



Cite this: *RSC Sustainability*, 2026, 4, 255Received 9th September 2025  
Accepted 30th October 2025

DOI: 10.1039/d5su00739a

rsc.li/rscsus

# First sustainable synthesis of biobased ethyl and methyl formates by ecocatalysis

Arthur Lasbleiz, Pierre-Alexandre Deyris, Franck Pelissier, Yves-Marie Legrand,   
Claude Grison \* and Claire M. Grison

We described the first synthesis of biobased ethyl and methyl formates. The synthetic strategy is based on the transesterification of natural geranyl and citronellyl formates derived from *Pelargonium* species essential oils with ethanol or methanol, promoted by an ecocatalyst<sup>®</sup>. Good yields (up to 80%) were obtained with an excellent selectivity.

## Sustainability spotlight

The work described in this article goes beyond the boundaries of sustainable chemistry: first, it adheres to all the principles of green chemistry described by Anastas and Warner. This study quantitatively assesses, through life-cycle analysis (LCA), the possible environmental benefits of replacing organometallic complexes (Ru, Pd, Co, Cu–Zn, or Fe-based catalysts) with biosourced catalysts, called ecocatalysts. Ecocatalysts are natural, non-toxic, non-ecotoxic, efficient and abundant. Elimination of hazardous substances in production and use is demonstrated. No synthetic or petroleum-based inputs are used. The process is simple and straightforward. It generates no waste and improves the quality of the raw material, *Pelargonium graveolens* essential oil. Second, the proposed strategy involves massive harvesting of the world's most invasive plant species, exotic knotweeds. Using the cut parts of these plants contributes to management efforts for these plant species by weakening them. Their use in organic synthesis also supports the repeated harvesting of these plants. In other words, this article shows how sustainable chemistry can contribute to ecological solutions aimed at controlling the development of invasive plant species. This is an additional principle that can inspire future research in sustainable chemistry.

## Introduction

Ethyl and methyl formates (EF and MF, respectively) are small, polar and reactive molecules with ever-expanding applications. They are good solvents for polymers such as cellulose nitrate, cellulose acetate, and also for vegetable oils, fatty acids and resins.<sup>1</sup> Their low boiling points, 54 °C for EF and 32 °C for MF, allow an easy removal during chemical processes and facilitate drying. Initially appreciated for their volatility and high vapor pressures, these formates are also known for their pleasant odor. EF is particularly present in raspberries.<sup>2</sup> Its fruity odor is used in the food industry.<sup>3</sup> With a relatively low toxicity to mammals<sup>4,5</sup> and being recognized as safe by the Food and Drug Administration and the Occupational Safety and Health Administration of the United States,<sup>6</sup> EF is also used as an insecticide to replace toxic compounds such as methyl bromide.<sup>7</sup> Its fumigant insecticide activity is effective and used in Australia and China to protect dried fruits, seeds and cereals.<sup>8</sup> EF and MF are also very useful in the domain of organic synthesis in which they are described as reactants of interest. They are particularly good formylation agents allowing the creation of N–CHO bonds from amines<sup>9–11</sup> and amides.<sup>12</sup>

They also promote C–CHO bond formation by aldol condensation reactions<sup>13–15</sup> or by attacking positive halogens in aromatic series.<sup>16,17</sup> They can participate in cyanation reactions in the presence of phosphoryl oxytrichloride.<sup>18–20</sup> More recently, EF and MF have been described as co-catalysts for the alkoxylation of inactivated aryl halides in the presence of cuprous halides.<sup>21–24</sup> This is an elegant and eco-friendly alternative to *O*-arylation reactions promoted by expensive and toxic liganded palladium<sup>25–29</sup> or cuprous<sup>30–32</sup> catalysts.

Different methods for the preparation of EF and MF are described in the literature. Industrially, they are derived from the carbonylation of ethanol or methanol.<sup>33</sup> However, this carbonylation requires high-purity CO<sub>2</sub> gas,<sup>34</sup> which is difficult to obtain without any trace of CO, which is an inhibitor of ruthenium-based catalysts used in the reaction.

At the laboratory scale, these two esters have usually been prepared by esterification of formic acid.<sup>35</sup> Nowadays, many research articles are devoted to the reduction of CO<sub>2</sub> to small organic molecules. The *O*-formylation of methanol or ethanol using CO<sub>2</sub> and Ru, Pd, Co, Cu–Zn or Fe-based catalysts has been reported<sup>36–38</sup> but in each case, the yields remained moderate. Cannon *et al.* showed the importance of the pH effect in these reactions.<sup>39</sup> Unlike the above syntheses performed in basic medium, the hydrogenation of CO<sub>2</sub> in acidic medium, catalysed by phosphine-ligated Ru catalysts, favours the formation of MF.<sup>39</sup> Electrochemical reduction of CO<sub>2</sub> in acidic ethanol on Pb

