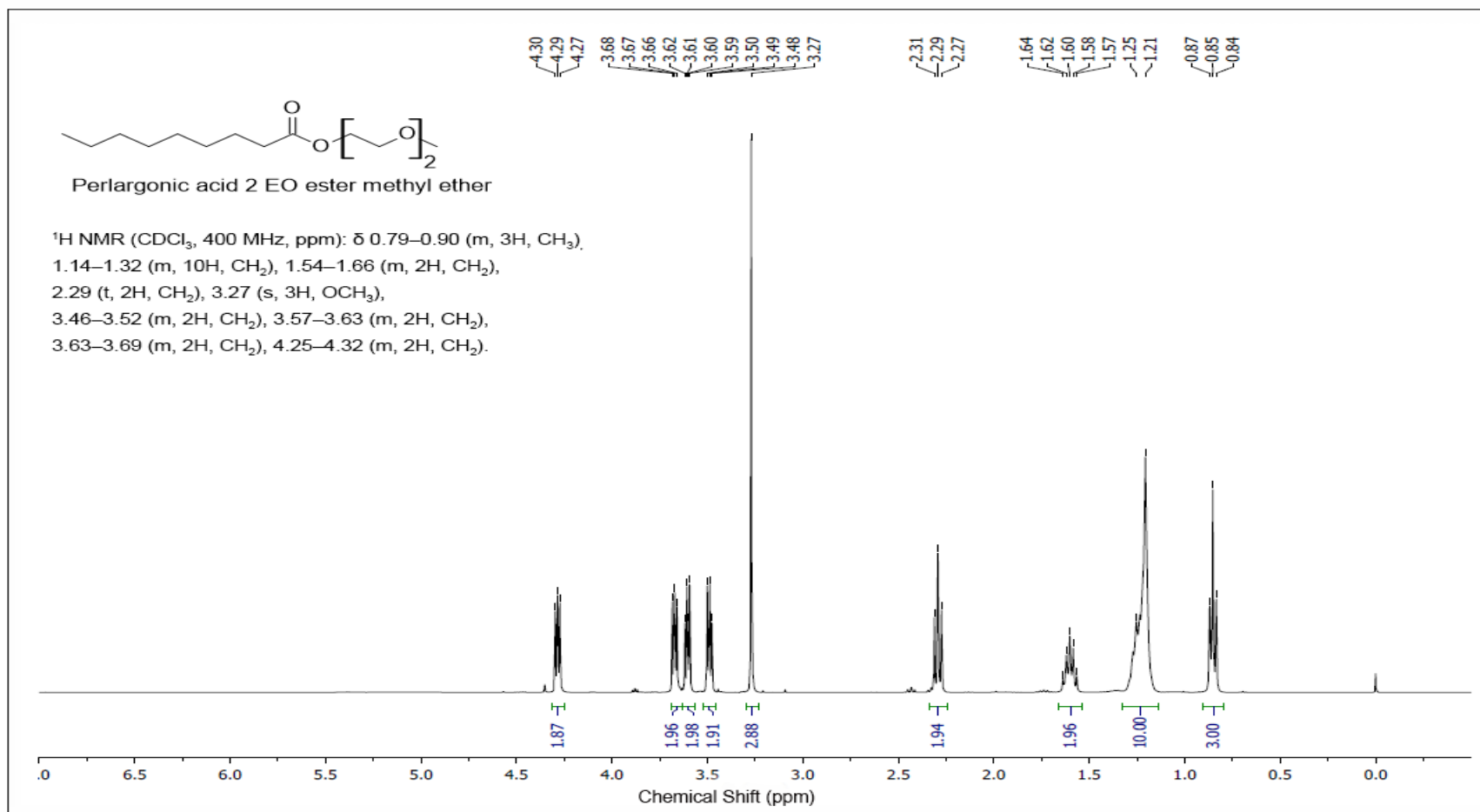










**Figure 7** -  $^1\text{H}$  NMR spectrum of test compound A7 (Pelargonic acid 2 EO ester methyl ether; Esterification synthesis route)

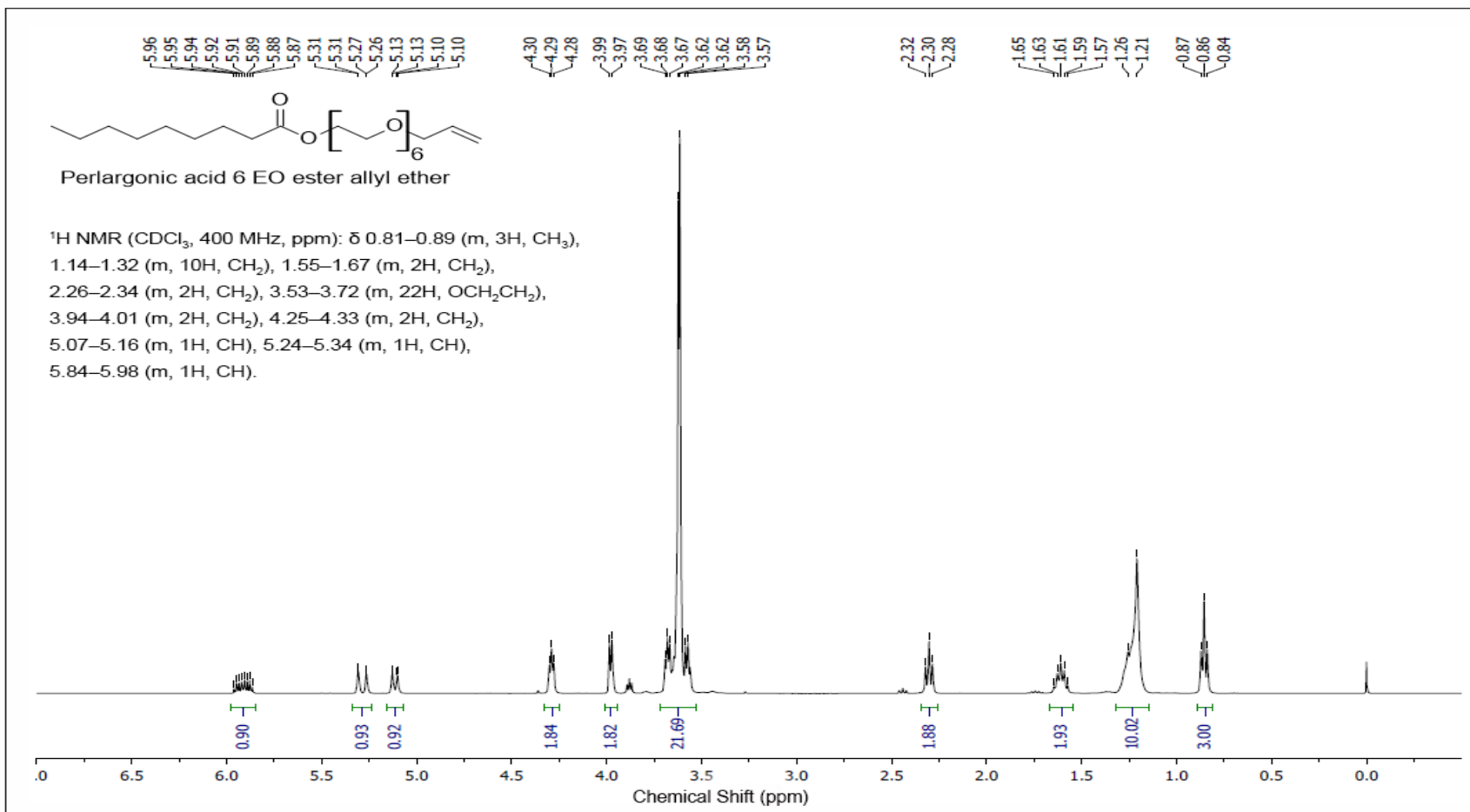


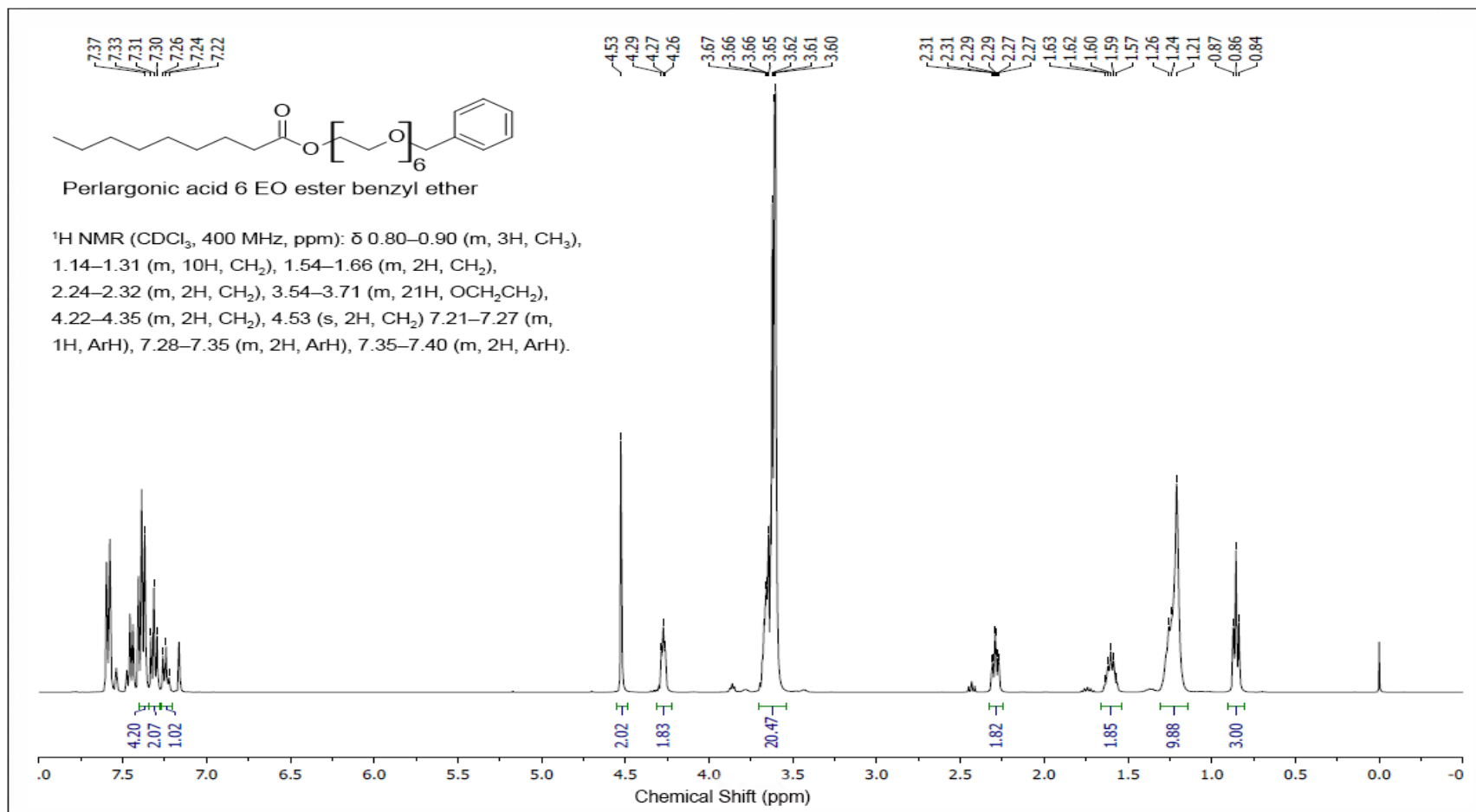








**Figure S12** -  $^1\text{H}$  NMR spectrum of test compound A12 (Pelargonic acid 6 EO ester allyl ether; Esterification synthesis route).

**Figure S13** -  $^1\text{H}$  NMR spectrum of test compound A13 (Pelargonic acid 6 EO ester benzyl ether; Esterification synthesis route).

Publication II

**Contact herbicidal activity  
optimization of methyl capped  
polyethylene glycol ester of pelargonic  
acid**

Chapter published as an original article in *Journal of Plant Diseases and Protection* (Journal indexed in Journal citation reports, JCR).

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## Contact herbicidal activity optimization of methyl capped polyethylene glycol ester of pelargonic acid

### Abstract

The loss of important contact herbicides like paraquat opens opportunities for more potentially sustainable solutions demanded by consumers and organizations. Frequently, for adequate weed control, the alternatives to classical synthetic products need well-defined and executed labels and even more detailed use descriptions. One novel candidate with rare contact activity is a pelargonic acid ester of methyl polyethylene glycol (PA-MPEG) with advantages over free pelargonic acid (PA), such as reduced volatility and ease of formulation. Here we report on the role of the application parameters such as spray volume, rate, sprayer setup, and climate conditions for weed control with PA-MPEG. At a dose rate of 12.8 kg ae ha<sup>-1</sup> in a spray volume of 500 L ha<sup>-1</sup>, control of *Digitaria sanguinalis* (L.) Scop. and *Solanum nigrum* L. was excellent. These values for product rate and spray volume are lower than applications with commercial PA herbicides, at equal or better efficacy. Coverage was too low at spray volumes of 100 to 200 L ha<sup>-1</sup>, for adequate contact activity of both PA-MPEG and PA. Weed control was significantly increased when PA-MPEG application was made at lower boom height with reduced distance to weed canopy, or under warm and dry climate conditions. The results indicate the potential of PA-MPEG under optimal use conditions as a new contact herbicide in integrated weed management.

### Keywords

Pelargonic acid; Weed canopy; Coverage; Climate conditions; Application parameters.



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## 1. Introduction

Free nonanoic acid, which is also commonly known as pelargonic acid (PA), its salts, or related octanoic and decanoic (C<sub>8</sub>-C<sub>10</sub>) fatty acids have been used to control weeds for over 30 years as nonselective contact herbicides that affect only the plant part in contact with the product (Coleman and Penner 2006; Dayan and Duke 2010; Ciriminna et al. 2019; EPA 2020). Therefore, good spray coverage given by high application spray volume and growing young plants is essential for good weed control (Webber and Shrefler 2006). PA is fast-acting and causes desiccation symptoms on the treated organ within only a few hours. This differs greatly from systemic herbicides, where visible symptoms may develop only after several days to weeks after application (Fukuda et al. 2004; Lederer et al. 2004; Jeschke et al. 2019). The root system is not directly affected because PA herbicidal activity is limited to the above-ground contact area with no translocation, thus weeds may show regrowth from their roots or rhizomes. Therefore, repeated applications might be required for long-lasting control by exhausting energy reserves in underground plant organs and also eroding leaf surface waxes (Webber et al. 2014; Krauss et al. 2020). The mechanism of action of PA is related to effective foliar uptake via the cuticle and erosion of surface waxes, and a moderate increase of cuticular transpiration can sometimes be observed (Ciriminna et al. 2019). The main mode of action (MoA) is related to the release of lipids after membranes disintegration (Fukuda et al. 2004; Lederer et al. 2004), and it was recently suggested that tissue desiccation and ultimately leaf death are related to an interruption of water cohesion in the cell walls (Campos et al. 2022) and thus the soil-plant-atmosphere continuum.

The withdrawal or restriction of contact herbicides like paraquat or diquat (Dinham 2004; EUR-Lex 2020) and the ongoing concerns about glyphosate use (Carvalho 2017; Van Bruggen et al. 2018) justify further investigation of the potential improvement of PA (Coleman and Penner 2008; Travlos et al. 2020). This burndown herbicide is considered one alternative to glyphosate in certain applications (Fogliatto et al. 2020), and it is suggested to be incorporated in weed management programs in agricultural (broadacre and plantations) (Kanas et al. 2020; Kanas et al. 2021) and non-agricultural (industrial, railways garden, etc.) uses (Barker and Prostack 2014).

