Review

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Herbicides based on pelargonic acid: Herbicides of the bioeconomy

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Abstract: Following the first generation of natural herbicide products based on pelargonic acid as an active ingredient, a number of new herbicides and blossom thinners based on C9:0 saturated fatty acid entered the marketplace in many countries, offering a long-awaited safer alternative to synthetic chemical herbicides. This study addresses key production and bioeconomy aspects prior to the expected widespread adoption of *n*-nonanoic acid as an alternative ingredient of new biobased herbicides, derived from the fatty acid first isolated from the leaves of *Pelargoniun roseum*. © 2019 Society of Chemical Industry and John Wiley & Sons, Ltd.

Keywords: pelargonic acid; herbicide; green chemistry; bioeconomy

Introduction

'H. Pless undertook some time ago the examination of the volatile ingredients of the plant *Pelargoniun roseum*, (so called from the known scent of the rose)'[1] wrote Redtenbecher in 1845 in an impressive article addressed to the *Memoirs and Proceedings of the Chemical Society*, in which he also reported *n*-nonaoic acid synthesis by treating oleic acid with nitric acid. 'He distilled the plant with water; the product had the scent of the plant, and an oil swain at the top. It was neutralized by baryta water, and the neutral, strongly-scented oil was distilled over. It was boiled in alcohol, and the first product precipitated by nitrate of silver… This is the reason, for want of a better, that I gave it the name pelargonic acid.'[1]

Pelargonic acid ($CH_3(CH_2)_7CO_2H$, *n*-nonanoic acid) is a saturated, nine-carbon fatty acid (C9:0) naturally occurring in numerous vegetables and fruits, including oranges, grape, apples, potatoes, but also in milk, cheese, and beef. At room temperature, it is a transparent oily liquid with a slight yellow color, a fatty odor, and a coconut taste.[2] It is practically insoluble in water (0.284 $g\,L^{-1}$ at 30 °C).[3]

Pointing to a strongly structured liquid in pure form, at 760 Torr pressure, the acid boils at 254 °C.[4] Indeed, recent computational simulations of the radial distribution functions of the carbonyl oxygen atom in the molecule in the liquid ascribe the difference in the boiling point of pelargonic acid compared with structural analogue 2-decanone (210 °C) to pronounced intermolecular interactions and molecular aggregation (strong hydrogen-bonded cyclic dimers and higher order aggregates).[5]

Approved in multiple countries as a safe food-flavoring agent, as an ingredient in solutions used commercially to peel fruits and vegetables, and as a sanitizing or

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antimicrobial compound for use on foods (up to a 1% solution), the substance is recognized in the USA by the Food and Drug Administration as a GRAS (Generally Regarded As Safe) chemical.[6] It is also approved for use in personal-care products and in transdermal drug delivery systems.

In 1994, the use of pelargonic acid as a blossom-thinning agent to prevent alternate-year cropping of apples was reported.[7] Two years before, the US Environmental Protection Agency had licensed for sale the first pesticide products containing ammonium nonanoate as 'biochemical herbicide' concluding that no risks to human health were to be expected from the use of ammonium salts of higher fatty acids (C8–C18 saturated and C18 unsaturated) based on their low toxicity and the fact that residues from pesticide uses are not likely to exceed the levels of naturally occurring or intentionally added fatty acids in commonly eaten foods.[8]

Following the first generation of natural herbicide products based on pelargonic acid as active ingredient, a number of new formulations based on C9: 0 have been developed and approved as herbicides or blossom thinners to protect plants and crops in agriculture against a wide spectrum of annual weed species. For example, as of February 2019, another biodegradable herbicide based on *n*-nonanoic acid, this time following a request from a company headquartered in Europe, was approved in the USA.[9]

These biobased herbicides are increasingly used to eliminate weeds also from gardens, lawns, golf courses, parks, walkways, roads, and industrial sites. This study addresses key production and bioeconomy aspects prior to widespread adoption of *n*-nonanoic acid as active ingredient of new generation herbicides and blossom thinners.

