# First sustainable synthesis of ethyl and methyl formates by ecocatalysis

## Electronic supporting information

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# Summary

# 1 Materials and Methods

## 1.1 Chemical reagents

Citronellol (95% purity), geraniol (98% purity), citronellyl formate (98% purity) and geranyl formate (95% purity) for calibration were purchased from Sigma-Aldrich company and were used without further purification. Biological *Pelargonium graveolens* L'Hér essential oil (batch number B448002) stemmed from Congo was purchased from Golgemma company and was used without further purification. Solvent anhydrous methanol (purchased from Sigma-Aldrich company) and anhydrous ethanol (purchased from VWR company) were used without further purification.

## 1.2 Mass Plasma – Atomic Emission Spectroscopy (MP-AES)

All reagents and solvents used in this work were purchased from commercial sources. Analyses by MP AES: The samples were digested in 10 mL of reversed aqua regia (1:2 hydrochloric acid (37%): nitric acid (65%)) under a microwave-assisted digestion (Multiwave-Go Anton Paar) with the following program: 20 to 165 °C in 20 min and then 10 min isothermal at 165 °C. Samples were filtered and then diluted to 0.4 $mg.L^{-1}$ in 1% aqueous nitric acid. Mineral compositions were determined by using a microwave plasma-atomic emission spectroscopy (MP-AES) 4200 (Agilent Technologies) equipped with a concentric nebulizer and a double-pass cyclonic spray chamber. The pump speed during analysis was kept at 10 rpm and the sample introduction tube diameter was 0.89 mm. The analytical cycle consisted of 30 s rinsing with aq. 1% nitric acid followed by 25 s of sample uptake (pump speed 40 rpm) and then 20 s of equilibration before the reading at preselected integration times (pump speed 10 rpm). The integration time was set to 3 s for all elements. Unless otherwise stated, the automatic background correction mode available in the software was used. An Agilent SPS3 autosampler was used throughout the study. The software Agilent MP Expert was used for the monitoring and the treatment of the data.

## 1.3 Gas Chromatography coupled with a Flame Ionisation Detector (GC-FID)

Gas chromatography analyses were performed using a Thermo Scientific Trace 1300 device with hydrogen as vector gas equipped with a Flame Ionisation Detector and a Thermo Scientific TR-5MS column (30m x 0.25mm x 0.25 µm). The used software was ThermoScientific Chromeleon 7.2. The oven temperature gradient was reported in Figure 1. An air flow of 350 $mL.min^{-1}$, a dihydrogen flow of 33 $mL.min^{-1}$ was used for the FID and the detector temperature was 280 ◦C. The reactions were monitored by using external standard for the calibration.

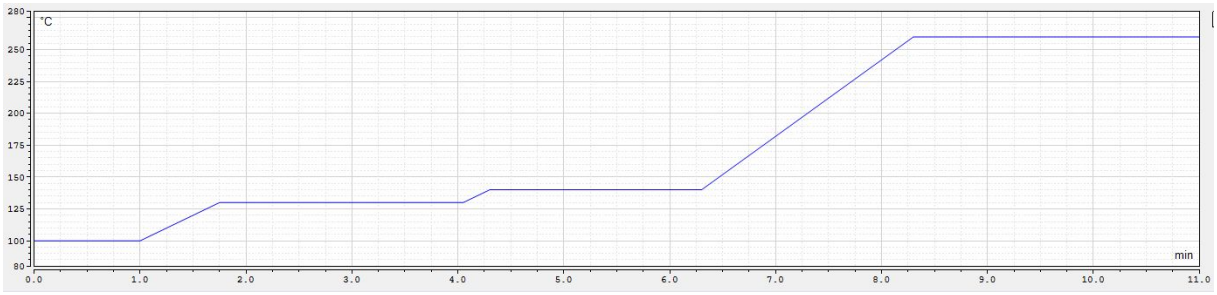



**Figure 1: Oven temperature gradient for GC-FID analyses**

### 1.3.1 Citronellol

The calibration curve of citronellol was obtained by the injection of samples (triplicates) at different concentrations. The curve is presented in Figure 2. The curve is linear, its equation is $y = 0.2411 x - 0.02$ and the $R^2 = 0.9994$.