However, PA remains largely unutilized by farmers even in those instances in which its use could be indicated. For example, in 2019, only 0.7 % of the potato fields in Belgium were treated with PA, and similarly, Spanish farmers used PA just in 0.3 % of the vineyard area (KLEFFMANN 2021). Also, PA is sometimes mistakenly compared to glyphosate; for example, applying it to well-established weeds (50 cm tall), which leads to a false expectation of efficacy and ill-use of the product (Baur and Campos 2019; personal communication). Besides the high use rate and prices of PA (Cirimina et al. 2019), this lack of knowledge by farmers to properly integrate this herbicide into weed management programs, and the undefined instructions on the label like on the role of weather conditions, continue to make PA a niche product for the plant protection market (Marrone 2019; Fogliatto et al. 2020).

The use of alternatives to conventional herbicides needs to be optimized. While PA products have been registered since 1992, optimum application parameters such as nozzles, pressure, boom height, or climate conditions are still barely known.

Recently, new compounds based on short-chain (C<sub>6</sub>-C<sub>12</sub>) fatty acids (FA) were suggested as promising contact herbicides (Baur et al. 2019). Particularly pelargonic acid ester of a methyl polyethylene glycol (PA-MPEG) showed excellent performance in weed control, being the lead compound for further studies (Campos et al. 2021). PA-MPEG gave an effective biological performance like PA herbicides, and as a liquid, it is non-volatile and has no unpleasant smell, unlike PA (Campos et al. 2021). This PA ester derivative with own herbicidal activity is identified with the Chemical Abstract Service (CAS) number 109909-40-2. PA-MPEG is not just a pre-drug of PA that is de-esterified to the active form of PA in contrast to many ester herbicides like cyhalofop-butyl (Ruiz-Santaella et al. 2006) or 2,4-D ester (Peterson et al. 2016). Yet, it acts as the ester. PA-MPEG can be directly diluted in water and ready to use without formulation efforts because of its physicochemical properties such as liquid state, high water-solubility, and wetting power due to both, low static and dynamic surface tension. Therefore, PA-MPEG may become a potential tool for weed control under optimum and well-defined use conditions.



In this study, we first define the optimum rate and spray volume of PA-MPEG for adequate weed control, then evaluate application factors such as sprayer parameters and environmental conditions on PA-MPEG efficacy.

## 2. MATERIALS AND METHODS

### *Chemicals*

Pelargonic acid ester of methylated polyethylene glycol (PA-MPEG) was provided by Clariant (Gendorf, Germany). For its synthesis, please refer to Campos et al. (2021). PA-MPEG was diluted directly in tap water without formulation ingredients for the application. For comparison purposes with PA herbicides, PA-MPEG content is 340 g of PA acid equivalent (ae) per liter. Beloukha® (BLK) from Belchim Crop Protection NV (Londerzeel, Belgium) and VOROX® Unkrautfrei Express (VRX) from Compo GmbH (Münster, Germany) were selected as commercial PA herbicides (Table 1).

**Table 1** – Basic data and application rates for the experimental herbicide and commercial PA products used in the trials.

Product	Active ingredient (ai) content (g L <sup>-1</sup> )	Acid equivalent (ae) content (g L <sup>-1</sup> )	Rate (L ha <sup>-1</sup> )	Other rates (kg ai or ae ha <sup>-1</sup> )	Spray volume (L ha <sup>-1</sup> )
PA-MPEG <sup>a</sup>	1001.0	340.0	5 – 50*	1.7 – 17*	100 – 1000*
Beloukha® (BLK) <sup>b</sup>	680.0	680.0	16	10.9	200 - 400
VOROX® Unkrautfrei Express (VRX) <sup>c</sup>	273.6	273.6	130	30.9	1000

\* Rates and spray volumes tested in this study.

<sup>a</sup> Clariant, Gendorf, Germany

<sup>b</sup> Belchim Crop Protection NV, Londerzeel, Belgium

<sup>c</sup> Compo GmbH, Münster, Germany

### ***Plant material***

Seeds of *Digitaria sanguinalis* (L.) Scop. and *Solanum nigrum* L. acquired from Herbiseed (Reading, UK) were sown separately in 9 x 9 cm plastic pots containing an artificial substrate (Typ B Hawita Fruhstorfer, Hawita Gruppe GmbH, Vechta, Germany). One week after emergence, weeds were thinned, and only one plant per pot was left. The weeds were grown in a phytotron under natural sunlight and augmented with supplemental sodium vapor lights with a photosynthetic photon flux density of 200  $\mu\text{mol m}^{-2} \text{s}^{-1}$ . The photoperiod was 16/8 light/dark. The temperature was regulated to 22 °C daytime and 17 °C nighttime. Relative humidity (RH) was fixed at  $55 \pm 5$  %. Weeds were bottom watered twice a week to maintain adequate moisture. Herbicide applications were performed to *Digitaria sanguinalis* at the start of the tillering, corresponding to growth stage 21-22 according to the *Biologische Bundesanstalt, Bundessortenamt und Chemische Industrie* (BBCH) scale and *S. nigrum* at the growth stage of six true leaves (BBCH 16).

### ***Spray application***

Treatments were applied with a custom-built spray chamber (Ing-Büro CheckTec, Braunschweig, Germany) with flat-flan nozzles from Lechler GmbH (Metzingen, Germany) mounted 50 cm above the weed canopy. The spray pressure was 300 kPa. Spray applications from 100 to 400 L ha<sup>-1</sup> were obtained by applying spray through a nozzle with an orifice size of 02 by adapting the speed of the sprayer in the spray chamber from 6.3 to 1.9 km h<sup>-1</sup>. Likewise, spray applications of 500 and 1000 L ha<sup>-1</sup> were gained using a tip nozzle with an orifice size of 06 at 2.4 and 1.5 km h<sup>-1</sup>, respectively.

### ***Experimental Design and data collection of phytotron trials***

Trials were conducted as randomized complete block design. Treatments were replicated four times for each weed species. A non-treated control was always included for comparison. Based on previous studies, evaluations were performed 2 and 7 days after treatment (DAT). Visible injuries (desiccated and necrotic tissues) were assessed for weed control on a 0 to 100 % scale, where the value “0 %” meant no weed control (no

dead plants) and “100 %” was complete weed control (all plants dead). Table 2 depicts the rating scale of weed control (Campos et al. 2021).

**Table 2** – Rating score used to interpret the weed control efficacy.

<b>Weed control efficacy (%)</b>	<b>Description</b>
0 - 19	No control. Plants are entirely tolerant (weeds alive).
20 - 39	Poor control. Plants are moderately tolerant with transient desiccated/wilted symptoms.
40 - 59	Moderate control. Plants are moderately susceptible. Desiccated tissues
60 - 79	Good control. Plants are susceptible. Necrotic tissues
80 - 100	Excellent control. Plants are highly susceptible (weeds killed).

***Impact of carrier volume and PA-MPEG concentration on weed control efficacy***

Two phytotron trials were performed. In the first experiment, PA-MPEG at 17 kg ae ha<sup>-1</sup> (dose selected based on Campos et al. (2021)) was sprayed at four spray volumes (100, 200, 500, and 1000 L ha<sup>-1</sup>). Commercial PA herbicides were used as positive controls according to label recommendations (Table 1). The second trial evaluated the efficacy of four PA-MPEG concentrations (2.5, 5, 7.5, and 10 % v/v) applied by using 200 and 500 L ha<sup>-1</sup> spray volumes. These concentrations represent PA-MPEG rates of 1.7, 3.4, 5.1, and 6.8 kg of PA acid equivalent (ae) ha<sup>-1</sup> for a spray volume of 200 L ha<sup>-1</sup>, and 4.3, 8.5, 12.8 and 17 kg ae ha<sup>-1</sup> for 500 L ha<sup>-1</sup>. No commercial reference was sprayed in this second test.

***Effect of nozzle type, spray pressure and spray boom height on weed control efficacy of PA-MPEG.***

In this experiment, changes in the variables pressure, nozzle and boom height were studied one at a time to examine their influence on PA-MPEG efficacy. The pressures were 100, 200 and 300 kPa, and the nozzles were a flat fan (LU-120-02) and an air

induction (ID-120-02), both from Lechler GmbH. The boom height used was 10, 25 and 50 cm from the target. The standard application was made using a flat nozzle (LU-120-02) at a spray pressure of 300 kPa, and fifty centimetres from the top of the weed species. PA-MPEG was applied with a suboptimal rate and spray volume (5.1 kg ae ha<sup>-1</sup> in 200 L ha<sup>-1</sup>) for better differentiation of sprayer parameters on efficacy.

### ***Influence of temperature and relative humidity on weed control efficacy of PA-MPEG***

Once the weed species had reached the right BBCH stage for treatment, they were placed under the test climatic conditions three days before spraying to avoid abiotic stress at the time of application. They were maintained under these conditions until 7 DAT (end of the experiment). Different sections of the Clariant phytotron were set to the test climatic conditions to carry out the study. A total of 5 scenarios were studied. Weeds were placed at temperatures (day/night) of either 10/5 °C, 22/17 °C, or 33/25 °C at a constant 55 % RH to examine the impact of temperature. To study the influence of RH, weeds were maintained at an RH of either 30, 55, or 97 % and 22/17 °C, day/night, respectively. Untreated weeds were always placed in each test climatic condition for comparison. PA-MPEG was applied with a suboptimal rate and spray volume (5.1 kg ae ha<sup>-1</sup> in 200 L ha<sup>-1</sup>) for better efficacy differentiation.

### ***Study of PA-MPEG spray coverage***

Individual leaves of *D. sanguinalis* and *S. nigrum* were used for determining PA-MPEG spray coverage. They were placed on a plate and sprayed with PA-MPEG containing the fluorescent tracer Blankophor CBB from Tanatex Chemicals (Ede, Netherlands) at 1 g L<sup>-1</sup>. The application was made using different pressures (100, 200 and 300 kPa) or tip nozzles (LU-120-02 and ID-120-02) in the sprayer. After spray evaporation, the leaves were placed on a black background, and the fluorescent blue signal was photographed under ultraviolet light (UPV® Black-Ray® B-100 High-Intensity UV Lamp) provided by Labortechnik (Wasserburg, Germany). A colour phase analysis was performed using the software LAS X from Leica Microsystems (Wetzlar, Germany) to quantify the

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percentage of the leaf covered by the spray. Obtained values represented the leaf surface covered by the PA-MPEG spray solution from the total area of the leaf.

### ***Influence of nozzle and pressure on spray droplet size of PA-MPEG***

Characterization of droplet size was conducted with the laser diffractometer MAL1082034 and the Spraytec 3.20 software from Malvern Instruments (Heidelberg, Germany), which were installed in a custom-built spray cabin from CheckTek (Braunschweig, Germany). Evaluations for the flat nozzle (LU-120-02) were conducted at 200 and 300 kPa. The air induction nozzle (ID-120-02) was only tested at 300 kPa. Before application, the required nozzles and pressures were set up on the sprayer. PA-MPEG spray solution was sprayed for twenty seconds. The obtained data was a volumetric population of droplets calculated from an average of 5000 droplets taken for five seconds and means of 6 repetitions.

### ***Cuticular penetration***

Cuticular penetration of PA-MPEG and VRX was studied after applying 10  $\mu$ L droplets of the spray solution to the outer surface of enzymatically isolated cuticular membranes (CM) placed on a steel chamber with a lid and measuring the acceptor in contact with the inner side of CM. Details are described elsewhere (Baur 1999; Baur and Schönherr 1997). Penetration was started after water evaporation of the droplet. The aliquots of the acceptor solution were drawn and analysed by a 1290 Infinity HPLC from Agilent (Santa Clara, USA). The geometric mean of the penetration values per treatment was obtained from 10 repetitions and two measurements (6 and 24 hours) after application. The kinetics indicated the mean of active ingredient (ai) penetration across the cuticle at different times.

Controlled conditions: HPLC was in an airtight chamber where the temperature was set up to the tested temperatures (5 and  $25 \pm 0.5$  °C). Humidity around CM was controlled by using saturated salt solutions that give constant humidities in the nearby air of the CM (Baur 1999; Baur and Schönherr 1997). The humidity points were tried with  $\text{CaCl}_2$  (30 % RH),  $\text{Ca}(\text{NO}_3)_2$  (56 % RH) and  $\text{KNO}_3$  (93 % RH).

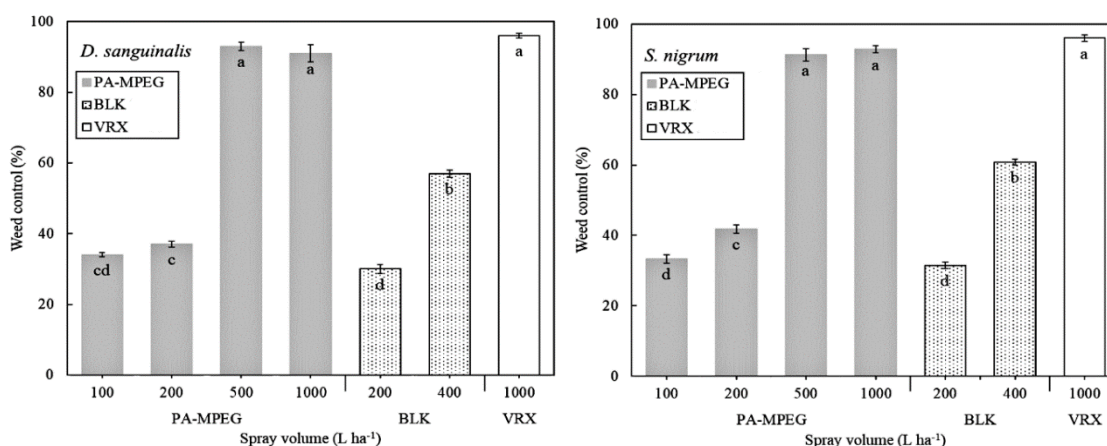
### Statistical analysis

The data were subjected to analysis of variance (ANOVA) using ARM software (Gylling Data Management Inc., Brookings, US). Individual treatment means were separated using Tukey's honestly significant difference (HSD) test at an alpha level of 0.05. Before the analysis, the normality and homoscedasticity of the assessment values were verified using the functionalities of the software. Data were automatically transformed by the software when needed.