Plant uses and mode of action

As mentioned above, pelargonic acid and its salts are used as active ingredients in emulsifiable concentrate formulations, sprayed to protect crops in open fields and in greenhouses against weeds and to thin blossoms so as to increase the quality and yield of apples and other fruit trees, allowing the trees to produce fruit every year instead of every other year.

The same formulations are increasingly used across the world to control both annual and perennial broadleaf and grass weeds, plus most mosses and other cryptogams at sites such as walkways, roads, railways, parks, urban, and domestic areas, schools, golf courses, gardens, and indoor sites.

The acid is a foliar-applied herbicide, which acts exclusively by contact, attacking and destroying the cell membranes of the plant epidermis and causing rapid tissue dehydration.

Above 15 °C, on a luminous day, drying action is extremely rapid. The treated plants begin to exhibit damage within 15–60 min of the application and begin to collapse within 1–3 h, with the herbicide being effective even in case of rainfall 2 h after application. The herbicide action is quick, non-selective, and broad spectrum, leading to necrotic lesions on plant aerial parts.

In 2004 a team of scholars from Germany and Japan first demonstrated that middle-chain length fatty acids, including pelargonic acid, attack cell membranes in a short time, causing cell leakage, collapse, and desiccation of the tissue.[10] The same team demonstrated the twofold herbicidal mode of action.[11]

The acid first intercalates into the cellular membranes leading to leakage, followed by breakdown of membrane acyl lipids (peroxidative activity) due to singlet oxygen formed by the action of sunlight on chlorophyll displaced from the thylakoids (the membrane-bound compartment inside the chloroplasts). The peroxidation causing necrosis and the rapid weed drying effect is driven by potent oxidative radical species.

For example, at pH 6.5 the highest formation for ethane and propane resulting from acyl lipid peroxidation in green cress seedlings occurs at about 1.2–1.8% pelargonic acid (Fig. 1). At the maximum concentration, the ethane amount is about 27-fold higher than propane formation.[11] Ethane is formed by peroxidation of the $\omega-3$ fatty acid residues in acyl lipids, whereas propane originates from the peroxidation of $\omega-4$ acids.[12]

A recent simulation of the interaction between nonanoic acid and plant plasma membrane phospholipids (the latter being one of the major components of plant plasma membranes) suggests that a mismatch in alkyl chain length between nonanoic

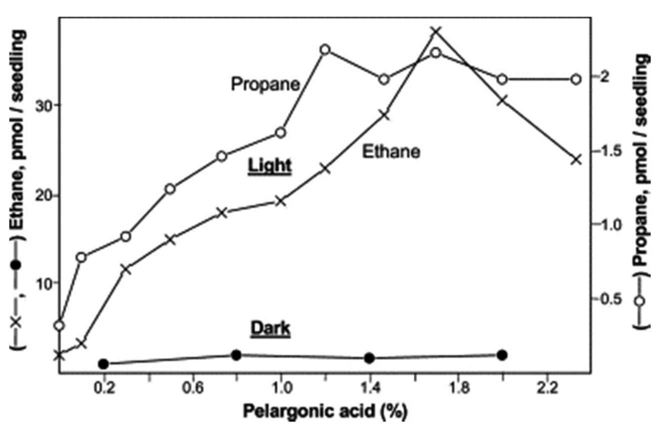

Figure 1. Formation of ethane and propane from green cress seedlings dependent on concentration of pelargonic acid (pH 6.5). Filled circles: Ethane + propane evolution. (Reproduced from ref. 11, with kind permission.)

acid and lipid hydrophobic tails is responsible for bilayer destabilization.[13]

In detail, the ability of the C9–C11 middle chain length fatty acids to penetrate and destabilize the plant plasma membranes would be due to a compromise between intermediate levels of affinity and mismatch, with C9–C11 acids presenting optimal combinations of these two factors and thus exhibiting the highest ability for lipid bilayer perturbation and eventually the highest phytotoxicity (whereas long-chain fatty acids have a high affinity for lipid bilayers but a low chain-length mismatch with them, and short chain fatty acids having a high degree of mismatch with lipid bilayers but a low affinity).