Bio-inspired Chemistry and Ecological Innovations (ChimEco), UMR 5021 CNRS-University of Montpellier, Cap Delta, 1682 rue de la Valsière, 34790 Grabels, France. E-mail: claude.grison@cnrs.fr



and Sn cathodes also leads to the production of EF. In this reaction, the formed formic acid serves as an autocatalyst to perform its own *in situ* Fischer esterification with ethanol and therefore produces EF with an interesting yield.<sup>40</sup> Promising results were obtained with the Ni-catalyzed hydrosilylation of CO<sub>2</sub> followed by an *O*-formylation of alcohols in the presence of HBF<sub>4</sub>.<sup>41</sup> The benefit of these acidic conditions was also described when using boryl formate in the TsOH-catalysed *O*-formylation of benzylic alcohols.<sup>42</sup> Similarly, the presence of triformatoborohydride, which is formed during the reaction of NaBH<sub>4</sub> with CO<sub>2</sub>,<sup>43</sup> could act as an *O*-formylation reagent with formic acid as a catalyst.<sup>44</sup> These acidic conditions suggest that the *O*-formylation step proceeds *via* a transesterification reaction.<sup>40</sup>

All these new approaches to the synthesis of formates are driven by the efforts to decarbonize industrial activity coupled with the valorisation of CO<sub>2</sub>, which is largely responsible for the greenhouse effect. However, these approaches suffer from the use of expensive, toxic and/or ecotoxic complex metal catalysts. Additionally, hydrosilane or borohydride reducing agents lead to the formation of problematic wastes regulated by REACH.

In this article, we propose to develop the first fully biobased synthesis of EF and MF using essential oils (EOs) derived from *Pelargonium* species, which are rich in geranyl and citronellyl formates (GF and CF, respectively) and an ecocatalyst<sup>®</sup> acting as a biosourced base catalyst, in accordance with an eco-responsible approach.

## Results and discussion

### Choice of *Pelargonium* essential oil and strategies

EOs of *Pelargonium* species are known and exploited for their high content in citronellol and geraniol, which can reach 35 and 29%, respectively, depending on their origin.<sup>45</sup> The global market for these EOs is substantial, with nearly 300 tons produced per year. Curiously, its abundance in CF and GF is less known and little exploited. While many hybrid cultivars (*Hybridum* cv) have been produced to optimise the levels of citronellol and geraniol, the highest levels are found in the native species *Pelargonium graveolens*, stemming from South Africa<sup>46</sup> (Table 1).

In this article, we propose to use the natural abundance of CF and GF contained in *Pelargonium graveolens* L'Hér. as a natural raw material to prepare EF and MF.

The synthetic strategy is based on the transesterification of these two formates with ethanol or methanol. The reaction is promoted by an ecocatalyst<sup>®</sup> (Eco1-E-FA-JA), a mineral catalyst of 100% plant origin. The selected plant species is *Fallopia japonica*, an invasive alien species (IAS) of wetlands. Its

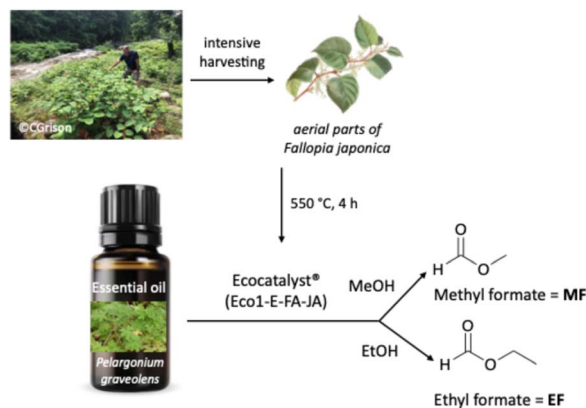


Fig. 1 Global strategy for EF and MF production from *Pelargonium graveolens* EO.

intensive harvesting helps weaken it and control its proliferation by exhaustion (Fig. 1).

### Characterization of the ecocatalyst<sup>®</sup>

The aerial parts of *Fallopia japonica* collected in large quantities were crushed directly in their wet form. They then underwent a heat treatment under air at 550 °C (SI, part 1.6.1). The thermal residue, called ecocatalyst<sup>®</sup> Eco1-E-FA-JA, has an unusual mineral composition, which was analysed by Mass Plasma – Atomic Emission Spectroscopy (MP-AES) (Table 2 and SI part 1.2).

The Mg content is 3.64 wt%, which is high in comparison to classical plants, but reasonable given the high chlorophyll content in the aerial parts. The K content (30.75 wt%) is remarkably high but falls within the main specificities of many IAS.

Ion chromatography analyses give the concentration of the anions from the ecocatalyst<sup>®</sup> soluble in water. Phosphate PO<sub>4</sub><sup>3-</sup>, sulfate SO<sub>4</sub><sup>2-</sup>, carbonate CO<sub>3</sub><sup>2-</sup> and chloride Cl<sup>-</sup> anions were detected in significant quantities (Table 3 and SI part 1.4 & 2.2).

The amount of the analysed sulfates is particularly high (4 times higher than phosphates). Chlorides and carbonates are also formed in significant quantities. Given the high carbonate content, the pH of the solution was measured and found to be 11.9 (200 mg of the ecocatalyst<sup>®</sup> in 10 mL of water). This basicity is higher than the pK<sub>a2</sub> of a simple carbonate, which makes the ecocatalyst<sup>®</sup> interesting and appropriate to be used in organic synthesis.