## 3. RESULTS

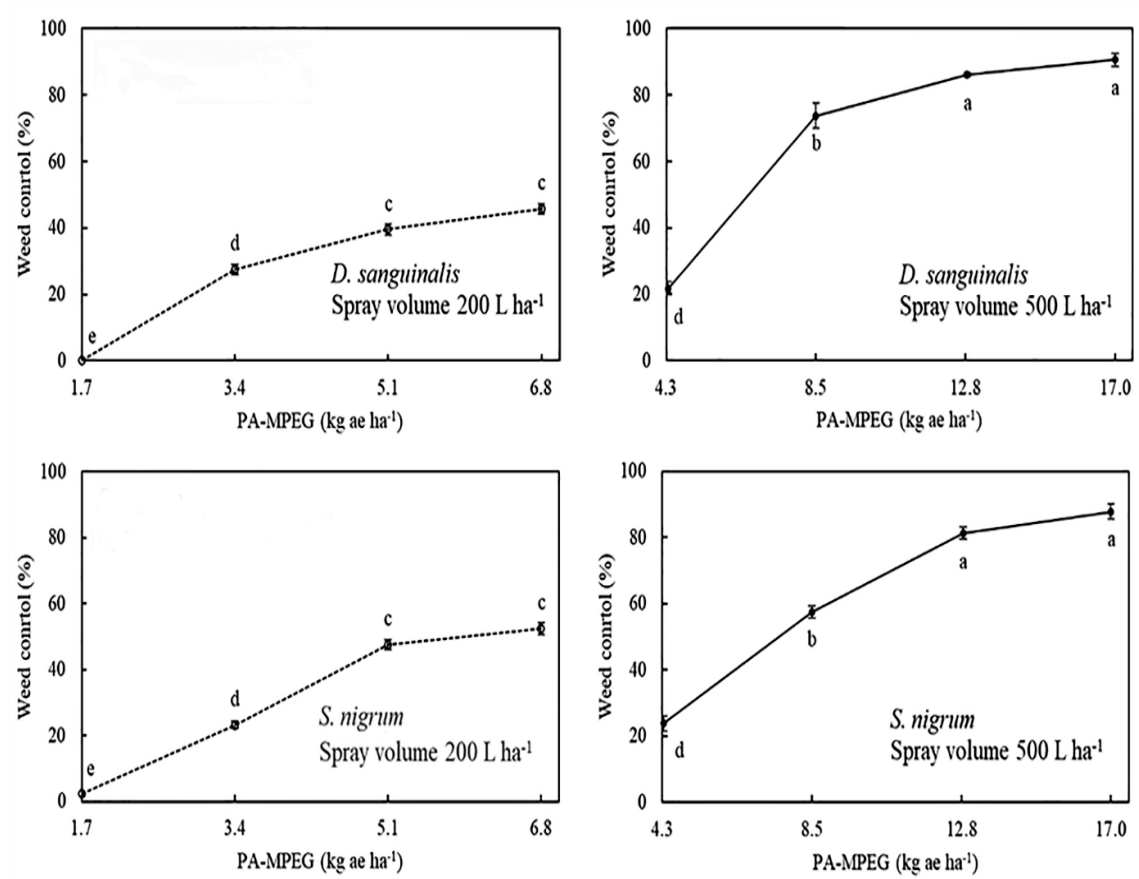
### Impact of carrier volume and PA-MPEG concentration on weed control efficacy

PA-MPEG and BLK became more effective as the spray volume increased, not affected by the decreasing concentration (Figure 1). At water volumes above 500 L ha<sup>-1</sup>, PA-MPEG weed control was higher than 90 % and equal to that provided by the commercial PA herbicide (VRX) with a spray volume of 1000 L ha<sup>-1</sup>. PA-MPEG in 100 or 200 L ha<sup>-1</sup> gave a weed control efficacy of around 40 % for both weed species as BLK did at label recommendation.



**Figure 1.** Control of *Digitaria sanguinalis* and *Solanum nigrum* treated with pelargonic acid ester methyl polyethylene glycol (PA-MPEG) at 17 kg ae ha<sup>-1</sup> as influenced by spray volume. Beloukha (BLK) applied at 10.9 kg ai ha<sup>-1</sup> in 200 and 400 L ha<sup>-1</sup> spray volume, and VOROX® Unkrautfrei Express (VRX) at 30.9 kg ai ha<sup>-1</sup> in 1000 L ha<sup>-1</sup> were used as standard references. Means labelled with common letters are not significantly different by the Tukey HSD Test at the 5% level of significance. Bars represent standard errors.

At a given water volume, PA-MPEG efficacy was highly dose-dependent (Figure 2). While the maximum weed control was achieved at a dose of 6.8 kg ae ha<sup>-1</sup> at spray volume of 200 L ha<sup>-1</sup>, and 17 kg ae ha<sup>-1</sup> at 500 L ha<sup>-1</sup>, weed control was not significantly higher than the one given by 5.1 or 12.8 kg ae ha<sup>-1</sup>. Accordingly, the threshold doses of PA-MPEG could be established at 5.1 kg ae ha<sup>-1</sup> for a 200 L ha<sup>-1</sup> spray volume and 12.8 kg ae ha<sup>-1</sup> for a spray volume of 500 L ha<sup>-1</sup> (Figure 2). *Digitaria sanguinalis* and *S. nigrum* control decreased drastically for PA-MPEG rates below 5.1 kg ae ha<sup>-1</sup> in the tested spray volumes.



**Figure 2.** Control of *Digitaria sanguinalis* and *Solanum nigrum* as affected by PA-MPEG rate at 200 and 500 L ha<sup>-1</sup> spray volumes. Means labelled with the same letter are not significantly different by the Tukey HSD Test at the 5% level of significance. Bars represent standard errors.

### ***Effect of nozzle type, spray pressure and spray boom height on weed control efficacy of PA-MPEG***

PA-MPEG efficacy was not significantly affected by using different nozzles or pressures in the application (Table 2). In contrast, boom height was a significant factor for PA-MPEG efficacy on both weeds, with the shorter boom height of 10 cm achieving greater weed control than the 25 and 50 cm boom height.

**Table 2.** Control of *Digitaria sanguinalis* and *Solanum nigrum* with pelargonic acid ester methyl polyethylene glycol (PA-MPEG) applied at 5.1 kg ae ha<sup>-1</sup> in a spray volume of 200 L ha<sup>-1</sup> through different tip nozzles, spray pressures, and boom height.

Nozzle type	Spray pressure (kPa)	Spray height (cm)	Weed control (%)	
			<i>D. sanguinalis</i>	<i>S. nigrum</i>
ID-120-02 <sup>a</sup>	300	50	34.8 ± 1.7 c <sup>*</sup>	45.0 ± 0.8 c <sup>*</sup>
LU-120-02 <sup>b</sup>	100	50	33.8 ± 1.5 c	47.3 ± 1.0 bc
LU-120-02	200	50	32.0 ± 1.7 c	47.3 ± 1.0 bc
LU-120-02	300	50	32.0 ± 1.2 c	46.0 ± 0.6 bc
LU-120-02	300	25	54.8 ± 1.7 b	51.0 ± 2.1 b
LU-120-02	300	10	64.3 ± 2.7 a	59.3 ± 1.4 a

<sup>a</sup> Air induction nozzle (Lechler GmbH, Metzingen, Germany).

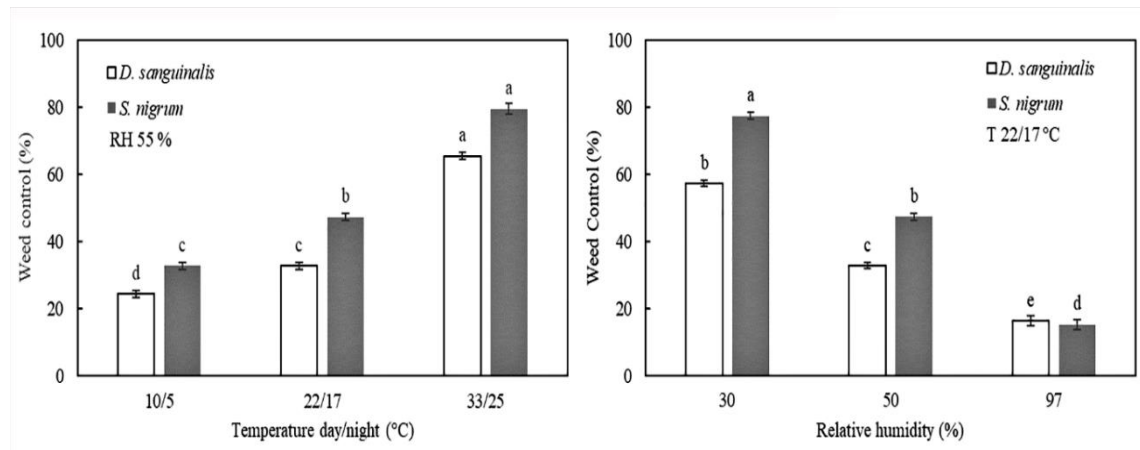
<sup>b</sup> Flat nozzle (Lechler GmbH, Metzingen, Germany).

<sup>\*</sup> Means followed by common letters in a column are not significantly different by the Tukey HSD Test at the 5% level of significance.

### ***Influence of temperature and relative humidity on weed control efficacy of PA-MPEG***

Maximum weed control of PA-MPEG was found when plants were located at elevated day/night temperatures (33/25 °C), as shown in Figure 3. A decrease in the RH from 97 % to 30 % also caused an increase in PA-MPEG efficacy, particularly on *S. nigrum*. At low temperature (10/5 °C) or the ambient temperature of 22/17 °C combined with high relative humidity (97 %), weeds were quite tolerant and did not show clear PA-MPEG injuries.

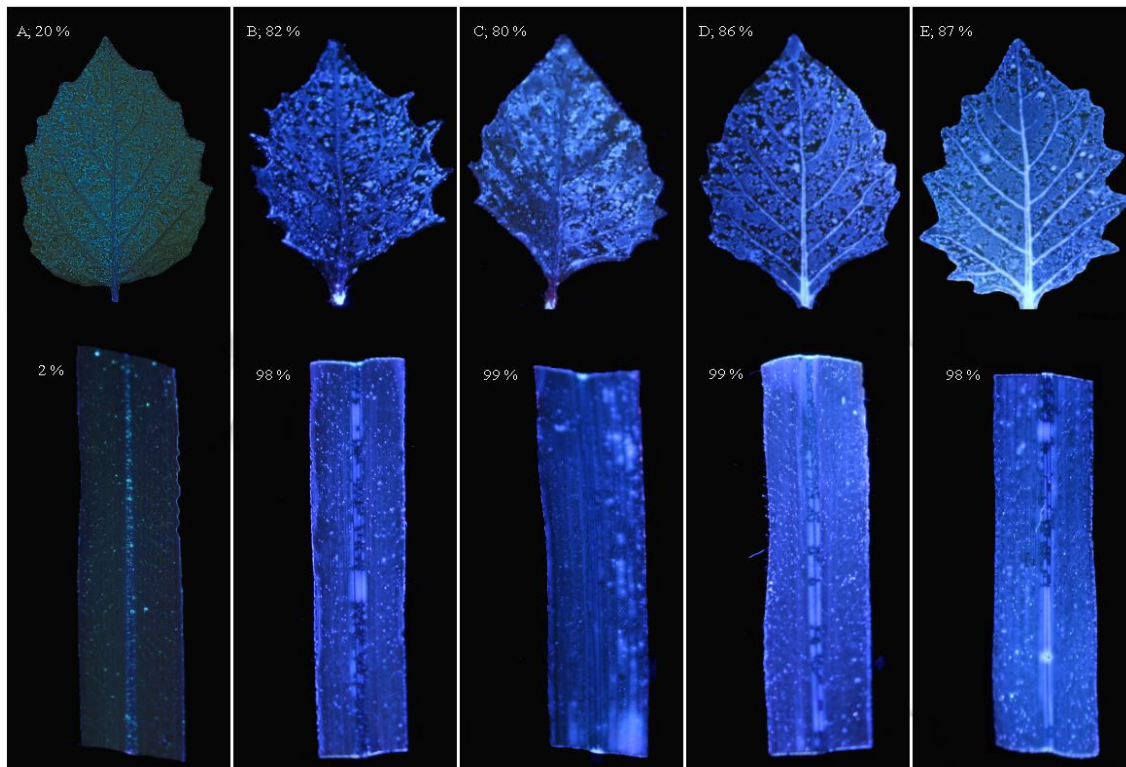




**Figure 3.** Effect of temperature and relative humidity on *Digitaria sanguinalis* and *Solanum nigrum* control with PA-MPEG at 5.1 kg ae ha<sup>-1</sup> in a spray volume of 200 L. Values within each weed species with the same letters are not significantly different ( $p \leq 0.5$ , Tukey's test). Bars represent standard errors.

#### ***Spray coverage of PA-MPEG with different nozzle types and spray pressure***

There was no striking difference in spray coverage percentage in PA-MPEG when varying nozzle or pressure for both weed species. PA-MPEG application gave a uniform and complete coverage of the surface leaf (above 80 %) in all tested variations. For a plant with a non-wettable surface like *D. sanguinalis*, coverage was generally at least 10 % higher as shown in Figure 4 (blue-coloured areas)



**Figure 4.** Spray coverage on individual leaves of *Digitaria sanguinalis* and *Solanum nigrum* with PA-MPEG at a rate of 5.1 kg ae ha<sup>-1</sup> in a spray volume of 200 L ha<sup>-1</sup> through different tip nozzles and spray pressures. The blue colour represents the leaf area covered by the spray, denoted as a percentage (%). A) water, LU-120-02 tip nozzle at 300 kPa; B) PA-MPEG, LU-120-02 tip nozzle at 100 kPa; C) PA-MPEG, LU-120-02 tip nozzle at 200 kPa; D) PA-MPEG, LU-120-02 tip nozzle at 300 kPa and E) PA-MPEG, ID-120-02 tip nozzle at 300 kPa.

#### ***Droplet size distribution of PA-MPEG at different spray applications***

The droplet diameter decreased as the pressure increased. The  $D_{v0.5}$  value fell by 25 % when increasing the pressure from 200 to 300 kPa (Table 3). The air induction nozzle also caused an increase in droplet diameter in comparison to LU-120-02, decreasing the driftable fines droplet (%  $V < 105$ ) by more than 50 %.

**Table 3.** Droplet size distribution of pelargonic acid ester methyl polyethylene glycol (PA-MPEG) at 5.1 kg ae ha<sup>-1</sup> in 200 L ha<sup>-1</sup>.

	Nozzle	Pressure (kPa)	D <sub>v0.1</sub> <sup>a</sup>	D <sub>v0.5</sub> <sup>a</sup>	D <sub>v0.9</sub> <sup>a</sup>	V < 90 <sup>b</sup>	V < 105 <sup>b</sup>	V < 150 <sup>b</sup>	V < 210 <sup>b</sup>	RS <sup>c</sup>
Water	LU-120-02	200	76	156	327	16.1	23.9	47.4	70.0	1.6
Water	LU-120-02	300	70	146	323	19.5	28.0	51.8	72.9	1.7
Water	ID-120-02	300	209	629	1370	1.6	2.5	5.7	10.1	1.8
PA-MPEG	LU-120-02	200	77	419	1302	13.2	17.1	27.5	36.5	2.9
PA-MPEG	LU-120-02	300	65	319	1199	18.9	24.0	36.3	45.8	3.6
PA-MPEG	ID-120-02	300	98	348	1073	8.7	11.3	19.6	30.4	2.8

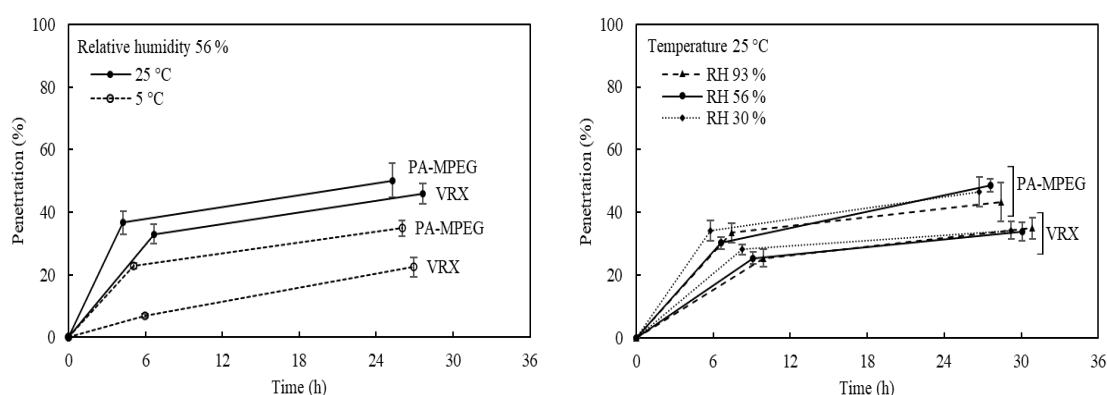
<sup>a</sup> Values represent droplet diameter.