In brief, pelargonic acid penetrates the waxy layer (cuticle) of the leaves and destroys the cell membranes of the plant's epidermal cells causing rapid and non-selective 'burn-down' of green tissues. The mode of action, namely the stripping of the cuticular waxes covering photosynthetic organs resulting in rapid dessication of the foliage, is similar to other contact herbicides such as herbicidal soaps. The photosynthetic electron transport rate (ETR), for example in cucumber cotyledon discs exposed to pelargonic acid, is rapidly suppressed, in comparison with other herbicides targeting lipid biosynthesis and waxes (Fig. 2).[14]

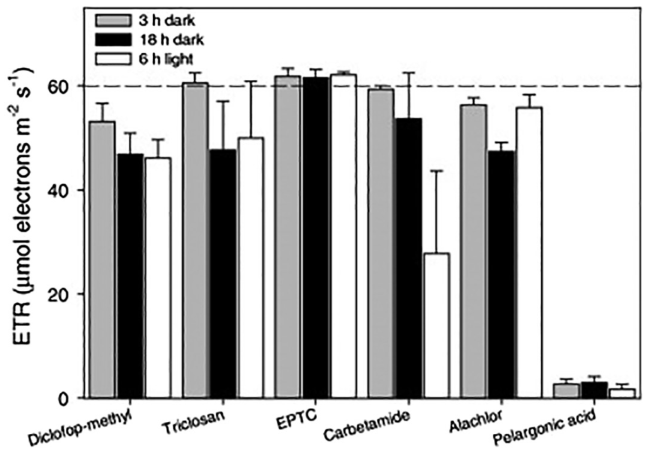

Figure 2. Photosynthetic electron transport rate (ETR) in cucumber cotyledon discs exposed to herbicides targeting lipid biosynthesis and waxes. Data represent means of three replications with standard deviation. The dotted line represents ETR of untreated solvent control. (Reproduced from ref. 14, with kind permission.)

Given the mode of action, it is not surprising that, in shaded areas, and with cloudy weather, the action on the plant leaves is delayed. The acid does not translocate through woody tissues, does not attack the roots, and has no soil activity, thereby preserving the soil's fertility, biodiversity, and resistance to erosion.

Due to the excellent cuticular penetrating properties, insects that are in weeds at the time of spraying will be killed, which explains the 'non-target arthropods' warning placed on most pelargonic acid-based commercial herbicides (a positive side effect with aphids, whitefly, and thrips spending time in weeds before migrating to the crop).

Toxicity tests on non-target organisms, such as birds, fish, and honeybees, revealed little or no toxicity.[15] The chemical decomposes rapidly in both land and water environments, so it does not accumulate. To minimize drift and potential harm to non-target plants, users are required to take precautions such as avoiding windy days and using large spray droplets.

The acid is a skin[16] and eye irritant, and product labels describe precautions that users should follow to prevent the products from getting in their eyes or on their skin.

'Assuming the farmer would obtain a lower price for the herbicide with a volume discount and an increase in yields due to experience, quality soils, and protected or shielded herbicide application' concluded an experimental research conducted in 2016 in a southern USA state to determine the impact of pelargonic acid on weed control efficacy, crop injury, green pepper (*Capsicum annuum*) yields, 'the data indicate a positive return from use of pelargonic acid as a natural herbicide'.[17]

In closer detail, the experiment indicated that the 15 lb/y (9% v:v) pelargonic acid treatment resulted in the maximum smooth crabgrass control (56% of weed injured) and broadleaf weed control (66%) at 1 day after the initial spray treatment with pelargonic acid, producing significantly greater fruit per acre (58 012 fruit / year) than the non-treated weedy control (14 516 fruit / year), which translates into 2.8 times the gross revenue.

On the other hand, noting that the 166 L ha^{-1} recommended dose for 'the best known natural herbicide in Switzerland normally used in home gardens in ornamentals, lawns and turfs' comprised 188 g pelargonic acid per L 'amounts to €2185/ha', scholars in Switzerland concluded that 'to become a true alternative to … synthetic, contact herbicides, the price of these natural products needs to be similar to the price of the conventional herbicides.'[18] The cost of a competing non-selective foliar active herbicide at the recommended dose of 4.5 L ha^{-1}, the same scholars noted, amounts to €120/ha.