X-Ray Powder Diffraction (XRPD) studies were carried out to determine the nature of the combinations between the different

Table 1 Essential oils (EO) of *Pelargonium* composition determined by Gas Chromatography-Mass Spectrometry (GC-MS) or Gas Chromatography-Flame Ionisation Detection (GC-FID) analyses (% of total area)

EO (origin)	<i>P. graveolens</i> (South Africa) <sup>47</sup>	<i>P. hybridum</i> cv. 'Rosat' (China) <sup>48</sup>	<i>P. hybridum</i> cv. 'Rosat' (Egypt) <sup>49</sup>
Citronellyl formate (CF)	13	12	7
Geranyl formate (GF)	8	2	3



Table 2 Mineral analysis by MP-AES of Eco1-E-FA-JA

Element	Al	Ca	Fe	K	Mg	Na
wt% rsd	0.10 ± 0.00	6.78 ± 0.08	0.15 ± 0.02	30.75 ± 0.13	3.64 ± 0.02	0.15 ± 0.00

Table 3 Anion composition of water-soluble ions from Eco1-E-FA-JA detected by ion chromatography

Anion	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	CO <sub>3</sub> <sup>2-</sup>	Cl <sup>-</sup>
wt% (g of anion/100 g ecocatalyst) ± rsd	1.90 ± 0.02	7.20 ± 0.11	11.10 ± 0.10	5.40 ± 0.09

Table 4 Eco1-E-FA-JA crystalline species identified by XRPD analysis

Name	Formula
Sylvite	KCl
Potassium calcium phosphate	KCaPO <sub>4</sub>
Potassium sulfate	K <sub>2</sub> SO <sub>4</sub>
Potassium carbonate sesquihydrate	K <sub>2</sub> CO <sub>3</sub> (H <sub>2</sub> O) <sub>1,5</sub>
Fairchildite	K <sub>2</sub> Ca(CO <sub>3</sub> ) <sub>2</sub>
Calcite	CaCO <sub>3</sub>
Periclase	MgO

mineral elements in the crystalline state (Table 4 and SI part 1.5 & 2.1).

During heat treatment, the self-assembly of the mineral elements led to the formation of two unusual but interesting salts, which are rarely used in organic synthesis:

- a double carbonate of potassium and calcium, fairchildite, K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>
- a mixed phosphate of potassium and calcium, KCaPO<sub>4</sub>.

The presence of carbonates, and fairchildite (K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>) in particular, was expected in Eco1-E-FA-JA, as it has been found previously in other ecocatalysts<sup>®</sup> derived from *F. japonica*.<sup>50</sup> Likewise, the presence of mixed phosphates was consistent with previous ecocatalysts<sup>®</sup> derived from *F. japonica*.<sup>50</sup> However, the phosphate species differed from only one cation from previous work, as KCaPO<sub>4</sub> was observed here, instead of KMgPO<sub>4</sub>. This slight difference might be attributed to the harvesting period of *F. japonica* and hence its physiological composition.

Moreover, another crystalline species with basic properties was detected: MgO, despite the modest temperature of the heat treatment. The presence of MgO is advantageous since this salt brings a dual character to the ecocatalyst<sup>®</sup>: the presence of oxide confers Brønsted basic properties while the magnesium shows Lewis acid properties.<sup>51</sup>

Regarding these analyses, Eco1-E-FA-JA exhibits advantageous properties to act as an excellent catalyst for transesterification reactions.

### Synthesis of ethyl and methyl formates

The reaction was first studied with ethanol as a model nucleophile (Scheme 1).

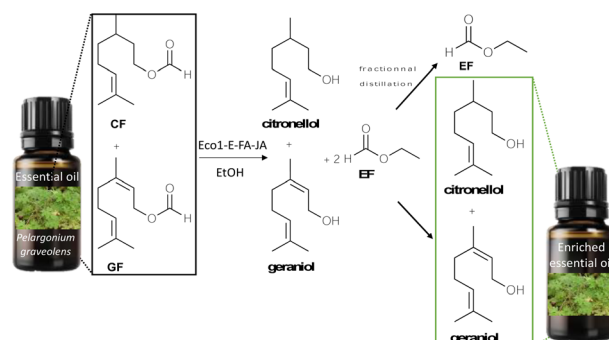
Taking as a reference the total quantity of GF and CF present in the native *Pelargonium graveolens* EO, 10 eq. of ethanol were used.

A detailed study of the impact of the catalytic charge on CF and GF conversion rates was carried out over 28 h (Fig. 2). While the reaction without a catalyst only gave 10% conversion of CF and GF, the reaction was studied between 0.04 and 0.21 equivalents of carbonates relative to both citronellyl and geranyl formates. According to the ion chromatography results, the ecocatalyst comprises 42% soluble carbonates, and therefore, 42% of the potassium salts are in the form of carbonates. Thus, 0.5 equivalents of potassium correspond to 0.21 equivalents of potassium carbonates (including fairchildite and potassium carbonate).

The monitoring was performed by GC-FID using external quantification of the two esters (see SI, part 1.3). Comparing the curves depicted in Fig. 2(a and b), the conversion times for the same catalytic load follow the same trend, suggesting that GF and CF exhibit a comparable reactivity.