<sup>b</sup> Percentages of spray volume contained in droplets less than 105, 150, and 210 µm.

<sup>c</sup> RS is the relative span of the spray droplet spectrum.

### Cuticular Penetration

PA-MPEG and PA penetration were quite dependent on temperature for a liquid adjuvant. Increasing temperature from 5 to 25 °C caused a 2 and 3-fold increase in initial penetration of PA-MPEG and PA (formulated as VRX). PA-MPEG penetrated particularly faster at lower temperature while PA-MPEG and PA were similar at 25 °C (Figure 5). In contrast, while penetration of PA-MPEG was faster at different relative humidities, the dependence of weed control on relative humidity was low.



**Figure 5.** Effect of temperature and relative humidity on the penetration of PA-MPEG and a commercial formulation of PA (VRX) at 25 g ae L<sup>-1</sup> across leaf cuticle membrane of *Malus domestica* (apple).

## 4. DISCUSSION

Pelargonic acid ester of methylated polyethylene glycol (PA-MPEG) is a new active ingredient not depending on formation and thus different from PA. However, both active substances, PA-MPEG and PA, cause similar symptoms on the treated plant and have the same MoA, which is still unclear (Campos et al. 2021, Campos et al. 2022). While PA-MPEG contains 340 g of PA acid equivalent (ae) per litre, PA-MPEG is neither a new formulation nor a pre-drug of PA that is hydrolysed to PA again. Results on hydrolysis stability have shown that PA-MPEG is hydrolytically stable at different pH (data not shown). Furthermore, other FA ester derivatives did not show herbicidal activity (Campos et al. 2021). This novel active ingredient, which can be directly diluted in water and applied, has been previously reported as a fast-acting contact herbicide with equal or even

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better weed control than PA herbicide at lower or equal rates (Baur et al. 2019). More importantly, PA-MPEG does not have the disadvantages of PA, such as the need for a complex formulation, combinability with other actives, high volatility, and the unpleasant smell (Campos et al. 2021). With these properties, PA-MPEG is a better alternative to conventional contact herbicides than PA. However, PA-MPEG use rates are still high, and consequently, further efforts and research on reducing them are needed.

Weed size has a significant impact on foliar applied herbicides efficacy (Eure et al. 2013). Post-emergence herbicides achieve maximum weed control when applications are made on plants in early growth stages (up to 10 cm high; BBCH 10-14) (Bayer Cropscience 2019; Pintar et al. 2021). For contact herbicides like PA, weed size is even more relevant due to the need for maximum coverage and thus total plant area. Crmaric et al. (2018) and Webber and Shrefler (2006) observed higher PA efficacy on younger weeds. Accordingly, the trials reported here were done with medium-sized weeds (18-20 cm height) for better differentiation of factors of influence on PA-MPEG efficacy. As the effect of PA-MPEG and PA is a very rapid non-selective contact activity, practically not depending on the metabolism of specific weeds (Baur et al. 2019; Muñoz et al. 2020), only *D. sanguinalis* and *S. nigrum* were sufficient in the context of this research. Both plants are representative monocot and dicot weeds of difficult control, particularly *D. sanguinalis* in corn and *S. nigrum* in potatoes fields (Kraehmer and Baur 2013). Moreover, these weeds are also commonly used in studies.

PA-MPEG and PA efficacy depend first on the dose (Muñoz et al. 2020; Travlos et al. 2020) and second on the spray volume, which gives the maximum plant coverage. For example, PA-MPEG applied at a rate of 4.3 kg ae ha<sup>-1</sup> in a spray volume of 500 L ha<sup>-1</sup> did not perform well and was not at all effective, neither did PA-MPEG at 17 kg ae ha<sup>-1</sup> in a spray volume of 100 L ha<sup>-1</sup>. There is an interaction (dose – spray volume) that needs careful use recommendations with these types of herbicides (Webber and Shrefler 2006; Webber et al. 2014; Crmaric et al. 2018).

From the results with *D. sanguinalis* and *S. nigrum*, PA-MPEG applied at a rate of 12.8 kg ae ha<sup>-1</sup> in 500 L ha<sup>-1</sup> spray volume is the most efficient and optimum application rate. This dose allows reducing the PA by 13.9 kg and water volume by 420 L per hectare

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compared to the commercial standard (VRX) recommendation. The significant reduction is partly due to the superior wetting properties of PA-MPEG, which improve weed coverage and canopy penetration despite the spray volume reduction, particularly on monocot weeds. The dynamic surface tension of straight PA-MPEG is below  $45 \text{ mN m}^{-1}$  at 200 ms, which guarantees excellent spray retention and capillarity spreading (Baur and Pontzen 2007), the latter giving even better coverage with the monocot (Figure 4).

The maximum burndown effect was observed 2 days after application (Coleman and Penner 2008) with no significant differences in weed control even after 7 days, like in previous studies (Campos et al. 2021; Campos et al. 2022). The efficacy of a single application of PA-MPEG at  $12.8 \text{ kg ae ha}^{-1}$  in a spray volume of  $500 \text{ L ha}^{-1}$  was higher than 80 %, which could provide long-lasting weed control. Thus, the second application in a short time interval (15 days) might not be needed. This differs from Krauss et al. (2020) and Webber et al. (2014), who suggested repeated PA applications to achieve sufficient weed control. However, the regrowth of the weed under field conditions needs observation to determine if a second application is required (Travlos et al. 2020).

PA-MPEG ( $5.1 \text{ kg ae ha}^{-1}$ ) at lower spray volumes ( $200 \text{ L ha}^{-1}$ ) resulted in full coverage only on individual leaves (Figure 4) and caused rapid necrotic symptoms of these leaves (data not shown). However, the control of complete plants of *D. sanguinalis* and *S. nigrum* with PA-MPEG was poor, even weaker than expected from a study with other weeds by Muñoz et al. (2020). From Figure 2, we concluded that PA-MPEG applied at  $5.1 \text{ kg ae ha}^{-1}$  in a spray volume of  $200 \text{ L ha}^{-1}$  showed better performance than BLK at label recommendation ( $10.9 \text{ kg ai ha}^{-1}$  in  $200 \text{ L ha}^{-1}$  spray volume), though on an insufficient control level around 40%. The poor weed control observed might be due to insufficient spray penetration into the weed canopy at the lower spray volumes. PA-MPEG and PA were applied on medium-sized plants (18-20 cm height), in contrast to other studies where smaller weeds were used (Muñoz et al. 2020; Travlos et al. 2020).

There are notable differences between PA-MPEG and PA-based contact herbicides and systemic ones. With systemic herbicides, an increase of concentration by reducing carrier volume often results in better weed control and often due to the several advantageous effects of higher concentration. It reduces the dynamic surface tension and

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increases spray coverage, and for glyphosate, a more concentrated spray deposit also increases cuticular penetration possibly via reducing dissociation (Knoche 1994; Schönherr and Baur 1994; Creech et al. 2015). This interaction on weed control was not observed with PA-MPEG and PA, where coverage effects are relevant (Figure 1) and required for excellent weed control with the FA-based herbicides (Crmaric et al. 2018).

At a spray volume of 200 L per hectare, commonly used for herbicides in broadacre agriculture, higher dose rates of PA-MPEG did not cause a significant enhancement in *D. sanguinalis* and *S. nigrum* control. PA-MPEG achieved an efficacy between 40 to 50 % on medium-sized plants. Application parameters like adjuvants or weed size can impact PA efficacy (Webber and Shrefler 2006; Coleman and Penner 2008). With PA-MPEG, the adjuvant functionalities are already included with a liquid physical state above zero °C and excellent wetting properties. A low dynamic surface tension compensates differences of nozzles, which was also observed with PA-MPEG, where related differences in mean drop size or driftable fines had no impact but driftable fines, e.g., also did not vary much. Although the optimal boom height depends on the mounted tip nozzles, PA-MPEG efficacy was increased when boom height was adjusted to 10 and 25 cm above the target. This finding could be a valuable insight in order to reduce PA-MPEG and PA use rates. While the application with a boom height of 50 cm could have provided a greater spray coverage at the top of the weeds than at lower boom heights, other effects have had a higher impact on PA-MPEG performance. One possible effect is a larger fraction of spray liquid collecting in the leaf axils. It has been found in previous single droplet studies that locally high concentrations at the axil and similarly also on the leaf petiole or stem, respectively, showed higher damage (de Ruiter et al. 1999) and caused the death of the leaf organ, even with low direct damage of the leaf blade (data not shown). We recently suggested that the effect of PA-MPEG and PA might be related to the interruption of capillary water flow in the apoplast in the presence of high amounts of the surfactant or acid and lipids from membrane disintegration (Campos et al. 2022). Another effect could be a higher fraction of stomatal penetration into the leaf of the two weeds that are both amphistomatic.

Weather conditions like light, temperature, or humidity have a significant impact on the success of weed control (Kudsk and Kristensen 1992; Zimdahl 2018). For example,

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light conditions impact both, the development of the plant midterm as well as the plants' immediate response to herbicides (Kudsk and Kristensen 1992; Larcher 2003). More importantly, several active ingredients like the contact herbicide glufosinate-ammonium are significantly better penetrating at high relative humidity, mainly due to better hydration of spray deposits which increases the driving force across the cuticle, achieving higher weed control (Anderson et al. 1993; Baur 1998, 1999). For PA herbicides, the label recommendation is to apply during sunny days, but Dayan and Watson (2011) and Lederer et al. (2004) reported that PA action was not light-dependent. We think that light could also have a direct effect as transpiration, which is at least tenfold higher with open stomata, and imbalanced water loss is the main MoA of PA-MPEG and PA (Campos et al. 2022). Weed control at constant light and relative humidity (55%) increased with temperature for both the monocot and dicot weed species (Figure 3). Higher control was also observed in PA field trials during the warmer season (Kanas et al. 2021). This can have two different causes. Cuticular penetration studies showed that both PA-MPEG and PA penetrate at a significantly slower rate and to a lower level within one day at 5°C (Figure 5). The penetration of PA-MPEG at low temperature is higher than with PA and notably, weed control at low temperature was always found to be better with PA-MPEG (data not shown). PA-MPEG is related to fatty alcohol ethoxylates, which are good penetration enhancers but still show temperature-dependent penetration and effect on the penetration of other actives (Baur 1999). Another reason for the observed temperature dependence is that low temperature also slows plant growth and the water requirement by the plant (Larcher 2003). So, the plant could be less affected by the discontinuity of the water flow in the cell walls and xylem, and thus not facing water shortage. There was even a more pronounced antagonistic effect of high relative humidity on PA-MPEG efficacy, suggesting that the temperature below 10 °C combined with more than 75 % RH could cause even lower activity of PA-MPEG, while the temperature of 20 °C or more and relative humidities below 60 % are beneficial (Figure 3). To our knowledge, there are no references in the literature considering the humidity for FA herbicides' efficacy. The high humidity could also increase the penetration of these herbicides by likely extending droplet evaporation time or accessing the stomatal route (Baur 1998). However, this was not relevant for PA-MPEG penetration. PA-MPEG and PA performed better at the lowest



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relative humidity (Figure 5), opposed to other contact herbicides like glufosinate-ammonium (Anderson et al. 1993). As a liquid and moderately lipophilic PA-MPEG solute penetration was not better at higher relative humidity but similar at 55 and 93% RH and slightly better at 30% RH. At this relative humidity, hydration of the ethoxy chain is reduced, which increases solubility and thus penetration across the cuticle (Baur 1999). PA-MPEG has a closer number of ethylene oxide (EO) than the fatty alcohol ethoxylate Genapol C 050, about 6 EO. Both PA-MPEG and Genapol C 050 showed similar results on penetration, depending only slightly on the humidity in contrast to higher ethoxylates with 8-17 EO units (Baur 1999). Thus, the low weed control cannot be explained by a low PA-MPEG penetration.

Cuticular transpiration rate does not have a vital role in PA-MPEG efficacy (Campos et al. 2022), and stomatal transpiration measurement after application of the high rates of PA and PA-MPEG does not give a clear response. As mentioned above, the saturated atmosphere could reduce the transpiration by a decreased gradient of water potential and PA-MPEG and PA also via shortage in supply (flow) of water via cell walls. Therefore, the combination of reduced damage at suboptimal used rates and the reduction in water loss due to climate conditions (cold temperature and/or high humidity) could maintain leaf vitality eventually with the healing of weak injuries (Georgieva et al. 2010).

In conclusion, PA-MPEG efficacy depends on its used concentration. However, maximum spray coverage and penetration into the weed canopy, which are given by high spray volumes, are also key factors for high efficacy with PA-MPEG as well as with PA. This work shows the most efficient PA-MPEG dose rate that provides better weed control than PA benchmarks at different spray volumes and also presents the most suitable spray volume for achieving good weed control on medium-sized weeds. Applications made outside the recommended arrangement of parameters can lead to possible decreases in weed control. However, boom height, weed size, or adequate climate conditions could decrease product rates while maintaining efficacy. Nevertheless, rates are high compared to conventional herbicides, and further research should be carry out to solve this problem for PA-MPEG, e.g., using synergists and particularly co-formulations with synthetic active ingredients or biological control agents.

**CONFLICT OF INTEREST DECLARATION**

The authors declare that they have no conflict of interest.

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Publication III

**Mechanistic aspects and effects of  
selected tank-mix partners on  
herbicidal activity of a novel fatty acid  
ester**

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## **Mechanistic aspects and effects of selected tank-mix partners on herbicidal activity of a novel fatty acid ester**

### **Abstract:**

Only a limited number of contact herbicides exist in agricultural production. While systemic herbicides are more efficient also at suboptimum spray coverage with long-lasting weed control, contact herbicides provide several advantages. There is no translocation to fruits or roots of plantation and other crop, low risk for resistance development, and minor risk for spray-drift damage. Besides, synthetic products that often have toxicological or residues issues, natural fatty acids, particularly pelargonic acid (PA), have contact activity and are safer for home and garden use. We recently described a methyl capped polyethylene glycol ester of pelargonic acid (PA-MPEG) that acts independent of acid formation. Both, PA-MPEG and PA are applied at high rates per hectare to achieve excellent weed control. Here, we report about potential additives to increase PA-MPEG efficacy. The herbicidal active, 1-decanol, and the non-phytotoxic alkylated seed oil-based adjuvant, Hasten<sup>TM</sup>, improved performance and outperformed a commercial PA herbicide. Both, PA-MPEG and PA appear to mainly act by the disintegration of bio-membranes besides having effects on transpiration. The main suggested effect is desiccation due to cutting the water continuum at the site of evaporation in the intercellular spaces. The synergistic action of the adjuvant Hasten<sup>TM</sup> and its practical uses are also discussed.

### **Keywords**

Contact herbicide; pelargonic acid; esterified seed oil; foliar penetration; adjuvant; tank-mix partner



## 1. Introduction

Most herbicides normally used for agricultural weed control are based on synthetic active ingredients (AIs) and possess systemic properties (Hatcher and Froud-Williams 2017; Jeschke et al. 2019). The majority of foliar AIs are low to moderately water-soluble non-electrolytes, with an octanol/water partition coefficient ( $\log P$ ) below 4, that allows acropetal movement in the xylem. Other active substances are weak organic acids or form such acids from pre-drug esters that move both basipetally and acropetally through the plant (mobility in the phloem) (Jeschke et al. 2019). In many cases, systemic soil-applied herbicides are only xylem mobile after root or hypocotyl uptake, and/or when sufficiently volatile to also distribute in the gas phase of soils (Jeschke et al. 2019; Baur and Aponte 2014). Selective weed control by such systemic herbicides is based on several complex and sophisticated plant-herbicide interactions, such as herbicide-tolerant transgenic crops, combinations with safeners, timing of applications or tolerance by a higher biomass, or the quick growth compensation of damaged assimilation areas (Duke and Powles 2008; Gatzweiler et al. 2012; Hatcher and Froud-Williams 2017; Zimdahl 2018; Jeschke et al. 2019).