More recent emulsifiable concentrates contain 680 g/L nonanoic acid (71.96%), and have a similar price (€19.65/L)[19] but require a drastically lower dosage (16 L ha^{-1}) leading to a €314.4/ha unit treatment cost.[20]

Considering, however, that regrowth of the weed is a problem with contact herbicides like pelargonic acid, to further reduce the overall cost of using natural herbicides

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based on nonanoic acid and to make them competitive with conventional herbicides, a significant reduction in its production cost must be achieved.

This, in turn, requires a switch from oil to vegetable raw materials *and* from conventional stoichiometric to new, catalytic green chemistry processes affording a fine chemical such as pelargonic acid at significantly lower cost.[21]

Production and economic aspects

Being manufactured by liquid-phase continuous oxidation of *n*-nonanal, an aldehyde obtained by the highly selective and costly hydroformylation of 1-octene, for decades, pelargonic acid has been a value-added derivative of ethylene. The olefin 1-octene is indeed an ethylene oligomerization petrochemical product. Adding cost to the acid, the byproduct of the hydroformylation reaction (2-methyloctanoic acid) needs to be separated from the pelargonic acid by rectification.[22]

Developed and employed on an industrial scale by an oleochemicals company (Emery Oleochemicals), pelargonic acid is also commercially produced from oleic acid by ozonolysis of the double-bond in a two-step oxidation process, an old reaction of great importance in the development of olefin chemistry,[23] with azelaic acid as a coproduct. 'Several 10^4 t/y of the acid' reads a 2014 encyclopedia article, 'are produced by Oxea and Emery.'[22]

In 2005, however, industrial researchers based in Italy described an improved process for the production of saturated fatty acids based on the oxidative scission of oleic acid into pelargonic and azelaic acid with an aqueous solution of hydrogen peroxide mediated by a small amount of a tungsten catalyst involving the use of a surfactant to disperse the two phases.[24]

A process that was further improved, using a phase-transfer catalyst to transfer the oxidant from the aqueous to the lipophilic phase,[25] was scaled up in collaboration with a company based in France, which developed a number of herbicides formulated with pelargonic acid obtained from oleic acid from sunflower oil.

In a typical process, oleic acid is oxidized in a batch reactor with a biphasic organic-aqueous system consisting of 30% H_2O_2 as an oxidant and peroxo–tungsten complex $[C_5H_5N(n\text{-}C_{16}H_{33})]_3\{PO_4[WO(O_2)_2]_4\}$ as phase-transfer catalyst with 1/5/0.02 substrate/H_2O_2/catalyst molar ratio kept under stirring at 85 °C for 5 h. Oleic acid is entirely converted into azelaic and pelargonic acid, with yields exceeding 80%, whereas the catalyst is recovered and reused.[26]

The new process should be compared to the double bond oxidation of unsaturated oleic acid with ozone, which requires special high-technology equipment for the dielectric barrier discharge production of ozone. This implies a large capital investment (estimated by Garti and co-workers back in 1998 at $17 000/kg ozone/h installed capacity)[27] and significant annual operating costs (electricity consumption), whereas highly toxic and explosive ozone in the feed must be diluted at not higher than 1.5–2 wt% concentration, 'which implies an increase in the volume of gases to be processed with a negative influence on the kinetics of the oxidation reaction.'[27]

The global production and availability of hydrogen peroxide, the cleanest oxidant along with oxygen, has gone from 0.5 million tonnes in the 1970s to 4.5 million tonnes in 2014, and is still growing.[28]

Similarly, oleic acid, once mostly obtained from beef tallow, is currently mostly obtained from vegetable oils (sunflower, palm, and rape oils). Driven by the global demand for natural surfactants, emulsifying agents, personal care, and cosmetic products, its annual output dramatically grew in the last two decades, with the main producers now being based in the Asia Pacific region due to the presence of large sources of natural raw materials such as vegetable oils.[29]

Due to an ever more abundant supply, the price of oleic acid (free on board, in Asia) has gone from $1000–1050/t in December 2017[30] to $830–860/t in August 2018.[31] Again, for comparison, the price of oleic acid derived from animal tallow in mid 2012 exceeded $1800/t.[32]

In brief, the price of the raw material (oleic acid) has more than halved in less than 5 years, and will continue to remain low because, as explained elsewhere, detailing the glycerol bioeconomy,[33] Asia-based oleochemicals companies will increase their supply and will continue to displace petrochemical products with their oleochemicals, regardless of lower prices.