The catalytic loading had a significant impact on the kinetics of the reaction. Indeed, using 0.04 or 0.08 eq. CO<sub>3</sub><sup>2-</sup> did not allow the reaction to reach full conversion after 28 h. While 0.13 and 0.17 eq. CO<sub>3</sub><sup>2-</sup> provided 98% conversion of both formates in 24 and 20 h, respectively, 0.21 eq. CO<sub>3</sub><sup>2-</sup> allowed the same conversion to be reached in 8 h. It is also important to note that the other terpenes contained in the EO of *P. graveolens* were not affected by the reaction and no byproducts were observed, highlighting the selectivity of the reaction at the same time (see SI, part 3.2 and Fig. 2).

The efficiency of the reaction was evaluated by recovering the formed EF by distillation of the reaction medium. Indeed, its boiling point at atmospheric pressure is 54 °C, which allows its separation from the EO and solvent by fractional distillation. This process yielded EF at 80% as a colourless liquid, and the



Scheme 1 Synthetic strategy towards EF formation.



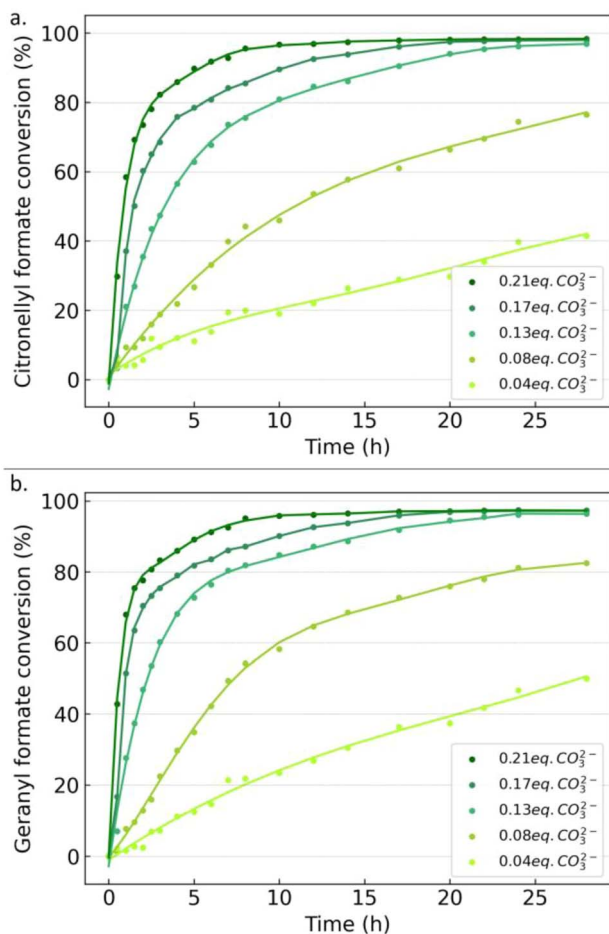


Fig. 2 Effects of different Eco-1-E-FA-JA loads (0.04 to 0.21 eq. soluble carbonates) on the conversion of citronellyl (a) and geranyl (b) formates versus time.

excess of ethanol was recovered by increasing the bath temperature. The difference between the optimum yield and the conversion of the substrates is explained by losses of materials during distillation, linked to the fact that the product has a very low boiling point. However, this result remains very satisfactory and shows that the transesterification of the formates naturally present in the EO is a good method for producing EF. The remaining EO collected in the distillation residue was separated from the catalyst by simple filtration. Its composition was evaluated by GC-FID and compared to the starting EO (Fig. 3).

A comparison of the activity of the ecocatalyst Eco1-E-FA-JA with common basic catalysts and reagents was carried out (Table 5). This comparative study was carried out under the best conditions obtained with the ecocatalyst (0.21 equivalents of soluble carbonates ( $\text{K}_2\text{Ca}(\text{CO}_3)_2 + \text{K}_2\text{CO}_3$ ), 6 h at ethanol reflux). Eco1-E-FA-JA was first compared to KOH, a reagent classically used in transesterification reactions. Initially, 0.21 equivalents of KOH were used to mimic the 0.21 equivalents of soluble carbonates present in Eco1-E-FA-JA (see ion chromatography analyses, Table 3). The conversion rates of citronellyl and geranyl formates were low (46 and 30%, respectively) instead of 90 and 90% with Eco1-E-FA-JA. By introducing excess KOH (0.87

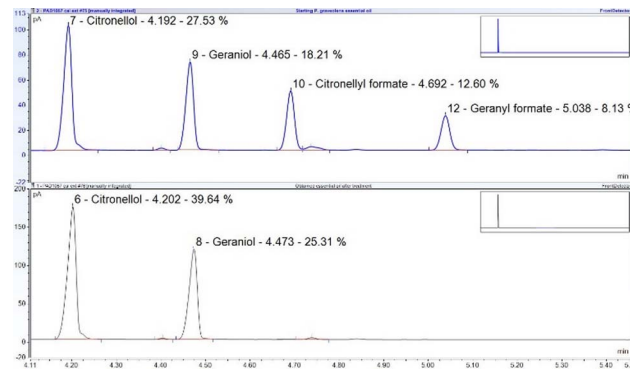


Fig. 3 GC-FID comparison of starting EO (up) with the resulting oil after treatment (bottom).

equiv. then 1 equiv.), the conversion rates of citronellyl and geranyl formates reached 88–89% and then 95–97%. However, treatment of the aqueous phase (see SI Section 3.3) revealed the formation of potassium formate (23 and 91%, respectively, see SI Fig. 14 and 15), resulting from the hydrolysis of citronellyl and geranyl formates. The ecocatalyst Eco1-E-FA-JA is therefore much more advantageous than KOH; it is both more reactive (90% conversion rate) and does not lead to any secondary hydrolysis reactions.