In contrast to more effective and systemic AIs, only a few available herbicides are not translocated in plants. They are commonly known as contact herbicides and act only on treated organs (Hatcher and Froud-Williams 2017; Zimdahl 2018). The most important ones are quaternary ammonium compounds of bipyridines, and 1,1'-dimethyl-4,4'-bipyridylium dichloride (paraquat) is the most widely used (Eddleston 2017). The advantages of such compounds are the rare occurrence of herbicide-resistant weeds (paraquat resistance is documented in 30 plant species in 72 situations vs. 53 species in 339 scenarios for glyphosate use) and the low risk that sensitive weeds become resistant over generation (ISHRW 2021). Other benefits are that they are harmless to non-target plants by spray drift and their lack of translocation, e.g. to fruits in orchards (WHO 1984). However, given the bipyridines' mode of action (MoA) - formation of reactive oxygen species after accepting electrons from photosystem I, causing the inhibition of photosynthesis – there are concerns regarding safety. Nonselective, nonspecific damage and continuous action occur due to the active ingredient regeneration causing oxidation

of cell components, including membranes. The toxicity and side effects of these herbicides on human and non-target organisms are substantial (Eddleston 2017). Therefore, paraquat and related products are increasingly banned in various regions (Dinham 2004; Eddleston 2017).

Contact herbicides also include natural alternatives with practically zero toxicity such as nonanoic or pelargonic acid (PA) and related octanoic (caprylic) and decanoic (capric) acids (Coleman and Penner 2006; Fukuda et al. 2004; Lederer et al 2004). Several commercial formulations of short chain fatty acids (FA) and their salts are available for weed control (BELCHIM 2018; CERTIS 2020; WESTBRIDGE 2020). With the advantage of having extremely rapid action and being rainfast, they do not pose residual problems, and no resistant weed biotypes have been reported (Ciriminna et al. 2019; Chiotti et al. 2020). However, FA herbicides are volatile, have an unpleasant odor and are difficult to formulate (Baur et al. 2019; BPDB 2021). For good and long-lasting effects on weed control, FA should be applied at extremely high rates, and repeated applications must be performed within short time intervals, which makes them very expensive for users (Merritt et al. 2016; Crmaric et al. 2018; Campos et al. 2021). Given their fast herbicidal activity, the combination with other synthetic or natural AIs is a challenge. It is often impossible to achieve a synergistic or an additive effect on weed control, particularly with systemic AIs (Wehtje et al. 2009; Little and Nadel 2014).

We have recently shown that novel short chain FA derivatives, particularly the methyl polyethylene glycol esters (MPEG) of C<sub>8</sub>–C<sub>10</sub> FA, are as effective as the free acid, and do not merely act as pre-drug (Campos et al. 2021). Pelargonic acid ester of methyl polyethylene glycol (PA-MPEG) is the preferred candidate (Campos et al. 2021). PA-MPEG is liquid at the relevant temperature range, not volatile and can be used as a straight product without further formulation efforts (Campos et al. 2021). It is also combinable in-can or in tank-mix with other herbicides and acts as a wetting agent on its own (Baur et al. 2019). With its very low animal and human toxicity as known to date, the use is very encouraging in environmentally friendly and organic farming. The use rate and water volumes of PA-MPEG are lower than those of various current PA formulations, but are still higher than conventional herbicides (Campos et al. 2021). Therefore, further

reductions in the use rate and spray volume, and increasing PA-MPEG performance, are essential for it to become an alternative to the traditional contact herbicides.

Adjuvants and natural additives are often added to the spray tank of the herbicides to enhance final performance. They can modify the characteristics of the spray mixture or improve herbicidal activity (Hazen 2000; Pacanoski 2015). Thus, adjuvants also have the potential to enhance PA-MPEG activity by affecting spray deposition, bioavailability and/or the effect in the transport across cuticles (Hazen 2000; Pacanoski 2015; CLARIANT 2021; VICCHEM 2021). For example, a strong selected wetting agent can offer better coverage, which is fundamental for contact herbicides, or an alcohol ethoxylated can increase the mobility of a solute in cuticles (Pacanoski 2015; CLARIANT 2021).

In this study, we present the results of sustainable adjuvants and natural additives as potential enhancers of PA-MPEG weed control efficacy. New insights into the likely mode of action are also discussed.

## 2. Materials and methods

### *Plant Species and Biological Test Conditions*

Seeds of velvetleaf (*Abutilon theophrasti* M.), large crabgrass (*Digitaria sanguinalis* L.) and black nightshade (*Solanum nigrum* L.) were acquired from Herbiseed (Reading, UK). Tomato (*Solanum lycopersicum* L.), bell peppers (*Capsicum annuum* L.), soybean (*Glycine max* L.) and maize (*Zea mays* L.) seeds were kindly provided by a local farmer in Bad Soden am Taunus (Germany). Plant species seeds were sown separately in plastic pots (9 cm × 9 cm × 10 cm) containing an artificial substrate named Typ B Hawita Fruhstorfer from Hawita Gruppe GmbH (Vechta, Germany). One week after emergence, plants were carefully thinned to one plant per pot. Weeds and crops were grown in the Clariant phytotron (Frankfurt am Main, Germany) under natural light and augmented with supplemental sodium vapor lights that produced a photosynthetic photon flux density (PPFD) of 200  $\mu\text{mol m}^{-2} \text{s}^{-1}$ . The photoperiod was 16/8 h light/dark. Daytime temperature was  $23 \pm 1$  °C, and night-time temperature was kept at  $18 \pm 1$  °C. Relative humidity

(R.H.) fell within  $55 \pm 5\%$  range. Enough moisture was maintained in soil until the end of trials to avoid water stress and keep plants in the optimum stage. Crop plants were irrigated with a standard fertilizer solution once a week to prevent nutrient deficiencies.

### ***Experimental Design of the Phytotron Trials***

Trials were conducted as a randomized complete block (RCB) design with four replicates per weed species. An untreated control was always included for comparison purposes. Spray preparations were applied to *D. sanguinalis* in phenological stage 22 (with two tillers) and *S. nigrum* in stage 16 (true six leaves) according to the *Biologische Bundesanstalt, Bundessortenamt und Chemische Industrie* (BBCH) scale. They were approximately 18-20 cm tall. Applications were carried out with a custom-built spray chamber (Ing-Büro CheckTec, Braunschweig, Germany) equipped with two off-center flat nozzles and a mobile carrier of the spray tank. Spray volumes of 200 and 400 L ha<sup>-1</sup> were set by adapting the application carrier speed, using OC2 nozzles from Lechler GmbH (Metzingen, Germany) mounted 50 cm above the weed canopy. Spray pressure was 300 kPa.

Herbicide efficacy was visually assessed at 1, 2 and 7 days after application (DAA) on a percentage scale, where the value “0%” represents no weed control (weeds alive) and one of “100%” denotes complete weed control (weeds killed) (Campos et al. 2021).

### ***Herbicidal Compound and Tank-Mix Partners Tested***

The experimental herbicide was the pelargonic acid ester of methylated polyethylene glycol (PA-MPEG) which was synthesized by Clariant (Gendorf, Germany). This active is liquid and was diluted directly in tap water. For comparison purposes, PA-MPEG content is 340 g of PA acid equivalent (a.e.) per liter. Based on previous knowledge, PA-MPEG was used at 7.5% v/v, alone or with selected tank-mix partners, at a spray volume of 200 L ha<sup>-1</sup>. Phosphoric acid, D-glucose, potassium carbonate and *l*-decanol were selected as non-synthetic amendments. They were purchased from Sigma-Aldrich Chemie GmbH (Merk KGaA, Darmstadt, Germany). The tested commercial adjuvants



were Synergen<sup>®</sup> TS 7, Polyglykol 400, Genapol<sup>®</sup> C 050 from Clariant (MuttENZ, Switzerland) and Hasten<sup>™</sup> from Victorian Chemicals (Victoria, Australia). Table 1 is a more detailed description of the tested compounds and the applied rates.

**Table 1.** Test compounds, applied concentrations used and the pH of spray solutions with PA-MPEG.

Test Compounds	Description	Use Rate (% v/v) <sup>1</sup>	pH Spray Mixture <sup>2</sup>
Phosphoric acid	Solution–85 wt. % in H <sub>2</sub> O.	0.60	1.9
D-glucose	97.5% purity.	1.00	5.8
Potassium carbonate	99.0% purity.	1.00	10.3
1-decanol	99.0% purity.	1.00	6.1
Synergen <sup>®</sup> TS 7 <sup>3</sup>	Blend of docusate sodium and ethoxylated fatty alcohol (sum 100%).	0.15	5.8
Polyglykol 400 <sup>3</sup>	Polyethylene glycol (PEG) with a molar weight of 400.	1.50	5.9
Genapol <sup>®</sup> C 050 <sup>3</sup>	Coconut fatty alcohol polyglycol ether with 5 EO.	1.00	5.8
Hasten <sup>™</sup> <sup>4</sup>	Emulsifiable concentrate of esterified vegetable oil and non-ionic surfactants.	2.50	6.1

<sup>1</sup> Rate based on label recommendation and previous trials.

<sup>2</sup> Pelargonic acid ester of methyl polyethylene glycol (PA-MPEG) at 7.5% v/v. PA-MPEG pH: 5.8.

<sup>3</sup> Clariant, (MuttENZ, Switzerland).

<sup>4</sup> Victorian Chemicals (Coolaroo, Australia).

### ***Interaction of the Hasten Concentration and the PA-MPEG Rate and Spray Volume***

Two experiments were carried out to check the optimum conditions for the PA-MPEG and Hasten. The first trial was conducted with a factorial arrangement of three Hasten use concentrations (0, 1, 2, and 2.5% v/v), two spray volumes (200 and 400 L ha<sup>-1</sup>) and a single PA-MPEG concentration of 7.5%. A commercial emulsifiable concentrate (EC) formulation of PA (Beloukha, 680 g AI L<sup>-1</sup>, Belchim Crop Protection, Londerzeel, Belgium) according to the label recommendation (10.9 kg a.i ha<sup>-1</sup>), was used as a standard

reference. In the second experiment, different PA-MPEG concentrations alone or with 2.5% Hasten were applied at 200 L ha<sup>-1</sup>. Based on earlier studies, the following herbicide concentrations were employed: 5, 6, 7, 8, 9, and 10%. No commercial reference was used because we explored Hasten enhancement at different PA-MPEG concentrations and PA-MPEG and the commercial PA herbicide gave closer weed control values at the selected 200 L ha<sup>-1</sup> in previous trials.

### ***Phytotoxicity of Spray Tank Partners after Spraying and Single Droplet Application***

The species used for this experiment were *D. sanguinalis* and *S. nigrum*, as described in 2.1. The tested tank-mix partners were mixed in tap-water at the aforementioned concentrations (Table 1). No herbicide (PA-MPEG) was employed in the spray solutions at this time. Test preparations were applied by spraying the weeds and also using 10 µL droplets. In the first experiment, spray applications were performed in the customized spray chamber with the parameters described in Section 2.2. (OC2; 300 kPa; 200 L ha<sup>-1</sup>). Treatments were replicated four times per weed species. The second trial evaluated the phytotoxicity of a single droplet application on the adaxial leaf surface of weeds at room temperature (25 °C and 56% RH). In addition, 10 µL droplets were also applied on the adaxial leaf of *A. theophrasti* (BBCH 14), tomato (BBCH 16), soybean (BBCH 16), and maize (BBCH 14), whose characteristics and wettability differ. An adjustable volume pipette (Eppendorf, Hamburg, Germany) was used for droplet applications. Two leaves were treated per plant, and two plants were treated for each plant species (four leaves in tall for each plant species). After droplet evaporation, plants were placed in the phytotron. Phytotoxicity was visually evaluated 1 day after treatment and was then assessed as described in Table 2.

**Table 2.** Phytotoxicity assessment.

<b>Rate</b>	<b>Description</b>
1	No damage
2	Slight symptoms (discoloration of tissue)
3	Slight necrotic spots
4	Strong symptoms (Complete necrosis)

### ***Cuticular Penetration***

The penetration tests of PA-MPEG and free PA (99%, Matrica, Porto Torres, Italy), with and without additive, were studied with enzymatically isolated cuticular membranes as described in detail in the literature (Cronfeld et al. 2001; Baur et al. 2014). Mature leaves of apple trees (*Malus domestica* B.) cv. Gala, from plantations in Hofheim am Taunus (Germany), were taken in June, and after a quick transfer to the laboratory, 2-cm diameter discs were punched with cork borers. Leaf discs were vacuum-infiltrated in a pectinase-cellulase solution. After incubation in the enzymatic solution for about 2 weeks, cuticles were separated, cleaned with deionized water, and dried on Teflon plates.

Adaxial cuticles (stomata-free) were mounted on stainless steel chambers with original outer surfaces exposed to air, and the inner cuticle surface came into contact with the aqueous-acceptor solution from the chamber's interior (Baur et al. 2014 ). Under controlled conditions (25 °C and 56% R.H.), 10 µL droplets of the spray solution were applied to the external cuticle surface of the cuticles and dried in room ambient with air circulation (approx. 25 min.). The aliquots of the acceptor solution that were drawn after different time points were analyzed by a 1290 Infinity HPLC (Agilent, Santa Clara, CA, USA).

A geometric mean of the penetration values per treatment was obtained from 10 repetitions and three measurements (6, 24, 48 h after application). The kinetics indicated the mean of active ingredient penetration across the cuticle at different times.

### ***Characterization of Spray Deposits on Glass Slides.***

Spray deposits of PA-MPEG and PA with and without inert ingredients were characterized on silanized glass slides on parallel to the cuticular penetration test. The physical appearance of the 10 µL droplet was analyzed with a research light microscope (DM4000M, Leica, Wetzlar, Germany) in the polarized light modus connected to a high-resolution color digital camera (DFC450, Leica, Wetzlar, Germany).

### ***Scanning Electron Microscope (SEM)***

The adaxial leaf samples of *D. sanguinalis* and *S. nigrum* were observed by a scanning electron microscope JSM-5600 LV from JEOL (Tokyo, Japan). Test preparations (0.3  $\mu$ L droplets) were applied to leaves. After allowing for water evaporation under room conditions (25 °C and 56% R.H.), for approx. 30 min., samples were prepared as described in detail by Pathan et al. 2010 (Pathan et al. 2010), frozen at  $-170$  °C and sputtered with gold. Then samples were analyzed at different magnifications. The resulting image of the adaxial leaf surface showed minimal distortion, which allowed the product deposit characteristics on leaves to be examined.

### ***Cuticular Transpiration***

The effect of PA and PA-MPEG on cuticular transpiration was measured with the enzymatically isolated cuticles of mature ivy (*Hedera helix* L.) leaves. The method first determined transpiration in the steady state before treatment, and then after applying and drying the test compounds. In this experiment, 10 repetitions (individual cuticles) were performed, where each cuticle is control (without treatment) and later treated, allowing paired observations. This method is described in detail in the literature (e.g., Geyer and Schönherr (1998)).