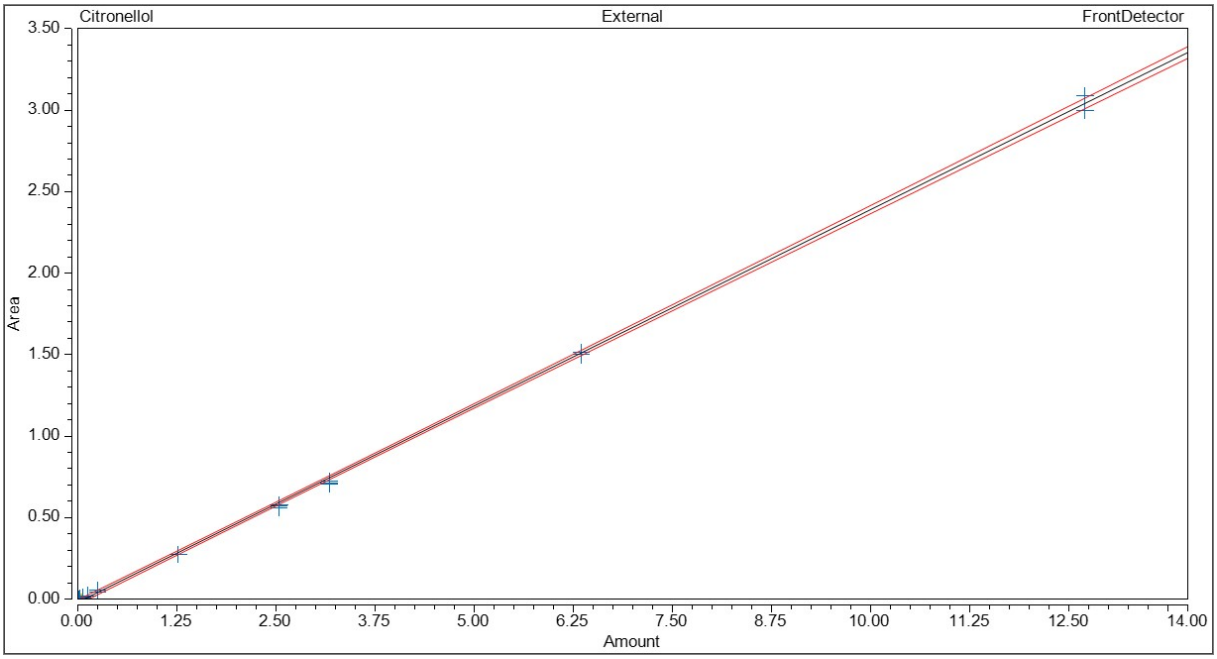



**Figure 2: Calibration curve of citronellol**

The calibration values were reported in Table 1. Regarding the relative standard deviation for the calibration levels, the limit of detection (LoD) was set at 0.1270 mmol.L$^{-1}$ and the limit of quantification (LoQ) was set at 0.2541 mmol.L$^{-1}$.

| Calibration level | Citronellol Concentration (mmol.L$^{-1}$) | Detector response (pA*min) | Calculated Concentration (mmol.L$^{-1}$) | Relative Standard Deviation (%) |
|---|---|---|---|---|
| 8 | 0.0635 | 0.009 | 0.1205 | 89.70 |
| 8 | 0.0635 | 0.009 | 0.1205 | 89.71 |
| 8 | 0.0635 | 0.009 | 0.1189 | 87.27 |
| 7 | 0.1270 | 0.020 | 0.1644 | 29.43 |
| 7 | 0.1270 | 0.020 | 0.1640 | 29.10 |
| 7 | 0.1270 | 0.020 | 0.1677 | 32.07 |
| 6 | 0.2541 | 0.052 | 0.2971 | 16.93 |

| | | | | |
|---|---|---|---|---|
| 6 | 0.2541 | 0.045 | 0.2694 | 6.03 |
| 6 | 0.2541 | 0.042 | 0.2557 | 0.65 |
| 5 | 1.2704 | 0.273 | 1.2167 | -4.23 |
| 5 | 1.2704 | 0.275 | 1.2218 | -3.83 |
| 5 | 1.2704 | 0.275 | 1.2227 | -3.76 |
| 4 | 2.5408 | 0.574 | 2.4619 | -3.11 |
| 4 | 2.5408 | 0.578 | 2.4795 | -2.41 |
| 4 | 2.5408 | 0.561 | 2.4093 | -5.18 |
| 3 | 3.1760 | 0.713 | 3.0390 | -4.31 |
| 3 | 3.1760 | 0.707 | 3.0164 | -5.02 |
| 3 | 3.1760 | 0.721 | 3.0726 | -3.26 |
| 2 | 6.3521 | 1.511 | 6.3503 | -0.03 |
| 2 | 6.3521 | 1.504 | 6.3216 | -0.48 |
| 2 | 6.3521 | 1.500 | 6.3042 | -0.75 |
| 1 | 12.7041 | 3.089 | 12.8958 | 1.51 |
| 1 | 12.7041 | 3.091 | 12.9031 | 1.57 |
| 1 | 12.7041 | 2.998 | 12.5191 | -1.46 |

**Table 1: Calibration values for citronellol**

### 1.3.2 Geraniol

The calibration curve of citronellol was obtained by the injection of samples (triplicates) at different concentrations. The curve is presented in Figure 3. The curve is linear, its equation is $y = 0.2903 x - 0.0111$ and the $R^2 = 0.9998$.

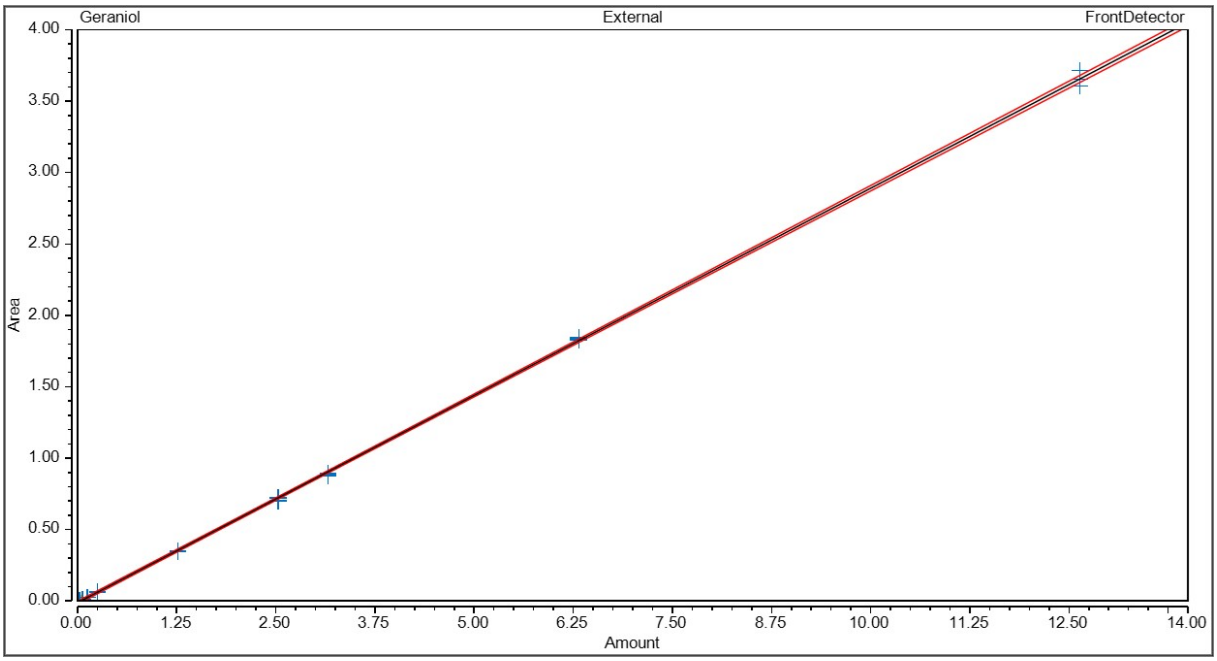



**Figure 3 : Calibration curve of geraniol**

The calibration values were reported in Table 2. Regarding the relative standard deviation for the calibration levels, the limit of detection (LoD) was set at 0.0253 $mmol.L^{-1}$ and the limit of quantification (LoQ) was set at 0.0632 $mmol.L^{-1}$.