Each mineral species of Eco1-E-FA-JA ( $\text{MgO}$ ,  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{Ca}(\text{CO}_3)_2$ ,  $\text{KCaPO}_4$ ) and a synthetic mixture of these salts were tested under the best conditions obtained with the ecocatalyst (6 h at ethanol reflux, Table 5).  $\text{K}_2\text{CO}_3$  and  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  were used to mimic  $\text{K}_2\text{Ca}(\text{CO}_3)_2$  and  $\text{KCaPO}_4$ , respectively, because the two salts are unavailable and cannot be synthesized. As expected, conversion rates of citronellyl formate and geranyl formate were very low with  $\text{CaSO}_4$  (33–17%) and the three poorly soluble bases in EtOH,  $\text{CaCO}_3$  (19–2%),  $\text{MgO}$  (42–49%) and  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  (2–20%). Only  $\text{K}_2\text{CO}_3$  led to satisfactory conversion rates (83–77%). However, they remained slightly lower than those of the ecocatalyst. It was necessary to introduce 1 equivalent of  $\text{K}_2\text{CO}_3$  to exceed the efficiency of 0.21 equivalents of soluble carbonates in Eco1-E-FA-JA (100–92% instead of 90–90%).

Finally, a synthetic mixture reconstituted from the constituent salts (0.21 equiv.  $\text{K}_2\text{CO}_3 + 0.16$  equiv.  $\text{MgO} + 0.43$  equiv.  $\text{CaSO}_4 + 0.17$  equiv.  $\text{KCl} + 0.02$  equiv.  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) has been studied. This composition corresponds to the results of ionic chromatography for each soluble salt (sulfate, chloride, phosphate, carbonate) and the MP-AES analysis for  $\text{MgO}$ . The conversion rates (86–82%) were slightly higher than those of  $\text{K}_2\text{CO}_3$  (83–77%) and slightly lower than those of the ecocatalyst (90–90%). We can therefore conclude that the ecocatalyst Eco1-E-FA-JA is a very good transesterification catalyst. It is more active than simple petroleum-based carbonates. Its natural composition in mixed salts reinforces its reactivity.

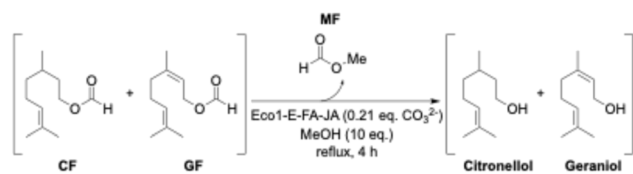
A comparison with a catalyst frequently used in ester transesterification reactions,  $\text{Ti}(\text{O}i\text{Pr})_4$ , was also performed.<sup>52</sup> The reaction of transesterification of *Pelargonium graveolens* EO with EtOH and 4 mol% of this catalyst was set up in order to



**Table 5** Comparative study of the activity of Eco1-E-FA-JA and its constituent salts

Catalyst or reagent	Formate equivalent	Citronellyl formate conversion (%)	Geranyl formate conversion (%)
KOH	0.21	46	30
KOH	0.87	89	88
KOH	1	97	95
CaSO <sub>4</sub>	0.21	33	17
CaCO <sub>3</sub>	0.21	2	19
MgO	0.21	47	29
MgO	1	88	72
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	0.21	2	20
K <sub>2</sub> CO <sub>3</sub>	0.21	83	77
K <sub>2</sub> CO <sub>3</sub>	0.44	84	84
K <sub>2</sub> CO <sub>3</sub>	1	100	92
Synthetic mixture	0.21 <sup>a</sup>	86	82
Eco1-E-FA-JA	0.21 <sup>b</sup>	90	90

<sup>a</sup> 0.21 equiv. K<sub>2</sub>CO<sub>3</sub> + 0.16 equiv. MgO + 0.43 equiv. CaSO<sub>4</sub> + 0.17 equiv. KCl + 0.02 equiv. Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>. <sup>b</sup> 0.21 equivalents of soluble carbonates.



**Scheme 2** Synthesis of MF from *P. graveolens* EO.

reproduce the conditions described by Corsi *et al.*<sup>52</sup> After 8 h of reaction at reflux of EtOH, the conversions of CF and GF were measured at 42 and 58%, respectively. These conversions were far lower than the proposed ecocatalysts. The GC-FID analyses are added in part 3.4 of the SI.

Compared to the initial EO, the chemical composition of the remaining EO is significantly enriched in citronellol (40% instead of 28%) and geraniol (25% instead of 18%). This result is of significant interest, because these two terpenes are used in various applications as repellents for arthropods that carry infectious diseases,<sup>53</sup> in fragrances<sup>54,55</sup> and as key intermediates in organic synthesis.<sup>56,57</sup> Moreover, the pH of the remaining EO was measured at 7, while the value of the initial EO was assessed at 2.7. The ecocatalyst<sup>®</sup> is thus able to perform quantitative transesterification reactions and also to neutralise the acidity of the initial EO in order to obtain a citronellol- and geraniol-enriched EO more suitable for human skin applications. These very encouraging results led us to extend the principle of this reaction to the transesterification of formates present in the *P. graveolens* EO with methanol (Scheme 2). More reactive than ethanol, methanol allows a total conversion in 4 hours.