### ***Stomatal Conductance***

The impact of PA-MPEG on leaf transpiration was investigated on bell pepper leaves because they have stomata on both leaf sides, with lower adaxial density, which are similar to *S. nigrum*, but they do not have trichomes (*S. nigrum* leaves have them) that can interfere with porometer measurements. Stomatal conductance was measured adaxially and abaxially with an SC-1 Leaf Porometer (Meter, Pullman, US) at room temperature (25 °C and 56% R.H.). PA-MPEG was only adaxially applied as 10  $\mu$ L droplet, which was spread over an area of about 1 cm<sup>2</sup>. Porometry measurement was carried out after droplet evaporation on the treated surface (adaxial) and on the abaxial side for the first four hours after application.

### ***Statistical Analysis***

The results of the efficacy trials were subjected to an analysis of variance (ANOVA) using the ARM software (Gylling Data Management Inc., Brookings, OR, USA). The individual treatment means were compared by the Student-Newman-Keuls least significant difference (LSD) test at the 5% level of significance ( $p < 0.05$ ). Prior to the analysis, data normality and homoscedasticity were verified using the software's functionalities. Data were automatically transformed by the software whenever necessary. Data transformations are indicated in the Tables as footnotes.

## **3. Results and discussion**

### ***PA-MPEG Herbicidal Activity Affected by the Test Compounds Added to the Spray Tank***

We have previously reported that PA-MPEG is not just a pre-drug of PA, in contrast to the esters of auxins (Campos et al. 2021). For example, the *iso*-octyl ester form of 2,4-D (2,4-dichlorophenoxyacetic acid) is rapidly hydrolyzed to free acid, which is the active (Zhang et al. 2019). Other PA ester derivatives have not shown any herbicidal activity (Campos et al. 2021). A comparable extremely rapid action with symptoms of wilt and necrosis on treated organs only a few hours after application, is observed with both PA and PA-MPEG (Campos et al. 2021).

Various adjuvants have been tested with PA in other studies (Coleman and Penner 2008; Webber et al. 2014). The impact of salts *versus* free acid was also tested (Data not shown). As far as we know, no significant economically reasonable PA efficacy enhancement is known by means of formulation or using tank-mix adjuvants. Since PA-MPEG is different from PA, being potentially both, pre-drug and drug, nonelectrolyte, surface-active, and having a molecular weight 2.5-fold higher (Campos et al. 2021), we also explored some potential enhancers of its herbicidal activity. Previous works have shown that PA-MPEG efficacy is best at 10% concentration with a 500 L ha<sup>-1</sup> spray volume on tested weeds (Campos et al. 2021). We evaluated the weed control of the test

compound at the 7.5% concentration with 200 and 400 L ha<sup>-1</sup> volumes on medium-sized plants (approximately 18–20 cm tall). Table 3 and Table S1 report the effect of the test compounds on weed control 2 days after PA-MPEG application. We also determined weed control after 1 week, but values were not significantly different and gave no further information on the performance of the test compounds.

**Table 3.** Impact of the test compounds on weed control (*Digitaria sanguinalis* and *Solanum nigrum*) 2 days after applications with 7.5% pelargonic acid ester of methylated polyethylene glycol (PA-MPEG) at 200 L ha<sup>-1</sup> spray volume.

Test Compound	Concentration (%) <sup>1</sup>	Weed Control (%)	
		<i>D. sanguinalis</i>	<i>S. nigrum</i>
None		29 d*	50 bc*
<i>I</i> -Decanol	1.00	43 a	74 a
Phosphoric acid	0.63	33 cd	59b
D-Glucose	1.00	29 d	47 c
Potassium Carbonate	1.00	30 cd	48 c
Genapol C 050	1.00	31 cd	52 bc
Polyglycol 400	1.50	31 cd	53 bc
Synergen TS 7	0.15	36 bc	58 b
Hasten	2.50	39 ab	68 a

<sup>1</sup> Concentration based on label recommendation and previous trials.

\* Means followed by common letters in a column are not significantly different by the Student–Newman–Keuls test at the 5% level of significance.

Except for *I*-decanol and Hasten, the proved products did not enhance the PA-MPEG activity at the selected and tested concentrations. These concentrations were chosen based on economic and potential maximum activity considerations. The extreme spray pH values of pH 2 with phosphoric acid and pH 10 with potassium carbonate (Table 1) did not affect PA-MPEG activity. Previous stability trials suggested that there is no hydrolysis of PA-MPEG in the spray liquid until two days at pH below 10 (Coleman and Penner 2008). Acid hydrolysis did even not occur on the time scale of weeks to months. Spray droplet evaporation was extremely quick and bulk droplet evaporation took only

minutes (Yu et al. 2009). However, the resulting spray deposit was hydrated because PA-MPEG is a liquid. Alkaline hydrolysis was particularly considered a possible process in the more concentrated spray deposit, resulting in free PA with differentially response. Nevertheless, the obtained results (Table 1) suggested that this was not the case. Thus, potential pH changes in the apoplast by phosphoric acid or potassium carbonate did not affect PA-MPEG stability or efficacy, respectively.

Glucose, as both an osmotic agent and a potential energy source for epiphytic organisms by enhancing the decay of damaged leaves, and PEG 400 as a hygroscopic liquid were neither effective. Since coverage is the key for the herbicidal activity of contact herbicides, another promising candidate was Synergen TS 7, which is a very strong wetting and spreading agent. However, it did not sufficiently improve PA-MPEG efficacy, but obtained better results on *D. sanguinalis*, with a slight increase in weed control than in *S. nigrum*, for which no additional control was observed. No superior spreading probably took place in the presence of the high already PA-MPEG concentration, which is also a wetting agent on its own (Baur et al. 2019; Campos et al. 2021). The lack of any significant influence on PA-MPEG efficacy by strong penetration enhancer, Genapol C 050, was at first surprising (Baur et al. 1997; Bauer et al. 1999). However, in the presence of 7.5% PA-MPEG in the spray, and assuming a cuticle/water partition coefficient of Genapol C 050 close to 1, the explanation of these results was that Genapol C 050 probably did not simply enter through leaf cuticles (Baur 1998, 1999). An 7.5% PA-MPEG application at a spray volume of 300 L ha<sup>-1</sup> by assuming 10% coverage on leaf area, resulted in an AI load of approximately 3 mg cm<sup>-2</sup>. This was 10- to 100-fold more than the cuticle specific mass and was, therefore, more than 10-fold in favor of the spray deposit (Baur et al. 1997). Hence, the amount of Genapol C 050 sorbed in cuticles was only 1% of the cuticle mass, or lower. This was too low to increase AI mobility in cuticles, where 5% is needed to obtain significant effects (Baur 1999; Cronfeld et al. 2001). Hasten and *l*-decanol are much more lipophilic, with a log *P* values of 4.5 for *l*-decanol and one above 8 for Hasten. Therefore, both products have a better potential to be quickly sorbed in cuticles after spray applications.

### ***Phytotoxicity of 1-Decanol and Hasten***

These two test compounds were also examined for their own phytotoxicity after spraying on complete plants and also applying individual 10  $\mu\text{L}$  droplets on the leaves of the selected plants. The droplet volume was large, and thus doses per area were much higher than with real sprays. Coarse spray droplets have mean droplet diameters close to 500  $\mu\text{m}$ , and most droplets are typically below the 0.5  $\mu\text{L}$  volume (Smith et al 2000; ASABE 2021). While *1*-decanol is usually applied as a plant growth regulator for the sucker control of tobacco (*Nicotiana tabacum* L.) plants and also can act as a contact herbicide, Hasten is an adjuvant that boosts the efficacy of many AIs without own activity (Janardhan et al 1990; GRDC 2021; VICCHEM 2021]. This was also reflected by the phytotoxicity results of both these products on the selected weeds and crops, respectively.

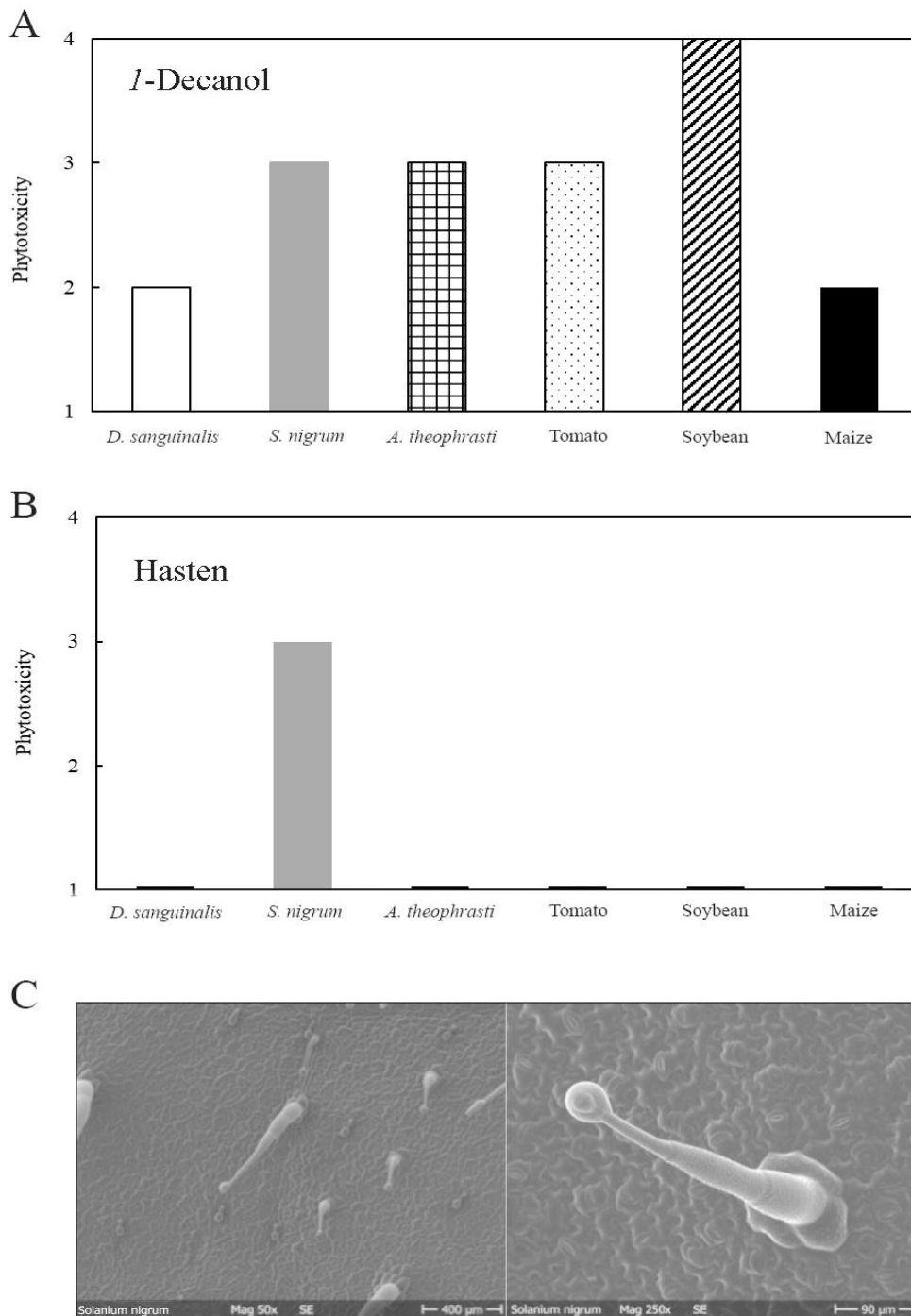
On all tested weeds and crops, *1*-decanol at 1% caused phytotoxicity symptoms when applied as an individual droplet (Figure 1A), while spray application did not lead any damage. The typical *1*-decanol use concentration, e.g., for sucker control in tobacco is above 3% (Janardhan et al 1990). In this experiment, necrotic tissues were already observed at the 1% use concentration due to the 2- to 3-fold higher dose rate per area with 10  $\mu\text{L}$  droplets. *1*-decanol volatility is very high with a vapor pressure of 1387 mPa, while PA-MPEG is non-volatile (Lewis et al. 2016; Campos et al. 2021). The log *P* of PA-MPEG is around 2.5, while, *1*-decanol has 100-fold higher lipophilicity and has therefore, completely different bioavailability characteristics. Alcohols with chain lengths of C<sub>8</sub>-C<sub>12</sub> also increase mobility in the cuticles of other solutes such as PA-MPEG (Baur and Schönherr 1997; Baur 1998). Adding of *1*-decanol to PA-MPEG enhanced its herbicidal efficacy probably by causing additional penetration besides the desiccation effect provoked by *1*-decanol itself.

The situation was completely different with the adjuvant Hasten. This product is very safe according to safety data sheet information and also possesses no herbicidal activity at typical use concentration up to 1% (Dubovik et al 2020; GRDC 2021; VICCHEM 2021; Wernecke 2021). When sprayed on plants, no phytotoxicity symptoms were observed up to the highest tested concentration (5%), which also indicates no own herbicidal activity. No phytotoxicity symptoms were observed on five of the six selected weeds and crops



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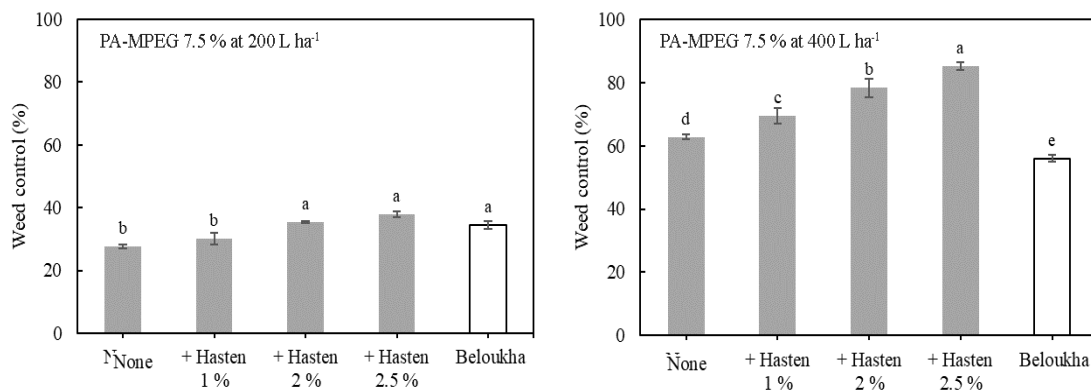
tested after droplet application of 2.5% Hasten (Figure 1B). Only *S. nigrum* showed necrotic spots after applying 10  $\mu$ L droplets, while spraying Hasten at even 5% exhibited no symptoms such as leaf curling, yellowing, or necrosis. The *S. nigrum* results were relevant because it is considered a strong allelopathic plant with herbicidal active secondary metabolites (Henriques et al. 2006). The glandular trichomes (Figure 1C) that exist on both leaf sides contain products such as flavonoids and alkaloids that could be released and enter leaf tissue to cause phytotoxicity even on *S. nigrum* itself (Henriques et al. 2006). Therefore, it is likely that the presence of Hasten caused the release of the allelopathic herbicidal compounds from *S. nigrum* trichomes, and it enabled to enter the mesophyll tissue of the leaf. When trichomes were damaged by a razor blade, no symptoms such as necrosis were developed in the absence of Hasten, but symptoms appeared when 2.5% Hasten was later applied. Apparently, Hasten also acted as a penetration enhancer for substances in glandular trichomes, but it did not cause phytotoxicity on its own (Wernecke 2021).