| Calibration level | Geraniol Concentration ($mmol.L^{-1}$) | Detector response (pA*min) | Calculated Concentration ($mmol.L^{-1}$) | Relative Standard Deviation (%) |
|---|---|---|---|---|
| 9 | 0.0253 | 0.004 | 0.0504 | 99.37 |
| 9 | 0.0253 | 0.003 | 0.0495 | 95.49 |
| 9 | 0.0253 | 0.003 | 0.0496 | 95.95 |
| 8 | 0.0632 | 0.011 | 0.0766 | 21.18 |
| 8 | 0.0632 | 0.012 | 0.0812 | 28.45 |
| 8 | 0.0632 | 0.012 | 0.0788 | 24.70 |
| 7 | 0.1264 | 0.027 | 0.1298 | 2.66 |
| 7 | 0.1264 | 0.027 | 0.1307 | 3.39 |
| 7 | 0.1264 | 0.026 | 0.1291 | 2.17 |
| 6 | 0.2528 | 0.063 | 0.2559 | 1.23 |
| 6 | 0.2528 | 0.063 | 0.2563 | 1.38 |
| 6 | 0.2528 | 0.063 | 0.2561 | 1.30 |
| 5 | 1.2639 | 0.347 | 1.2329 | -2.45 |
| 5 | 1.2639 | 0.349 | 1.2398 | -1.91 |
| 5 | 1.2639 | 0.349 | 1.2423 | -1.71 |
| 4 | 2.5277 | 0.717 | 2.5093 | -0.73 |
| 4 | 2.5277 | 0.722 | 2.5255 | -0.09 |
| 4 | 2.5277 | 0.701 | 2.4532 | -2.95 |
| 3 | 3.1597 | 0.887 | 3.0955 | -2.03 |
| 3 | 3.1597 | 0.879 | 3.0649 | -3.00 |
| 3 | 3.1597 | 0.895 | 3.1231 | -1.16 |
| 2 | 6.3193 | 1.844 | 6.3904 | 1.13 |
| 2 | 6.3193 | 1.835 | 6.3592 | 0.63 |
| 2 | 6.3193 | 1.828 | 6.3376 | 0.29 |
| 1 | 12.6386 | 3.654 | 12.6275 | -0.09 |
| 1 | 12.6386 | 3.713 | 12.8317 | 1.53 |
| 1 | 12.6386 | 3.607 | 12.4666 | -1.36 |

**Table 2 : Calibration values for geraniol**

### 1.3.3 Citronellyl formate

The calibration curve of citronellyl formate was obtained by the injection of samples (triplicates) at different concentrations. The curve is presented in Figure 4. The curve is linear, its equation is $y = 0.3231 x - 0.009$ and the $R^2 = 0.9996$.

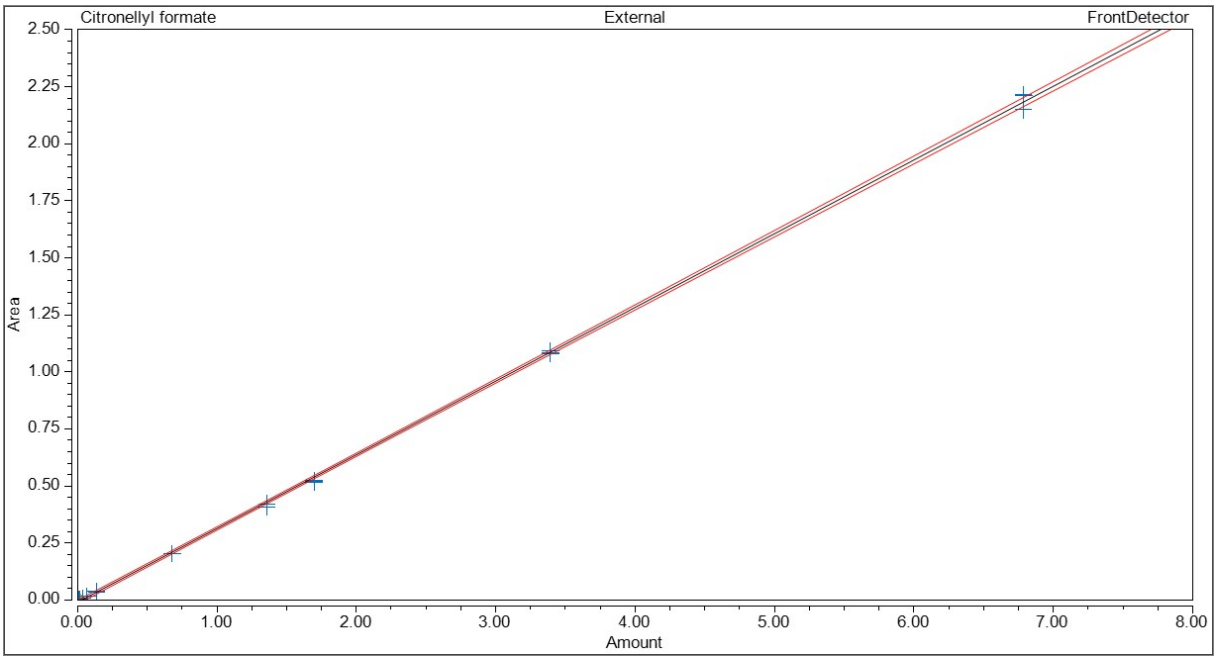



**Figure 4: Calibration curve of citronellyl formate**

The calibration values were reported in Table 3. Regarding the relative standard deviation for the calibration levels, the limit of detection (LoD) was set at 0.0339 mmol.L$^{-1}$ and the limit of quantification (LoQ) was set at 0.0679 mmol.L$^{-1}$.

