

Biobased herbicides based on pelargonic acid

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Reflecting their large-scale utilization across the world, the global market for herbicides exceeded \$25 billion revenues in 2017 only (1). The use of herbicide formulations is heavily regulated in most world's countries. Yet, the environmental and health problems associated to their use are significant and widespread (2).

Perhaps not surprisingly, the societal megatrends currently reshaping the chemical industry (3) can be observed also in this highly profitable segment of the industry. Several environmentally friendly herbicides, indeed, were lately introduced to meet the increasing demand of entirely safe herbicides exerting their function, without harming health or the environment.

Amid them herbicidal and blossom thinner formulations based on pelargonic acid as active ingredient hold large growth potential. Owing its name to *Pelargonium roseum* from whose essential oil it was first isolated in 1845, pelargonic acid ($\text{CH}_3(\text{CH}_2)_7\text{CO}_2\text{H}$, *n*-nonanoic acid) is a saturated, nine-carbon fatty acid naturally occurring in numerous vegetables and fruits. At room temperature, the acid is a transparent oily liquid poorly soluble in water (0.284 g/L at 30°C) with a slight yellow color, a strong fatty odor and coconut taste.

Sales of the first agrochemical products containing ammonium nonanoate as "biochemical herbicide" were first authorized in the United States in 1992 based on the low toxicity of ammonium nonanoate whose residues "are not likely to exceed the levels of naturally-occurring or intentionally-added fatty acids in commonly-eaten foods" (4).

New herbicides based on nonanoic acid lately approved in many countries protect plants and crops against a wide spectrum of annual weed species. The acid indeed has a broad spectrum activity, has uniquely rapid action and quickly biodegrades leaving no residues on water and soil (5).

The main limit to large-scale uptake of today's emulsifiable concentrates containing higher amounts of the active ingredient (> 70%), thus enabling lower dosage and lower unit treatment costs, is the higher cost of pelargonic acid based-formulations. A problem worsened by the fact that non

selective foliar herbicides based on the fatty acid do not kill basal meristems so that larger weeds and grasses may re-grow, requiring new herbicide application.

To make natural herbicides based on nonanoic acid competitive with conventional herbicides, its production cost must be lowered. Once again, this requires manufacturers of fine and specialty chemicals to shift from stoichiometric to catalytic process affording the product at higher yield, with no (or much lower) waste by-products, and under milder reaction conditions (6).

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The new catalytic route to pelargonic acid

Developed on industrial scale by an oleochemical company and employed also by other chemical firms, pelargonic acid has been mostly produced from oleic acid on a several 10^4 t/a production rate by ozonolysis of the double-bond in a 2-step oxidation process, affording azelaic acid as a co-product (7).

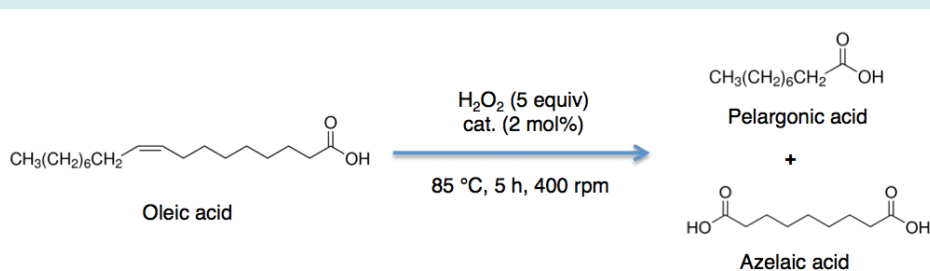
A largely improved process for the production of saturated fatty acids based on the oxidative scission of oleic acid into pelargonic and azelaic acid with an aqueous solution of hydrogen peroxide mediated by a small amount of a tungsten catalyst was described in 2005 (8).

Scaled up in collaboration with a company based in France, the process is carried out with the aid of a surfactant to improve the dispersion of the two phases as well as of the catalyst. In

France, the substrate oleic acid is obtained from sunflower oil, but several other vegetable oils can be used.

In a typical process (Scheme 1), oleic acid is oxidized in a batch reactor with a biphasic organic-aqueous system consisting of 30 wt% H_2O_2 and peroxy-tungsten complex ($C_5H_5N(n-C_{16}H_{33})_3\{PO_4(WO(O_2)_2)_4\}$) as phase-transfer catalyst with

1/5/0.02 substrate/ H_2O_2 /catalyst molar ratio. After stirring at 85 °C for 5 h, oleic acid is entirely converted into azelaic and pelargonic acids with yields exceeding 80%, whereas the catalyst is recovered and reused (9).



Scheme 1. Route to pelargonic and azelaic acid from oleic acid with aqueous H_2O_2 mediated by peroxy-tungsten complex in a two-phase reaction mixture. (Adapted from Ref.9, with kind permission.)

The old process used for the double bond oxidation of unsaturated oleic acid with ozone, for comparison, requires costly special equipment for the dielectric barrier discharge production of ozone (\$17,000/kg ozone/h installed capacity in 1998), (10) and significantly high operating costs (electricity consumption) whereas toxic and explosive ozone in the feed must be diluted at 1.5-2 wt% concentration, with a negative influence on the overall kinetics of the oxidation reaction (10).