**Figure 1.** Phytotoxicity of the 10  $\mu$ L droplet application on the adaxial side of mature leaves after 24 h. (A) *I*-Decanol at 1%. (B) Hasten at 2.5%. (C). SEM micrographs showing the glandular trichomes on the adaxial leaf of *Solanum nigrum*.

### ***Concentration Dependence of the Adjuvant Effect on PA-MPEG Herbicidal Activity***

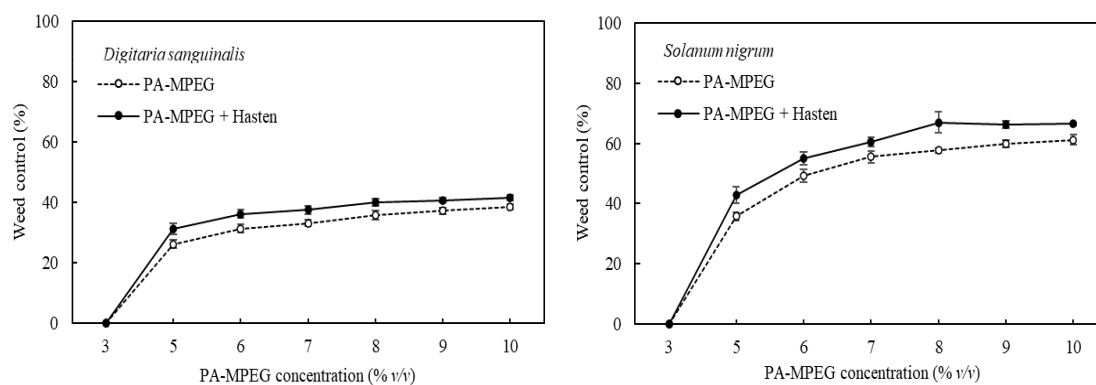
After considering the positive effect of Hasten on the herbicidal activity of PA-MPEG, this adjuvant was used in further experiments. As previously mentioned, PA-MPEG was tested at 7.5% instead of at the previously reported optimum 10% PA-MPEG to better differentiate its herbicidal activity (Campos et al. 2021). The employed benchmark, Beloukha, was a high load PA formulation (680 g/L) applied at the recommended use rate and water volumes (Figure 2 and Table S2). With a 400 L ha<sup>-1</sup> spray volume, Beloukha (10.9 kg a.i ha<sup>-1</sup>) showed an inferior efficacy than PA-MPEG at 7.5% (10.2 kg a.e ha<sup>-1</sup>). However, at 200 L ha<sup>-1</sup> both PA-MPEG 7.5% (5.1 kg a.e ha<sup>-1</sup>) and Beloukha achieved very low level weed control. The addition of Hasten at 1.0–2.5% to the spray tank positively affected the PA-MPEG efficacy in a concentration-dependent way. Weed control increased for both the water volumes tested up to 20%, with slightly stronger effects on weed control percentage at 400 L ha<sup>-1</sup>. With Hasten, PA-MPEG performance was clearly boosted and superior to the commercial PA formulation (Figure 2 and Table S2). Obviously, the effect of water volumes dominated the differences in PA *versus* PA-MPEG, and the adjuvant's impact on PA-MPEG efficacy. On the other hand, PA-MPEG efficacy was increased by the adjuvant even at 400 L ha<sup>-1</sup>, reaching a higher weed control level after 2 days, and being approximately 30% better than the benchmark.



**Figure 2.** Effect of the Hasten rate and spray volume on the weed control of *Digitaria sanguinalis* with pelargonic acid ester of methylated polyethylene glycol (PA-MPEG) at 7.5%. Visual assessment at 2 days after application. Common letters above bars indicate that the means are not significantly different by the Student-Newman-Keuls test at the 5% level. Bars represent standard errors. Beloukha's rate was 10.9 kg a.i. ha<sup>-1</sup>.

The beneficial impact of the larger water volume was not related to coverage *per se*, i.e., the absolute area of the treated weed plant surfaces. This was practically complete at 200 L ha<sup>-1</sup> for *D. sanguinalis* after treatment with both products, PA-MPEG and the benchmark. Both, spray liquid adhesion and capillary wetting of monocots with surfactant solutions below critical surface tension (35 mN m<sup>-1</sup>) ensure full treated leaf area coverage (Baur and Pontzen 2007). Spraying with fluorescent tracers displayed full coverage (Data not shown). At a higher load liquid (400 L ha<sup>-1</sup>) there was more run-off to the leaf angles of the vertical grass leaves. So, the better performance of 7.5% PA-MPEG at the 400 L ha<sup>-1</sup> spray volume could be caused by the higher dose per area of PA-MPEG and its basipetal run-off of spray liquid with uneven distribution (Baur and Pontzen 2007).

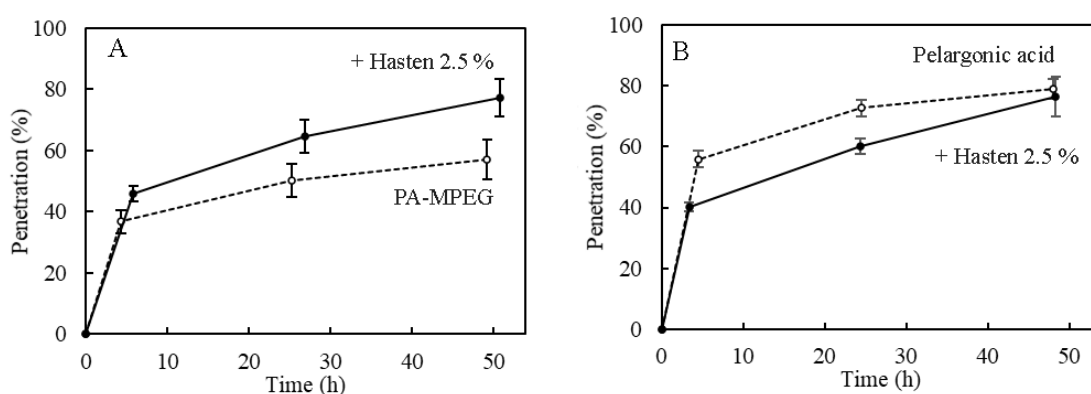
At the 2.5% adjuvant concentration and the 200 L ha<sup>-1</sup> spray volume, we examined the optimum use concentrations of PA-MPEG on *D. sanguinalis* and *S. nigrum* (Figure 3 and Table S3). Previous results have not shown either herbicidal activity or phytotoxicity at 3% PA-MPEG (Data not shown). While the maximum control with 10% PA-MPEG was not exceeded much by adding Hasten at 2.5%, there was a consistent increase at lower use PA-MPEG concentration. The results suggest that 7.5% PA-MPEG plus the adjuvant was comparable to 10% PA-MPEG. The enhancing effect of Hasten was given at all PA-MPEG concentrations for both weeds, but there was no hint for a particular ratio for optimum increases.



**Figure 3.** Effect of 2.5% Hasten on the weed control of *Digitaria sanguinalis* and *Solanum nigrum* at different concentrations of pelargonic acid ester of methylated polyethylene glycol (PA-MPEG), 2 days after application. Spray volume of 200 L ha<sup>-1</sup>. Bars represent standard errors.

### *Pelargonic Acid and PA-MPEG Cuticular Penetration*

Previous studies have demonstrated that Hasten does not significantly enhance PA activity (Coleman and Penner 2008). We have also found that it is neutral and sometimes antagonistic for salts such as ammonium PA and C<sub>8</sub>–C<sub>10</sub> FA at equal amounts of active substance per hectare (Data not shown). In contrast, PA-MPEG performance was significantly improved by Hasten (Figures 2 and 3 and Table S3). As wetting agent related effects and others such as drift or volatility can be excluded, we checked the potential effects on PA-MPEG penetration compared to free PA. Figure 4 illustrates how Hasten acts as penetration enhancer of PA-MPEG but conversely decreased PA penetration, which was faster penetrating than PA, with about 30 % more absorbed a few hours after application. The penetration level, at the very high doses per area, corresponding to the 25 g a.e. L<sup>-1</sup> solute concentration, was also generally high. The difference in penetration correlated well with the observed shifts in herbicidal activity in the presence of the adjuvant. Hasten belongs to the class of alkylated or methylated seed oil (MSO) type adjuvants that are swelling agents for cuticles (Baur et al. 2014). This increases the mobility of the AI and a several-fold faster penetration through more liquid-like cuticles (Baur 1998).

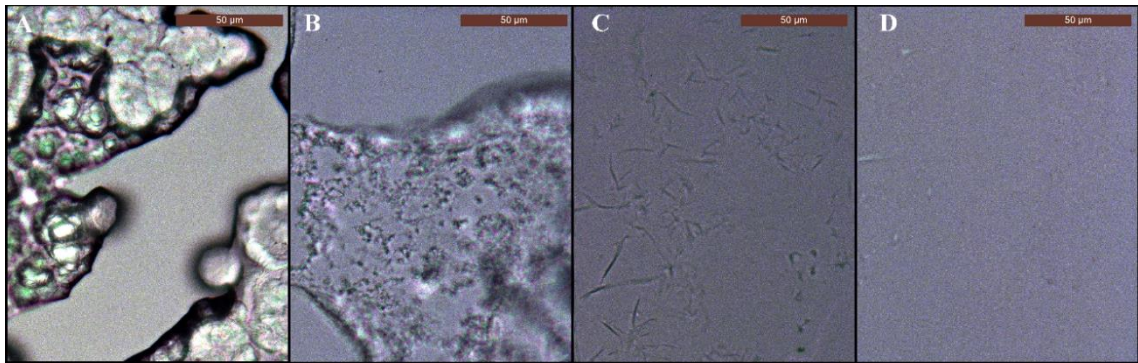


**Figure 4.** The impact of Hasten at 2.5% on the cuticular penetration of (A) pelargonic acid ester of methylated polyethylene glycol (PA-MPEG) at 25 g a.e. L<sup>-1</sup> and (B) straight pelargonic acid (PA) at 25 g a.i. L<sup>-1</sup>. Each curve is the mean of seven to nine repetitions. (Temperature was 25 °C and relative humidity was 56%). Bars represent standard errors.

In the presence of Hasten, PA-MPEG reached the PA penetration level after 2 days, while it was still slightly below PA at shorter times. The penetration of both PA and PA-MPEG was very fast and similar to the quickly penetrating alcohol ethoxylates, such as the previously mentioned Genapol C 050, where a fraction of 60-80% of the applied amount penetrates within one day the cuticle of different species (Baur and Schönherr 1997). Free PA is a very small molecule with  $110 \text{ cm}^3 \text{ mol}^{-1}$  (BPDB 2021). The PA mobility is so high that adjuvants such as Hasten cannot increase mobility (Baur 1998). The negative effect of Hasten on PA penetration was similar to the one observed effect with Genapol C 050 on PA-MPEG, and it is probably related to a change of partitioning coefficient (Baur 1998; Baur et al. 2014). The mixtures of Hasten with large amounts of PA reduced the sorption in cuticles. In contrast to the free PA, PA-MPEG is a bulkier molecule with a molecular weight over  $400 \text{ g mol}^{-1}$  which results in a 3-fold bigger molar volume than PA. Although linear molecules were found to have higher mobilities, this does not apply to PA-MPEG, which has a central ester group and, thus,  $sp^2$  hybridization. It was found that ethoxylates of fatty acids (esters) having the same degree of ethoxylation penetrate much slower than alcohol ethoxylates (ethers). This structure and molecular weight caused a 10-fold lower mobility in cuticles. Clearly, the swelling effect of Hasten increased mobility in such a way that enhanced cuticular permeability resulted in better weed control (Baur 1998).

#### ***Characterization of Spray Deposits on Glass Slides.***

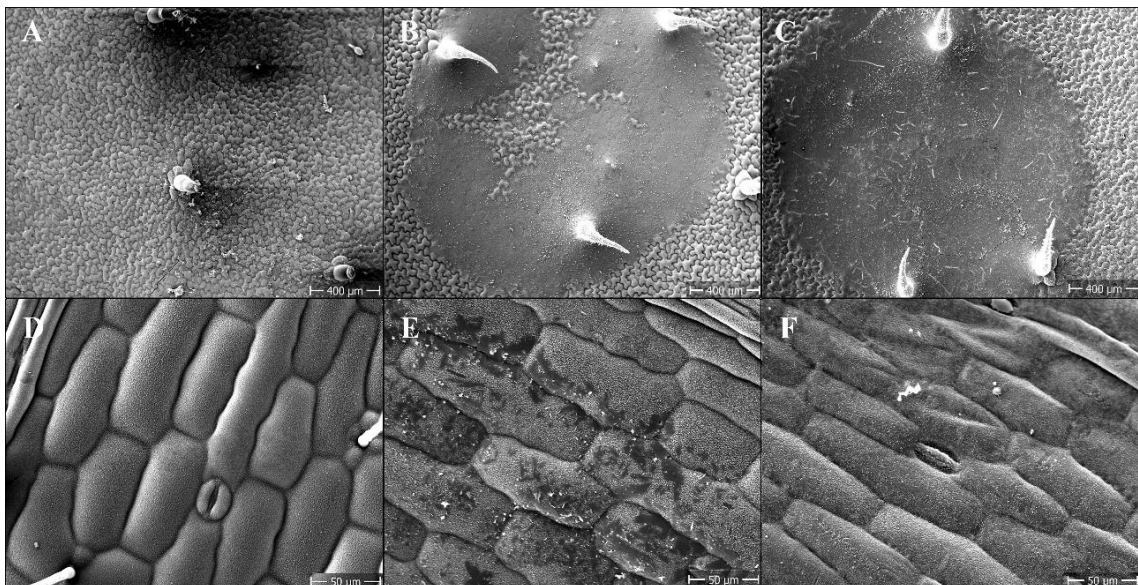
Spray deposits showed a homogeneous and amorphous PA-MPEG and Hasten mixture, which indicates good bioavailability (Figure 5). The light microscopic evaluation of deposits on glass slides suggested that PA always forms some crystalline particles with counterions from water, which were also visible in the presence of Hasten (Figure 5).



**Figure 5.** Optical microscope images of spray deposits on glass slides. (A) Straight pelargonic acid (PA) at 25 g a.i. L<sup>-1</sup>, (B) PA plus Hasten 2.5%, (C) pelargonic acid ester of methyl polyethylene glycol (PA-MPEG) at 25 g a.e. L<sup>-1</sup>, and (D) PA-MPEG plus Hasten 2.5%.

### *Scanning Electron Microscope (SEM)*

Figure 6 shows for single droplet application that Hasten closed the gaps not covered with PA-MPEG in the spray droplet deposits on *S. nigrum* leaves, which could result in the recovery of the leaf tissue below. On *D. sanguinalis*, the deposit area also appeared more homogeneous than with the straight PA-MPEG application.



**Figure 6.** SEM micrographs of the *Solanum nigrum* (upper row) and *Digitaria sanguinalis* (lower row) leaves, 2 h after the 0.3 μL droplet application of pelargonic acid ester of methyl polyethylene glycol (PA-MPEG) at 25 g a.e. L<sup>-1</sup> with (C,F) and without (B,E) Hasten 2.5%. Untreated leaves (A,D).

### ***The Mechanistic Aspects and High Use Rates of PA-MPEG and PA***

The high use rates of both PA-MPEG and PA are still a limiting factor for their use in conventional crop production, even though the products are comparable in costs per hectare to for example, glufosinate, and are more environmentally friendly. PA is quite volatile, and loss of product could be one reason for the necessity of high PA rates. However, also for non-volatile PA-MPEG, high rates are needed for good weed control (Campos et al. 2021). So, this property does not appear to be very relevant. The phytotoxic symptoms with both PA and PA-MPEG typically start with wilting several hours after application and desiccation of the treated plant parts and, if sufficiently extensive, weed death. A second application is sometimes needed to exhaust weeds. The generally suggested MoA for PA and PA-MPEG are changes in the leaf epidermal structure, such as erosion of surface waxes, a related higher leaf transpiration, the disintegration of bio-membranes, and likely as a consequence, decreased photosynthesis (Coleman and Penner 2006, 2008).