| Calibration level | Citronellol Concentration (mmol.L$^{-1}$) | Detector response (pA*min) | Calculated Concentration (mmol.L$^{-1}$) | Relative Standard Deviation (%) |
|---|---|---|---|---|
| 8 | 0.0339 | 0.009 | 0.0556 | 64.13 |
| 8 | 0.0339 | 0.009 | 0.0559 | 65.03 |
| 8 | 0.0339 | 0.009 | 0.0552 | 62.77 |
| 7 | 0.0679 | 0.018 | 0.0833 | 22.74 |
| 7 | 0.0679 | 0.018 | 0.0830 | 22.27 |
| 7 | 0.0679 | 0.018 | 0.0828 | 21.89 |
| 6 | 0.1357 | 0.038 | 0.1470 | 8.36 |
| 6 | 0.1357 | 0.038 | 0.1465 | 7.97 |
| 6 | 0.1357 | 0.036 | 0.1398 | 3.06 |
| 5 | 0.6786 | 0.203 | 0.6560 | -3.34 |
| 5 | 0.6786 | 0.204 | 0.6583 | -3.00 |
| 5 | 0.6786 | 0.205 | 0.6614 | -2.53 |
| 4 | 1.3572 | 0.419 | 1.3240 | -2.44 |
| 4 | 1.3572 | 0.422 | 1.3346 | -1.66 |
| 4 | 1.3572 | 0.409 | 1.2948 | -4.60 |
| 3 | 1.6965 | 0.518 | 1.6311 | -3.85 |
| 3 | 1.6965 | 0.515 | 1.6223 | -4.38 |
| 3 | 1.6965 | 0.524 | 1.6507 | -2.70 |
| 2 | 3.3929 | 1.094 | 3.4138 | 0.62 |
| 2 | 3.3929 | 1.085 | 3.3845 | -0.25 |
| 2 | 3.3929 | 1.081 | 3.3739 | -0.56 |
| 1 | 6.7858 | 2.212 | 6.8734 | 1.29 |

| | | | | |
|---|---|---|---|---|
| 1 | 6.7858 | 2.214 | 6.8806 | 1.40 |
| 1 | 6.7858 | 2.150 | 6.6812 | -1.54 |

**Table 3: Calibration values for citronellyl formate**

### 1.3.4 Geranyl formate

The calibration curve of geranyl formate was obtained by the injection of samples (triplicates) at different concentrations. The curve is presented in Figure 5. The curve is linear, its equation is y = 0.2337 x + 0.0064 and the $R^2$ = 0.9987.

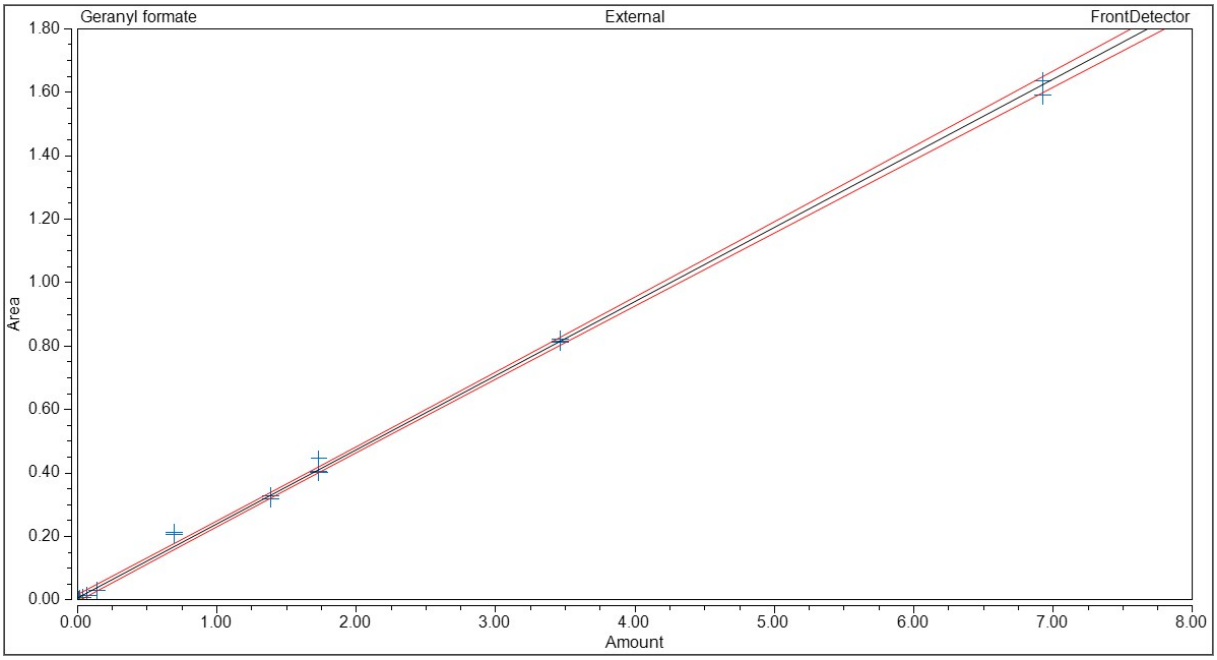



**Figure 5: Calibration curve of geranyl formate**

The calibration values were reported in Table 4. Regarding the relative standard deviation for the calibration levels, the limit of detection (LoD) was set at 0.0346 mmol.$L^{-1}$ and the limit of quantification (LoQ) was set at 0.6926 mmol.$L^{-1}$.