The new green process in the solvent-free and biphasic medium uses a cheap and readily prepared tungsten catalyst, and a clean abundant oxidant such as 30% aqueous H_2O_2 affording pelargonic and azelaic acids with an excellent 90.1% atom economy and E_{factor} ($m_{\text{waste}}/m_{\text{product}}$) of 13, lower than the usual processes.[34] Economic data concerning the industrial process have not yet been published. A conservative estimatem, without taking into account that the process can be shifted from batch to continuous, and the catalyst effectively heterogenized, suggests that the cost of the new green chemistry process could be significantly lower of the ozone-based oxidative scission of C18:1.

The global pelargonic acid market is currently a niche of the fine chemicals market, with revenues amounting to slightly more than $85 million in 2018. Market analysts estimate a compound annual growth rate of around 5.3% between 2018 and 2025.[35]

On the other hand, the global herbicides market had $25.88 billion revenues in 2017 and is expected to reach $37.99 billion by 2025,[36] with 'regulations leading to increase in the demand for bio-based herbicides' and the 'chemical industry gradually shifting from synthetic chemicals to bio-based chemicals by referring its eco-friendly nature'.[36]

With its broad-spectrum activity, uniquely rapid action and quick biodegradability, leaving no residues on water and soil herbicidal formulations based on bio-based pelargonic acid, this fatty acid holds the potential to largely exceed the $123 million market forecast recently by 2025.[35]

Can and will this potential be fulfilled?

Outlook and perspectives

Attracted by the possibility of entering the huge herbicide market as well as facing ever lower prices for their oleic acid, oleochemicals company controlling today's and tomorrow's global supply of oleic acid will most likely enter manufacturing of pelargonic (and azelaic) acid based on the green H_2O_2 chemocatalytic route.[26]

This should inevitably lead to a reduction in the price mentioned above and a concomitant increase in global supply and availability that will make herbicidal formulations based on *n*-nonanoic acid competitive with conventional herbicides.

Driven by newly discovered applications such as, for example, the control of duckweed (a tiny aquatic flowering plant that floats in large quantities on still water) in aquaculture using a pelargonic acid formulation as an aquatic herbicide at only $243/ha cost,[37] demand will expand to numerous sectors and customers well beyond the Vatican Gardens where weeds have been treated with pelargonic acid since 2016.[38]

Meanwhile, new large-scale applications such as the recently discovered highly effective mosquito repellent (a novel repellent having a longer lifespan than commercially available repellents with the added benefit of not only repelling mosquitoes but killing them too if they make contact with it),[5] based on a mixture of nonanoic acid and butylacetylaminopropionate, will be commercialized, further increasing the global demand for pelargonic acid.

Based on the outcomes of contemporary research,[39] green chemistry is the technology enabler of the bioeconomy because, coupled to the shift from oil to biological raw materials, preferably of vegetable origin, it allows production costs to be cut.

The economic and social dimensions of sustainable development are often overlooked in favor of the environmental dimension of sustainability.[40] Reporting the new green chemistry route for the oxidative cleavage of unsaturated fatty acids, Mouloungui and co-workers rightly emphasized how it could enable the introduction of 'short production chains' to obtain valued bioproducts starting from local sunflower crops growing in Mediterranean areas 'to strengthen economic activity in the areas concerned'.[34]

Focusing on selected production and bioeconomy aspects of *n*-nonanoic acid, this study will hopefully contribute towards the global emergence of new-generation bioherbicides based on the *Pelargonium roseum* acid, first isolated by Redtenbecher in 1845.

Acknowledgements

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