Considering the gap between MF and methanol boiling points (32 °C and 65 °C, respectively), the distillation step took place at the same time as the reaction. While MF was directly distilled after its formation, the equilibrium of the reaction was shifted, providing a drastic reduction of the reaction duration. MF was successfully obtained with 75% yield as a colourless

liquid. The excess methanol was then distilled in a subsequent fraction to be recycled. The same advantages as previously can be noted:

- Enrichment of the EO in citronellol and geraniol (SI, part 3.2 and Fig. 12 and 13).
- Neutralization of the acidity of the EO.
- Other compounds stayed untouched, and no byproducts were observed.

## Conclusions

Here we described the first preparation of biobased EF and MF by using an ecocatalyst<sup>®</sup> derived from the invasive alien species *Fallopia japonica*. The conception of this new type of catalyst contributes to supporting the control of the proliferation of this plant. The characterization of this biobased catalyst highlighted the presence of carbonates and phosphates of potassium and calcium, as well as MgO, which is known for its Lewis acid character and its Brønsted basicity. This ecocatalyst<sup>®</sup> proved to be highly efficient in the transesterification of CF and GF contained in the *Pelargonium graveolens* EO without the use of any additive or solvent, improving the green potential of the reaction. Good yields (up to 80%) of EF and MF were obtained with an excellent selectivity. To the best of our knowledge, the application of this catalytic system to this specific reaction has never been described. Finally, this study highlighted the triple advantage of this methodology:

- Highly efficient synthesis of biobased MF and EF.
- Production of a *Pelargonium graveolens* EO with higher citronellol and geraniol contents.
- Neutralisation of EO acidity.

The current international market of *P. graveolens* EO is substantial, with nearly 300 tons produced per year. The projection of the ecocatalytic process application to this annual production could lead to form more than 18 tons of biobased EF or MF.

## Author contributions

AL: investigation, formal analysis, data curation. PAD: investigation, formal analysis, data curation, writing and reviewing. FP: formal analysis, validation, data curation. YML: formal analysis, validation, data curation. CG: writing, reviewing and editing, supervision, funding acquisition, formal analysis, methodology, conceptualization. CMG: formal analyses, validation, data curation, funding acquisition, writing, reviewing and editing.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI) and are also available at



<https://osf.io/g24y7>. Supplementary information is available. See DOI: <https://doi.org/10.1039/d5su00739a>.