| Calibration level | Citronellol Concentration (mmol.$L^{-1}$) | Detector response (pA*min) | Calculated Concentration (mmol.$L^{-1}$) | Relative Standard Deviation (%) |
|---|---|---|---|---|
| 9 | 0.0139 | 0.002 | n.a. | n.a. |
| 9 | 0.0139 | 0.003 | n.a. | n.a. |
| 9 | 0.0139 | 0.002 | n.a. | n.a. |
| 8 | 0.0346 | 0.007 | 0.0027 | -92.10 |
| 8 | 0.0346 | 0.007 | 0.0042 | -87.80 |
| 8 | 0.0346 | 0.007 | 0.0012 | -96.59 |
| 7 | 0.0693 | 0.014 | 0.0332 | -52.14 |
| 7 | 0.0693 | 0.014 | 0.0340 | -50.96 |
| 7 | 0.0693 | 0.014 | 0.0334 | -51.77 |
| 6 | 0.1385 | 0.028 | 0.0940 | -32.16 |
| 6 | 0.1385 | 0.030 | 0.1025 | -25.96 |
| 6 | 0.1385 | 0.030 | 0.0998 | -27.91 |
| 5 | 0.6926 | 0.212 | 0.8785 | 26.84 |

| | | | | |
|---|---|---|---|---|
| 5 | 0.6926 | 0.212 | 0.8784 | 26.83 |
| 5 | 0.6926 | 0.207 | 0.8588 | 23.99 |
| 4 | 1.3852 | 0.326 | 1.3696 | -1.13 |
| 4 | 1.3852 | 0.329 | 1.3797 | -0.40 |
| 4 | 1.3852 | 0.319 | 1.3373 | -3.46 |
| 3 | 1.7316 | 0.401 | 1.6890 | -2.46 |
| 3 | 1.7316 | 0.445 | 1.8784 | 8.48 |
| 3 | 1.7316 | 0.406 | 1.7110 | -1.19 |
| 2 | 3.4631 | 0.821 | 3.4874 | 0.70 |
| 2 | 3.4631 | 0.816 | 3.4640 | 0.03 |
| 2 | 3.4631 | 0.812 | 3.4499 | -0.38 |

**Table 4: Calibration values for geranyl formate**

All the calibration values, which were presented in part 1.3. were summarized in the following Table 5.

| Compound | Correlation coefficient | LoD ($mmol.L^{-1}$) | LoQ ($mmol.L^{-1}$) | Curve's equation |
|---|---|---|---|---|
| Citronellol | 0.9994 | 0.1270 | 0.2541 | y = 0.2411 x - 0.02 |
| Geraniol | 0.9998 | 0.0253 | 0.0632 | y = 0.2903 x - 0.0111 |
| Citronellyl formate | 0.9996 | 0.0339 | 0.0679 | y = 0.3231 x - 0.009 |
| Geranyl formate | 0.9987 | 0.0346 | 0.6926 | y = 0.2337 x + 0.0064 |

**Table 5 : Summary of the calibration values for the GC-FID analyses**

### 1.4 Ionic Chromatography

Ionic chromatography analyses were performed on a Metrohm 930 Compact IC Flex apparatus equipped with a Metrohm 863 Compact Autosampler, a Metrohm Metro sep A trap 1 10/4 precolumn and a Metrohm Metro 7 A Supp 19 150/4 column, using the software MetrOhm MagIC Net 4.2. The elution solvent was a NaOH solution at 25 $mmol.L^{-1}$ and the gradient was realized with a NaOH solution at 100 $mmol.L^{-1}$. The gradient used was reported on Figure 6. A 500 $mmol.L^{-1}$ $H_2SO_4$ solution was used as regeneration solvent.

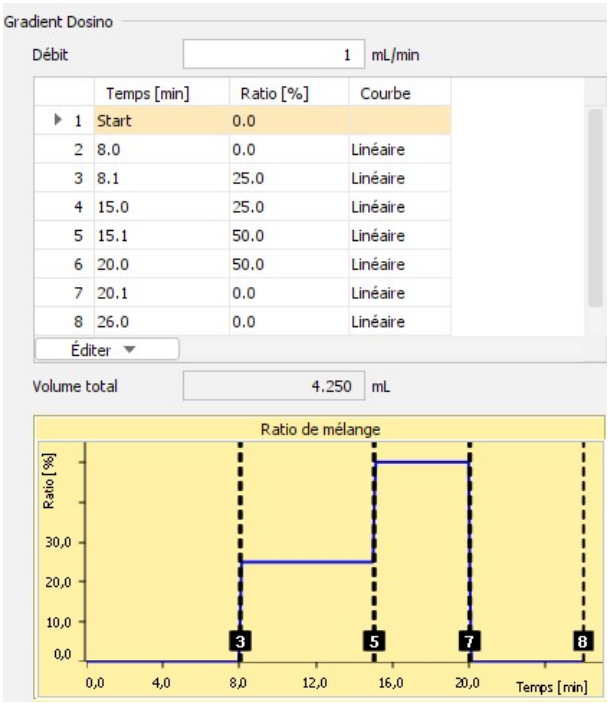


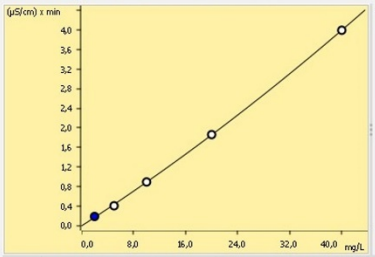

**Figure 6: Gradient of elution for ionic chromatography analyses**

The calibration curves, equations, $R^2$ and relative standard deviations for chlorides, carbonates, phosphates and sulfates were reported on Figure 7.

Courbe 1 - Eco1-E-FA-JA-18042023-CAP-NAT1

Anions

Chromatogramme
Courbe de calibration
Composé: Chlorure




Fonction: A = -5,91222E-3 + 0,0172148 × Q + 1,39719E-5 × Q²

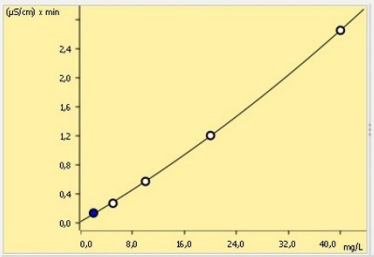
| | |
|---|---|
| Coefficient de variation (écart type relatif) | 1.654% |
| Coefficient de corrélation | 0.999939 |
| Courbe | Quadratique |
| Poids statistique | 1 |

| | Type d'échantillon | Index | Conc. | Volume | Dilution | Quantité d'échantillon | Surface | Ident | Date | Utilisée |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Standard 1 | 1 | 2.000 | 5.0 | 1.0 | 1.0 | 0.187 | s1 | 2024-03-05 17:04:50 UTC+1 | ☑ |
| 2 | Standard 2 | 1 | 5.000 | 5.0 | 1.0 | 1.0 | 0.406 | s2 | 2024-03-05 17:36:51 UTC+1 | ☑ |
| 3 | Standard 3 | 1 | 10.000 | 5.0 | 1.0 | 1.0 | 0.893 | s3 | 2024-03-05 18:08:51 UTC+1 | ☑ |
| 4 | Standard 4 | 1 | 20.000 | 5.0 | 1.0 | 1.0 | 1.861 | s4 | 2024-03-05 18:40:52 UTC+1 | ☑ |
| 5 | Standard 5 | 1 | 40.000 | 5.0 | 1.0 | 1.0 | 3.995 | S5 | 2024-03-05 19:12:55 UTC+1 | ☑ |