Unexpectedly, the application of individual droplets at the very high PA and PA-MPEG concentrations did not lead to striking changes in the epidermal fine structure (Figure 6). Later observable epidermal changes were the consequences of the destruction of the mesophyll structure, and thus, the quick initial increase in transpiration was not causing lethal desiccant effects. This was also suggested by the fact that the still high use PA-MPEG concentration of about  $30 \text{ g L}^{-1}$  increased transpiration, but did not cause any phytotoxicity, even though this concentration resulted (see the calculation above) in a 5-fold higher dose per area than the cuticle mass ( $0.03\text{--}0.3 \text{ mg cm}^{-2}$  for different species). Neither the increased efficacy with the used concentration nor the Hasten effect suggested a key role of transpiration. Although the transpiration effects of PA and PA-MPEG were measurable, they did not give a clear picture. For example, about 2 h after the adaxial application of PA-MPEG to amphistomatic pepper plants (experimentally preferred to *S. nigrum* due to lack of trichomes), adaxial transpiration rose from  $20 \text{ (SD } 4.6) \text{ mmol m}^{-2} \text{ s}^{-1}$  for untreated plants to  $35 \text{ (SD } 6.8) \text{ mmol m}^{-2} \text{ s}^{-1}$ . In contrast, on the abaxial side with a higher stomatal number, transpiration rates decreased on average from about  $66 \text{ mmol m}^{-2} \text{ s}^{-1}$  for the untreated plants to  $44 \text{ mmol m}^{-2} \text{ s}^{-1}$ , and the daily maximum transpiration rates were generally much higher with values of around  $200 \text{ mmol m}^{-2} \text{ s}^{-1}$ .



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Cuticular transpiration was also measured with enzymatically isolated cuticles (Schreiber and Schönherr 2009). The addition of PA-MPEG to very dense common ivy cuticles increased transpiration by more than 10-fold. Cuticular transpiration is only minor contributing to total leaf water loss (a few percent with open stomata) of mature leaves. Not even significantly increased cuticular transpiration alone can explain phytotoxicity. However, for young expanding leaves or growing weeds, cuticular transpiration is the main source of water loss, and at least juvenile plant organs might be completely damaged.

Thus, we conclude that even when cuticular and/or stomatal transpiration increased, the observed wilting and desiccation symptoms were not caused by them. Instead, we suggest a combination of three factors that makes PA and PA-MPEG contact herbicides with desiccant action. First, high amounts of both herbicides are needed because the main targets are thylakoid membranes or chloroplast lipids. Plants can flexibly react to temperature or other stress factors and permanently repair membranes, having distinct membrane lipids and lipid metabolism with galactolipids and sulfolipids that directly come from photosynthetic products (Cool et al. 2021; Hernandez and Cejudo 2021). Disturbing this key plant function and large lipid compartment and the permanently running repair mechanism, requires high amounts, and a 30% load of the lipid. To cause such damage, PA and PA-MPEG need to reach that target. To do so, not only cuticular penetration, but also migration in the apoplast of cell walls and the xylem are required. Some alcohol ethoxylates (non-ionic surfactants) have been reported to increase transpiration at 0.5%, which cause phytotoxicity as necrotic tissues (Baur 1999). However, not even very high use concentrations (of these surfactants) such as that typical for PA or PA-MPEG, bring about a comparable desiccant effect such as that with PA and PA-MPEG. The putative reason is that such alcohol ethoxylates are not mobile in the mesophyll, and do not even allow locosystemic movement in treated leaves. In contrast, PA and PA-MPEG are probably more mobile, given their lower affinity to biomembranes, but high amounts are still needed to disturb the thylakoid assembly. PA is a small anionic solute that is particularly mobile. We still do not know whether PA-MPEG is hydrolyzed after entering the epidermis or the mesophyll to form free PA, but with an octanol/water partition coefficient of a log  $P$  value of 2.5, it is already as nonmetabolized

PA-MPEG a very mobile solute once it has penetrated the cuticle (Briggs and Bromilow 1994). Yet still, high amounts of PA and PA-MPEG continue to be needed to disturb the thylakoid assembly.

Another aspect that we consider to be highly relevant, and even causal for desiccant action, is that as large amounts of PA or PA-MPEG enter the plant tissue, the biomembranes in the chloroplast disintegrate and cause the release of lipids galactolipids and sulfolipids as well as FA from membrane lipids and/or PA to the cell walls and xylem and thus the total apoplast (Fukuda et al. 2004; Cook et al. 2021). The surface tension of PA-MPEG is below  $30 \text{ mN m}^{-1}$ , and both phospholipids and soaps have surface tensions of  $35\text{--}40 \text{ mN m}^{-1}$ . This breaks the cohesion of water such that water supply for transpiration is reduced and causes wilting rather than increased transpiration rates at the cuticle or epidermal level. This could be the real cause of the observed desiccation effect. Further research is already underway to confirm these findings.

This should not be mixed up with recent observations showing that surfactants such as phospholipids in the xylem can contribute to stabilize water flow at negative pressure (Schenk et al. 2017). Schenk et al. (2017) suggest that xylem surfactants have a high affinity to lipophilic areas in vessels, and while surfactants increase the probability and number of air bubbles, they can reduce embolism by their action to limit bubble size and ease re-bubble dissolution in xylem sap. In contrast, we suggest that the large amounts of surfactants resulting from either PA or PA-MPEG applications together with those released from membrane disintegration, potentially destroy this very stable mechanism of water uptake via the cohesion-tension. The site of actions is in the cell wall where the capillaries of cellulose fibers supply water that evaporates at the interface to the intercellular. Negative effects of surfactants on water transport by increased embolism have been shown to occur in the xylem, but not in the context of the MoA for killing weeds by affecting the capillary system in mesophyll cell (Sperry and Tyree 1988). With PA, water can no longer follow the steep gradient to the more negative water potential of unsaturated air. This could be a new target for other novel contact herbicide principles by interfering with the water cohesion-tension in the apparent free space of the cell wall.

## **4. CONCLUSIONS**

Contact herbicides based on free PA have several disadvantages such as high use rates and water volumes, bad smell, and irritant factors, and they also require complex formulation. A novel ester, PA-MPEG, can reach and outperform the best PA benchmark, and is a ready-to-apply liquid with exceptional use properties. In contrast to free PA, the PA-MPEG is a significantly larger molecule that benefits from penetration enhancing adjuvants. An alkylated seed oil product (Hasten) increased cuticular permeability, directly giving better weed control. Even though performance was boosted with this adjuvant, the high application rates remained almost unchanged. Therefore, the product is preferred for precision application to specific sites, such as furrow application or with weed detection application systems, and drone application appears particularly interesting.

### **AUTHOR CONTRIBUTIONS**

Conceptualization, J.C., L.B. and P.B.; methodology, J.C.; formal analysis, J.C., L.B., P.B; investigation, J.C. and P.B.; data curation, J.C., and P.B.; writing—original draft preparation, J.C., M.V. and P.B.; writing—review and editing, J.C., L.B., M.V. and P.B.; supervision, P.B. All authors have read and agreed to the published version of the manuscript.

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### **CONFLICTS OF INTEREST**

The authors declare no conflict of interest.

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## SUPPLEMENTARY MATERIALS

**Table S1:** Weed control percentage (visual control ratings) of *Digitaria sanguinalis* and *Solanum nigrum*, 2 days after application of pelargonic acid ester methyl polyethylene glycol (PA-MPEG) at 7.5 % alone and with tested compounds. Spray Volume 200 L ha<sup>-1</sup>.

Pest Code				<i>Digitaria sanguinalis</i>	<i>Solanum nigrum</i>
Days After Application (DAA)				2	2
Herbicide	Rate (%)	Test compound	Concentration (%)		
Untreated Check				0.00	0.00
PA-MPEG	7.50	None		28.50 ± 0.87 d	50.25 ± 3.45 bc
PA-MPEG	7.50	1-Decanol	1.00	42.50 ± 1.44 a	73.50 ± 3.01 a
PA-MPEG	7.50	Phosphoric acid	0.63	32.50 ± 0.87 cd	59.00 ± 3.46 b
PA-MPEG	7.50	D-Glucose	1.00	28.50 ± 0.87 d	46.75 ± 1.18 c
PA-MPEG	7.50	Potassium carbonate	1.00	30.25 ± 2.36 cd	47.75 ± 0.75 c
PA-MPEG	7.50	Genapol C 050	1.00	30.50 ± 1.66 cd	51.50 ± 2.22 bc
PA-MPEG	7.50	Polyglycol 400	1.50	30.50 ± 1.66 cd	52.50 ± 2.63 bc
PA-MPEG	7.50	Synergen TS 7	0.15	35.75 ± 0.48 bc	58.25 ± 1.97 b
PA-MPEG	7.50	Hasten	2.50	38.50 ± 0.87 ab	68.00 ± 3.11 a

Means followed by a common letter in a column are not significantly different by the Student–Newman–Keuls test at the 5 % level of significance.

Untreated check is not included in the analysis.

**Table S2:** Weed control percentage (visual control ratings) of *Digitaria sanguinalis*, 2 days after application of pelargonic acid ester methyl polyethylene glycol (PA-MPEG) at 7.5 % with the addition into the spray tank of Hasten at different concentrations.

				200 L ha <sup>-1</sup>	400 L ha <sup>-1</sup>
Spray volume					
Days After Application (DAA)				2	2
Herbicide	Rate	Adjuvant	Concentration (%)		
Untreated Check				0.00	0.00
PA-MPEG	7.50 %	None		27.60 ± 0.60 b	62.80 ± 0.80 d
PA-MPEG	7.50 %	Hasten	1.00	30.00 ± 1.84 b	69.40 ± 2.40 c
PA-MPEG	7.50 %	Hasten	2.00	35.40 ± 0.40 a	78.40 ± 2.93 b
PA-MPEG	7.50 %	Hasten	2.50	37.80 ± 0.97 a	85.20 ± 1.28 a
Beloukha	10.9 Kg a.i. ha <sup>-1</sup>			34.40 ± 1.17 a	56.00 ± 1.00 e

Means followed by a common letter in a column are not significantly different by the Student–Newman–Keuls test at the 5 % level of significance.

Untreated check is not included in the analysis.

**Table S3:** Weed control percentage (visual control ratings) of *Digitaria sanguinalis* and *Solanum nigrum*, 2 days after application of pelargonic acid ester methyl polyethylene glycol (PA-MPEG) at 7.5 % alone and with tested compounds. Spray Volume 400 L ha<sup>-1</sup>.

Pest Code				<i>Digitaria sanguinalis</i>	<i>Solanum nigrum</i>
Days After Application (DAA)				2	2
Herbicide	Rate (%)	Adjuvant	Concentration (%)		
Untreated Check				0.00	0.00
PA-MPEG	5.00	None		26.25 ± 1.25 e	35.75 ± 1.49 e
PA-MPEG	5.00	Hasten	2.50	31.25 ± 1.75 d	43.00 ± 2.71 d
PA-MPEG	6.00	None		31.25 ± 1.25 d	49.25 ± 2.17 c
PA-MPEG	6.00	Hasten	2.50	36.25 ± 1.25 a-d	55.00 ± 2.04 bc
PA-MPEG	7.00	None		33.25 ± 1.18 cd	55.50 ± 2.10 bc
PA-MPEG	7.00	Hasten	2.50	37.50 ± 1.44 abc	60.50 ± 1.66 ab
PA-MPEG	8.00	None		35.75 ± 1.49 bcd	57.75 ± 0.75 b
PA-MPEG	8.00	Hasten	2.50	40.00 ± 1.22 ab	67.00 ± 3.39 a
PA-MPEG	9.00	None		37.25 ± 1.03 abc	60.00 ± 1.22 ab
PA-MPEG	9.00	Hasten	2.50	40.75 ± 0.75 ab	66.25 ± 1.25 a
PA-MPEG	10.0	None		38.50 ± 0.87 abc	61.25 ± 1.75 ab
PA-MPEG	10.0	Hasten	2.50	41.50 ± 0.87 a	66.50 ± 0.50 a

Means followed by a common letter in a column are not significantly different by the Student–Newman–Keuls test at the 5 % level of significance.

Untreated check is not included in the analysis.



Chapter VI

# **CONCLUSION**





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## CONCLUSION

This thesis has presented new derivatives of short-chain (C<sub>6</sub>-C<sub>12</sub>) fatty acids as promising herbicidal compounds, lacking some drawbacks of fatty acids like high volatility and consequently its strong bad odour and the complexity of formulation. Pelargonic acid ester of a methyl polyethylene glycol (PA-MPEG) has been suggested as the novel nontoxic contact herbicide for further studies.

PA-MPEG is both the active ingredient and the final herbicide, thanks to its physicochemical properties. Therefore, formulation efforts are not needed, and it can be diluted in water for its application, unlike other fatty acid herbicides. Moreover, PA-MPEG has no bad odour, and its application is comfortable for the final users, unlike PA, which releases a rancid aroma over days. This new compound was synthesised by the reaction of PA and PEG, which are non-toxic raw materials used in food, personal care and pharmaceutical industry. Accordingly, PA-MPEG could be recognised as a safe substance and a non-toxic, sustainable alternative for weed control.

Since PA is used as a starting material to obtain PA-MPEG, both herbicides, PA and PA-MPEG, share many characteristics, like their outcome on the target weeds and also the mode of action. PA-MPEG and PA could break the water cohesion in the cell walls, causing the desiccation of the tissue and, finally, the death of the leaf. The herbicidal activity of PA-MPEG is limited to the contact area, not being translocated to roots or other untreated parts of the plant. Therefore, PA-MPEG is also labelled as a non-selective contact herbicide like PA. Consequently, good spray coverage is essential to ensure that PA-MPEG reaches its maximum potential for weed control. PA-MPEG rate has been determined at a lower value than applications with PA benchmarks.

This study has also provided that besides applying the product on small-size weeds, which significantly impacts contact herbicide effectiveness, PA-MPEG efficacy can also be enhanced throughout taking into account different application factors. For example, a lower boom height gives better coverage of lower leaves and the base of the plant by the

sprays, or favourable climate conditions during and after application increase the cuticular penetration of the herbicide, and the loss of the water from the plant not allowing the repair of weak injuries. Thus, applications made following these recommendations can lead to a decrease in product rates while maintaining effectiveness. Adjuvants, particularly Hasten<sup>TM</sup>, added into the PA-MPEG spray tank have shown a positive impact on efficacy. Hasten<sup>TM</sup> increased the cuticular permeability by its swelling effect, allowing higher mobility of PA-MPEG, which also resulted in better weed control.

PA-MPEG clearly conquers the intrinsic problems of PA products. It showed better physicochemical properties than free PA and achieved higher weed control than PA benchmarks at lower or equal application rates, being a superior non-toxic contact herbicide to PA herbicides. PA-MPEG application rates, which are lower than PA use rates, are still high, and thus, it could not be easy to introduce this herbicide in conventional agriculture. Therefore, additional investigations should be carried out to work out this problem and to test the efficacy of the product on more weed species and field conditions. PA-MPEG could be an excellent alternative to traditional contact herbicides with toxic profile, being interesting to use in precision applications to specific sites, such as early post-emergence of weeds before crop sowing or with weed detection application systems.