## Notes and references

- J. Hietala, A. Vuori, P. Johnsson, I. Pollari, W. Reutemann and H. Kieczka, Formic Acid, DOI: [10.1002/14356007.a12013.pub3](https://doi.org/10.1002/14356007.a12013.pub3), accessed 26 November 2024.
- Redaction, Framboise : qu'est-ce que c'est ?, <https://www.futura-sciences.com/planete/definitions/botanique-framboise-7571/>.
- Redaction, Global Ethyl Formate Market By Type (Superior Grade, First Grade), By Application (Solvent, Pharmaceutical Intermediates), By Geographic Scope And Forecast, <https://www.verifiedmarketreports.com/en/product/ethyl-formate-market/>.
- Redaction, Occupational Safety and Health Administration Chemical Database Ethyl Formate, <https://www.osha.gov/chemicaldata/106>.
- Environment and Climate Change Canada, Screening assessment formic acid and formates substance group, 2023.
- International Symposium on Controlled Atmosphere Grain Storage, *Controlled Atmosphere and Fumigation in Grain Storages: Proceedings of an International Symposium 'Practical Aspects of Controlled Atmosphere and Fumigation in Grain Storages' Held from 11 to 22 April 1983 in Perth Western Australia*, ed. B. E. Ripp and H. J. Banks, Elsevier, Amsterdam New York, 2011.
- V. S. K. Bharathi and D. S. Jayas, *J. Stored Prod. Res.*, 2024, **106**, 102280, DOI: [10.1016/j.jspr.2024.102280](https://doi.org/10.1016/j.jspr.2024.102280).
- A. Zaitoon, L.-T. Lim and C. Scott-Dupree, *J. Agric. Food Chem.*, 2019, **67**, 13914–13921, DOI: [10.1021/acs.jafc.9b06335](https://doi.org/10.1021/acs.jafc.9b06335).
- B. Kapuku and D. S. Bohle, *Molecules*, 2024, **29**, 1084, DOI: [10.3390/molecules29051084](https://doi.org/10.3390/molecules29051084).
- M. Liu and X. Wang, CN118388452, 2024.
- H. Suzhou, WO2024149370, 2024.
- Y. Li, Z. Shi, Y. Pei, L. Chen, T. Shu, P. Wang, S. Shi, L. He, P. Tang, C. Zhang and P. Yan, WO2024017294, 2023.
- Q. Gao, S. Liu and Z. Kang, CN118420581, 2023.
- V. V. Leverov, Y. Panasiuk, O. Shablykin, O. Stashkevych, K. Sahun, A. Rassokhin, I. Sadkova, D. Lesyk, A. Anisiforova, Y. Holota, P. Borysko, I. Bodenчук, N. M. Voloshchuk and P. K. Mykhailiuk, *Angew. Chem., Int. Ed.*, 2024, **63**, e202319831, DOI: [10.1002/anie.202319831](https://doi.org/10.1002/anie.202319831).
- R. Bouzammit, I. Lakkab, M. El Fadili, Y. Kanzouai, M. Chalkha, A. Nakkabi, B. El Bali, S. Obbade, L. Jouffret, M. Lachkar and G. Al Houari, *J. Mol. Struct.*, 2024, **1312**, 138582, DOI: [10.1016/j.molstruc.2024.138582](https://doi.org/10.1016/j.molstruc.2024.138582).
- X. Ke, Q. Fang and Q. Sun, WO2024169773, 2024.
- F. Zhu and J. Huang, CN117776973, 2023.
- H. Zhao, V. D. Cuomo, J. A. Rossi-Ashton and D. J. Procter, *Chem*, 2024, **10**, 1240–1251, DOI: [10.1016/j.chempr.2024.01.020](https://doi.org/10.1016/j.chempr.2024.01.020).
- Z. Jiao, K. T. Jaunich, T. Tao, O. Gottschall, M. M. Hughes, A. Turluk and A. W. Schuppe, *Angew. Chem., Int. Ed.*, 2024, **63**, e202405779, DOI: [10.1002/anie.202405779](https://doi.org/10.1002/anie.202405779).
- Y. Wu, W. Cai, L. Yu, J. Chang and C. Song, *Org. Chem. Front.*, 2024, **11**, 89–93, DOI: [10.1039/D3QO01454A](https://doi.org/10.1039/D3QO01454A).
- Y. Guo, X. Fan, M. Nie, H. Liu, D. Liao, X. Pan and Y. Ji, *Eur. J. Org. Chem.*, 2015, **2015**, 4744–4755, DOI: [10.1002/ejoc.201500500](https://doi.org/10.1002/ejoc.201500500).
- X. Zhang, W. Li, Y. Yu, M. Luo, H. Bai, L. Shi and H. Li, *Green Chem.*, 2024, **26**, 2207–2212, DOI: [10.1039/D3GC04070D](https://doi.org/10.1039/D3GC04070D).
- S. S. Huang, Z. J. Zheng, Y. M. Cui, Z. Xu, K. F. Yang and L. W. Xu, *Synthesis*, 2019, **51**, 4249–4252, DOI: [10.1055/s-0039-1690617](https://doi.org/10.1055/s-0039-1690617).
- Y. Guo, Y.-D. Li, C. Chen, J.-H. Zhao, H.-W. Liu, D.-H. Liao and Y.-F. Ji, *Res. Chem. Intermed.*, 2016, **42**, 2525–2537, DOI: [10.1007/s11164-015-2165-4](https://doi.org/10.1007/s11164-015-2165-4).
- S. Gowrisankar, A. G. Sergeev, P. Anbarasan, A. Spannenberg, H. Neumann and M. Beller, *J. Am. Chem. Soc.*, 2010, **132**, 11592–11598, DOI: [10.1021/ja103248d](https://doi.org/10.1021/ja103248d).
- K. W. Anderson, T. Ikawa, R. E. Tundel and S. L. Buchwald, *J. Am. Chem. Soc.*, 2006, **128**, 10694–10695, DOI: [10.1021/ja0639719](https://doi.org/10.1021/ja0639719).
- X. Wu, B. P. Fors and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2011, **50**, 9943–9947, DOI: [10.1002/anie.201104361](https://doi.org/10.1002/anie.201104361).
- K. E. Torraca, X. Huang, C. A. Parrish and S. L. Buchwald, *J. Am. Chem. Soc.*, 2001, **123**, 10770–10771, DOI: [10.1021/ja016863p](https://doi.org/10.1021/ja016863p).
- A. V. Vorogushin, X. Huang and S. L. Buchwald, *J. Am. Chem. Soc.*, 2005, **127**, 8146–8149, DOI: [10.1021/ja050471r](https://doi.org/10.1021/ja050471r).
- S. V. Ley and A. W. Thomas, *Angew. Chem., Int. Ed.*, 2003, **42**, 5400–5449, DOI: [10.1002/anie.200300594](https://doi.org/10.1002/anie.200300594).
- G. Evano, N. Blanchard and M. Toumi, *Chem. Rev.*, 2008, **108**, 3054–3131, DOI: [10.1021/cr8002505](https://doi.org/10.1021/cr8002505).
- F. Monnier and M. Taillefer, *Angew. Chem., Int. Ed.*, 2009, **48**, 6954–6971, DOI: [10.1002/anie.200804497](https://doi.org/10.1002/anie.200804497).
- Y. Han, D. Jia, Z. Guo and Y. Zhang, CN116688896, 2023.
- E. Gérard, PhD thesis, University of Lille 1, 1994.
- L. Rong, Z. Xu, J. Sun and G. Guo, *J. Energy Chem.*, 2018, **27**, 238–242, DOI: [10.1016/j.jechem.2017.07.015](https://doi.org/10.1016/j.jechem.2017.07.015).
- B. An, Y. Meng, Z. Li, Y. Hong, T. Wang, S. Wang, J. Lin, C. Wang, S. Wan, Y. Wang and W. Lin, *J. Catal.*, 2019, **373**, 37–47, DOI: [10.1016/j.jcat.2019.03.008](https://doi.org/10.1016/j.jcat.2019.03.008).
- J. He, M. Wen, Y. Zhu, Z. An, X. Xiang, H. Song and X. Shu, CN113908849, 2020.
- W. Zhang, Y. Yao, S. Xie, K. Gubsch, Y. Yang, X. Lan and H. Lin, *Catal. Today*, 2021, **374**, 53–60, DOI: [10.1016/j.cattod.2020.12.027](https://doi.org/10.1016/j.cattod.2020.12.027).
- A. T. Cannon and C. T. Saouma, *Polyhedron*, 2021, **207**, 115375, DOI: [10.1016/j.poly.2021.115375](https://doi.org/10.1016/j.poly.2021.115375).
- D. T. Hofsommer, I. R. Zamborini, S. S. Uttarwar, C. A. Phipps, M. Gautam, F. Nkurunziza, C. A. Grapperhaus and J. M. Spurgeon, *ACS Sustainable Chem. Eng.*, 2024, **12**, 882–892, DOI: [10.1021/acssuschemeng.3c05853](https://doi.org/10.1021/acssuschemeng.3c05853).
- L. González-Sebastián, M. Flores-Alamo and J. J. García, *Organometallics*, 2013, **32**, 7186–7194, DOI: [10.1021/om400876j](https://doi.org/10.1021/om400876j).
- B. Zhang, G. Du, W. Hang, S. Wang and C. Xi, *Eur. J. Org. Chem.*, 2018, **2018**, 1739–1743, DOI: [10.1002/ejoc.201800320](https://doi.org/10.1002/ejoc.201800320).