Courbe 1 - Eco1-E-FA-JA-18042023-CAP-NAT1

Anions

Chromatogramme
Courbe de calibration
Composé: Sulfate



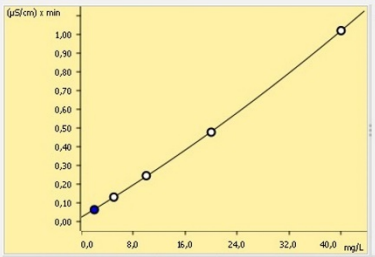

Fonction: A = 0,0209562 + 0,0104476 × Q + 1,37568E-5 × Q²

| | |
|---|---|
| Coefficient de variation (écart type relatif) | 1.627% |
| Coefficient de corrélation | 0.999941 |
| Courbe | Quadratique |
| Poids statistique | 1 |

| | Type d'échantillon | Index | Conc. | Volume | Dilution | Quantité d'échantillon | Surface | Ident | Date | Utilisée |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Standard 1 | 1 | 2.000 | 5.0 | 1.0 | 1.0 | 0.140 | s1 | 2024-03-05 17:04:50 UTC+1 | ☑ |
| 2 | Standard 2 | 1 | 5.000 | 5.0 | 1.0 | 1.0 | 0.274 | s2 | 2024-03-05 17:36:51 UTC+1 | ☑ |
| 3 | Standard 3 | 1 | 10.000 | 5.0 | 1.0 | 1.0 | 0.576 | s3 | 2024-03-05 18:08:51 UTC+1 | ☑ |
| 4 | Standard 4 | 1 | 20.000 | 5.0 | 1.0 | 1.0 | 1.209 | s4 | 2024-03-05 18:40:52 UTC+1 | ☑ |
| 5 | Standard 5 | 1 | 40.000 | 5.0 | 1.0 | 1.0 | 2.660 | S5 | 2024-03-05 19:12:55 UTC+1 | ☑ |

Anions

Chromatogramme
Courbe de calibration
Composé: Phosphate




Fonction: A = 0,0235453 + 4,15209E-3 × Q + 4,14857E-6 × Q²

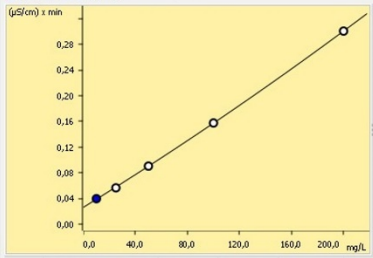
| | |
|---|---|
| Coefficient de variation (écart type relatif) | 0.904% |
| Coefficient de corrélation | 0.999980 |
| Courbe | Quadratique |
| Poids statistique | 1 |

| | Type d'échantillon | Index | Conc. | Volume | Dilution | Quantité d'échantillon | Surface | Ident | Date | Utilisée |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Standard 1 | 1 | 2.000 | 5.0 | 1.0 | 1.0 | 0.063 | s1 | 2024-03-05 17:04:50 UTC+1 | ☑ |
| 2 | Standard 2 | 1 | 5.000 | 5.0 | 1.0 | 1.0 | 0.131 | s2 | 2024-03-05 17:36:51 UTC+1 | ☑ |
| 3 | Standard 3 | 1 | 10.000 | 5.0 | 1.0 | 1.0 | 0.245 | s3 | 2024-03-05 18:08:51 UTC+1 | ☑ |
| 4 | Standard 4 | 1 | 20.000 | 5.0 | 1.0 | 1.0 | 0.478 | s4 | 2024-03-05 18:40:52 UTC+1 | ☑ |
| 5 | Standard 5 | 1 | 40.000 | 5.0 | 1.0 | 1.0 | 1.020 | S5 | 2024-03-05 19:12:55 UTC+1 | ☑ |

Courbe 1 - Eco1-E-FA-JA-18042023-CAP-NAT1

Anions

Chromatogramme
Courbe de calibration
Composé: Carbonate




Fonction: A = 0,0263809 + 2,49547E-4 × Q + 2,46471E-8 × Q²

| | |
|---|---|
| Coefficient de variation (écart type relatif) | 0.876% |
| Coefficient de corrélation | 0.999972 |
| Courbe | Quadratique |
| Poids statistique | 1 |

| | Type d'échantillon | Index | Conc. | Volume | Dilution | Quantité d'échantillon | Surface | Ident | Date | Utilisée |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Standard 1 | 1 | 10.000 | 5.0 | 1.0 | 1.0 | 0.040 | s1 | 2024-03-05 17:04:50 UTC+1 | ☑ |
| 2 | Standard 2 | 1 | 25.000 | 5.0 | 1.0 | 1.0 | 0.057 | s2 | 2024-03-05 17:36:51 UTC+1 | ☑ |
| 3 | Standard 3 | 1 | 50.000 | 5.0 | 1.0 | 1.0 | 0.090 | s3 | 2024-03-05 18:08:51 UTC+1 | ☑ |
| 4 | Standard 4 | 1 | 100.000 | 5.0 | 1.0 | 1.0 | 0.158 | s4 | 2024-03-05 18:40:52 UTC+1 | ☑ |
| 5 | Standard 5 | 1 | 200.000 | 5.0 | 1.0 | 1.0 | 0.301 | S5 | 2024-03-05 19:12:55 UTC+1 | ☑ |