- 43 I. Knopf and C. C. Cummins, *Organometallics*, 2015, **34**, 1601–1603, DOI: [10.1021/acs.organomet.5b00190](https://doi.org/10.1021/acs.organomet.5b00190).
- 44 G. Gastelu, D. Savary, M. Hulla, D. Ortiz, J. G. Uranga and P. J. Dyson, *ACS Catal.*, 2023, **13**, 2403–2409, DOI: [10.1021/acscatal.2c06218](https://doi.org/10.1021/acscatal.2c06218).
- 45 B. Blerot, S. Baudino, C. Prunier, F. Demarne, B. Toulemonde and J.-C. Caissard, *Phytochem. Rev.*, 2016, **15**, 935–960, DOI: [10.1007/s11101-015-9441-1](https://doi.org/10.1007/s11101-015-9441-1).
- 46 K. Ghedira and P. Goetz, *Phytotherapie*, 2015, **13**, 197–201, DOI: [10.1007/s10298-015-0955-x](https://doi.org/10.1007/s10298-015-0955-x).
- 47 B. Blerot, PhD thesis, University of Lyon, 2016.
- 48 N. S. Ravindra and R. N. Kulkarni, *Sci. Hortic.*, 2015, **184**, 31–35, DOI: [10.1016/j.scienta.2014.12.023](https://doi.org/10.1016/j.scienta.2014.12.023).
- 49 M. N. Boukhatem, A. Kameli and F. Saidi, *Food Control*, 2013, **34**, 208–213, DOI: [10.1016/j.foodcont.2013.03.045](https://doi.org/10.1016/j.foodcont.2013.03.045).
- 50 A. Lasbleiz, F. Pelissier, J.-H. Renault, C. M. Grison, Y.-M. Legrand and C. Grison, *C. R. Chim.*, 2024, **27**, 85–97, DOI: [10.5802/crchim.273](https://doi.org/10.5802/crchim.273).
- 51 L. Liénart, Y.-M. Legrand, F. Pelissier, P. Gaveau, P. Hesemann, E. Petit, C. Grison and C. M. Grison, *Appl. Catal. B Environ. Energy*, 2024, **349**, 123888, DOI: [10.1016/j.apcatb.2024.123888](https://doi.org/10.1016/j.apcatb.2024.123888).
- 52 M. Corsi, S. Magnolfi and F. Machetti, *Eur. J. Org. Chem.*, 2020, **2020**, 1720–1726, DOI: [10.1002/ejoc.202000050](https://doi.org/10.1002/ejoc.202000050).
- 53 C. Grison and A. Stanovych, WO2021005204A1, 2021.
- 54 W. Chen and A. M. Viljoen, *J. S. Afr. Bot.*, 2010, **76**, 643–651, DOI: [10.1016/j.sajb.2010.05.008](https://doi.org/10.1016/j.sajb.2010.05.008).
- 55 A. Lapczynski, S. P. Bhatia, C. S. Letizia and A. M. Api, *Food Chem. Toxicol.*, 2008, **46**, S110–S113, DOI: [10.1016/j.fct.2008.06.056](https://doi.org/10.1016/j.fct.2008.06.056).
- 56 P. A. Grieco, *J. Chem. Soc., Chem. Commun.*, 1972, **8**, 486, DOI: [10.1039/c39720000486](https://doi.org/10.1039/c39720000486).
- 57 E. J. Lenardão, G. V. Botteselle, F. De Azambuja, G. Perin and R. G. Jacob, *Tetrahedron*, 2007, **63**, 6671–6712, DOI: [10.1016/j.tet.2007.03.159](https://doi.org/10.1016/j.tet.2007.03.159).