**Figure 7: Calibration curves, equations, $R^2$ and relative standard deviation for ionic chromatography analyses**

| Anion | $PO_4^{3-}$ | $SO_4^{2-}$ | $CO_3^{2-}$ | $Cl^-$ |
|---|---|---|---|---|
| Correlation coefficient | 0.999980 | 0.999941 | 0.999972 | 0.999939 |
| Relative standard deviation | 0.904% | 1.627% | 0.876% | 1.654% |

**Table 6: Summary of the correlation coefficients and the relative standard deviations for each analysed anion**

### 1.5 X-Ray Powder Diffraction

X-ray powder diffraction (XRPD) analysis. XRPD data measurements were performed using a Bruker diffractometer (D6 Advance, with a Cu Kα radiation λ=1.54086 Å) equipped with a LYNXEYE SSD160-2 detector. The measurements were monitored and treated by the software Brüker Diffract.EVA 7.2 and the PDF-2 2004 database. The full width at half maximum (FWHM) is guaranteed to be inferior to 0.03° 2θ and the accuracy is evaluated at ± 0.01° 2θ.

### 1.6 Experimental protocols

#### 1.6.1 Preparation of Eco1-E-FA-JA ecocatalyst

Aerial parts of *Fallopia japonica* (stems and leaves) were collected along of the Coudoulous stream near Clapisse in the town of Aulas, France (43°59'41.1"N 3°35'22.2"E). The fresh biomass was directly shredded and sieved under 4 mm by a TBMI type HM600P shredder in order to obtain an homogeneous wet powder. The biomass powder was then heat treated at 550 °C for 4 h to obtain Eco1-E-FA-JA.

#### 1.6.2 General protocol for transesterification of *P. graveolens* essential oil by EtOH with Eco1-E-FA-JA

In a 250 mL two-neck round-bottom flask equipped with a magnetic stirrer and a condenser were added 100 g of *P. graveolens* essential oil, anhydrous EtOH (10 eq compared to formiate initial amounts) and Eco1-E-FA-JA (0.5 eq. K compared to formiate initial amounts). The mixture was stirred for 6 h (or 28 h for the monitoring experiments) at reflux of ethanol (bath at 80 °C). The resulting mixture was cooled at room temperature then distilled at atmospheric pressure. A colorless liquid was obtained (80% yield). The bath was then heated to 90 °C in order to recover the excess of ethanol.

#### 1.6.2. General protocol for transesterification of *P. graveolens* essential oil by MeOH with Eco1-E-FA-JA

In a 250 mL two-neck round-bottom flask equipped with a magnetic stirrer and a condenser were added 100 g of *P. graveolens* essential oil, anhydrous MeOH (10 eq compared to formiate initial amounts) and Eco1-E-FA-JA (0.5 eq. K compared to formiate initial amounts). The mixture was stirred for 4 h at reflux of Methanol (bath at 70 °C). The resulting mixture was cooled at room temperature then distilled at atmospheric pressure. A colorless liquid was obtained (75% yield). The bath was then heated to 80 °C in order to recover the excess of methanol.

## 2 Characterization of the catalyst Eco1-E-FA-JA

### 2.1 XRPD analyses

The diffractogram of Eco1-E-FA-JA was depicted in Figure 8.

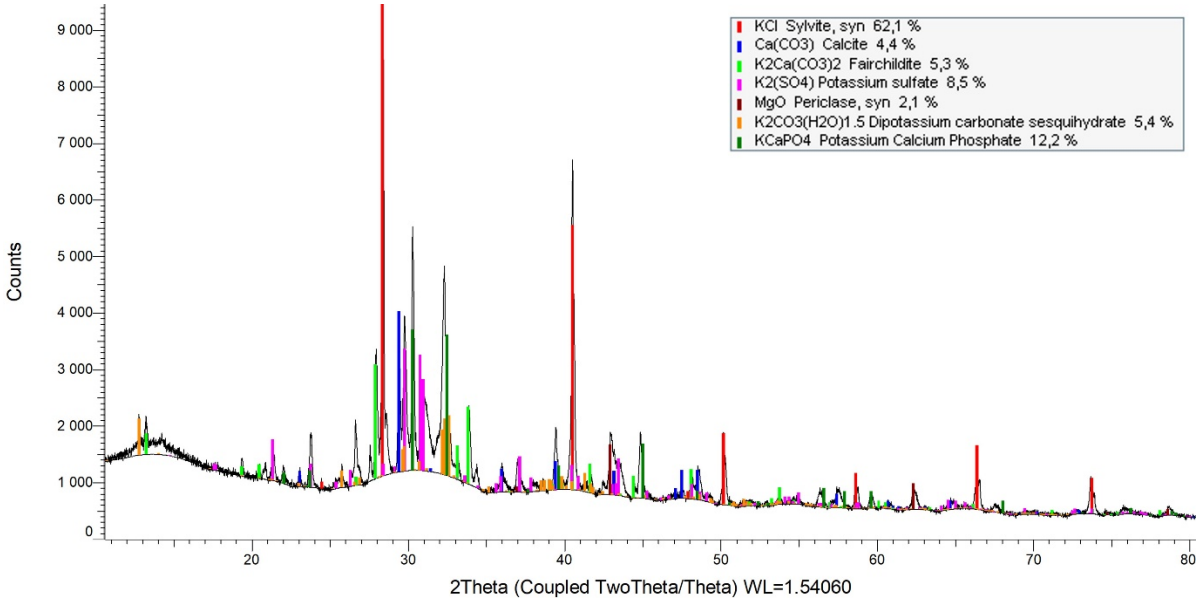



**Figure 8: XRPD diffractogram of Eco1-E-FA-JA**

### 2.2 Ionic chromatography

The chromatogram is depicted in Figure 9. The values of areas and the calculated concentration were resumed in Table 5.

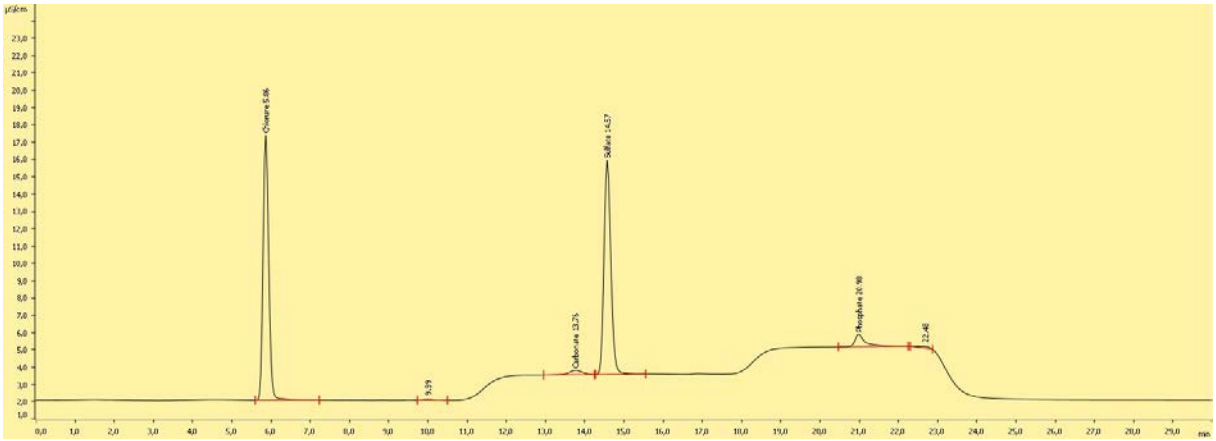


**Figure 9: Ionic chromatography analysis of Eco1-E-FA-JA**

| Anion | Retention time (min) | Surface (µS.cm$^{-1}$.min) | Concentration (mg.L$^{-1}$) |
|---|---|---|---|
| Chloride | 5.86 | 2.560 | 26.877 |
| Carbonate | 13.76 | 0.098 | 55.699 |
| Sulfate | 14.57 | 2.510 | 38.094 |
| Phosphate | 20.98 | 0.231 | 9.529 |

**Table 7: Ionic chromatography analysis results**

# 3 Results

## 3.1 Monitoring of citronellyl formate and geranyl formate conversion by GC-FID in transesterification reaction of *Pelargonium graveolens* essential oil by ethanol without catalyst

The monitoring of the conversion of citronellyl formate and geranyl formate without catalyst was reported in Figure 10.

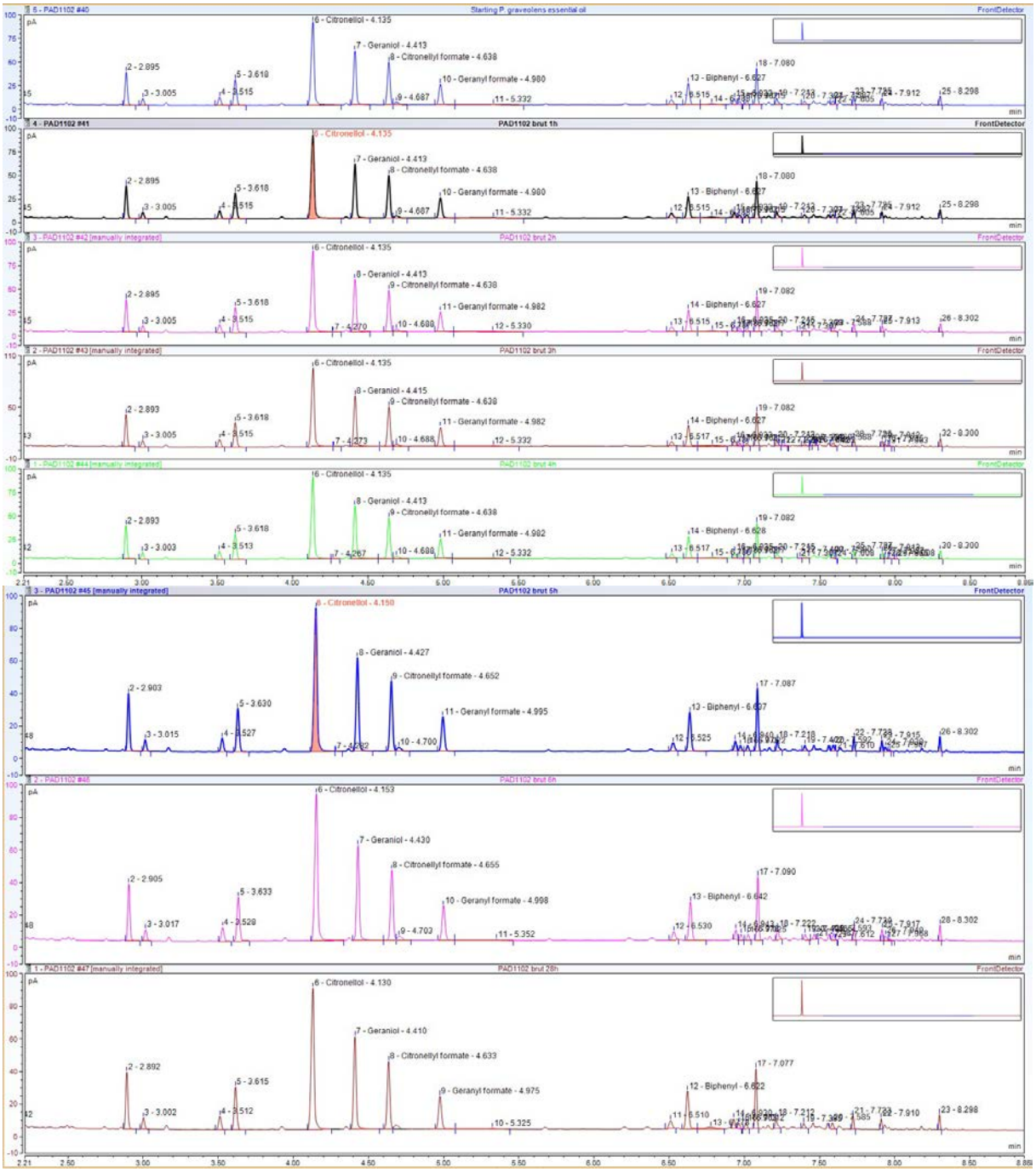
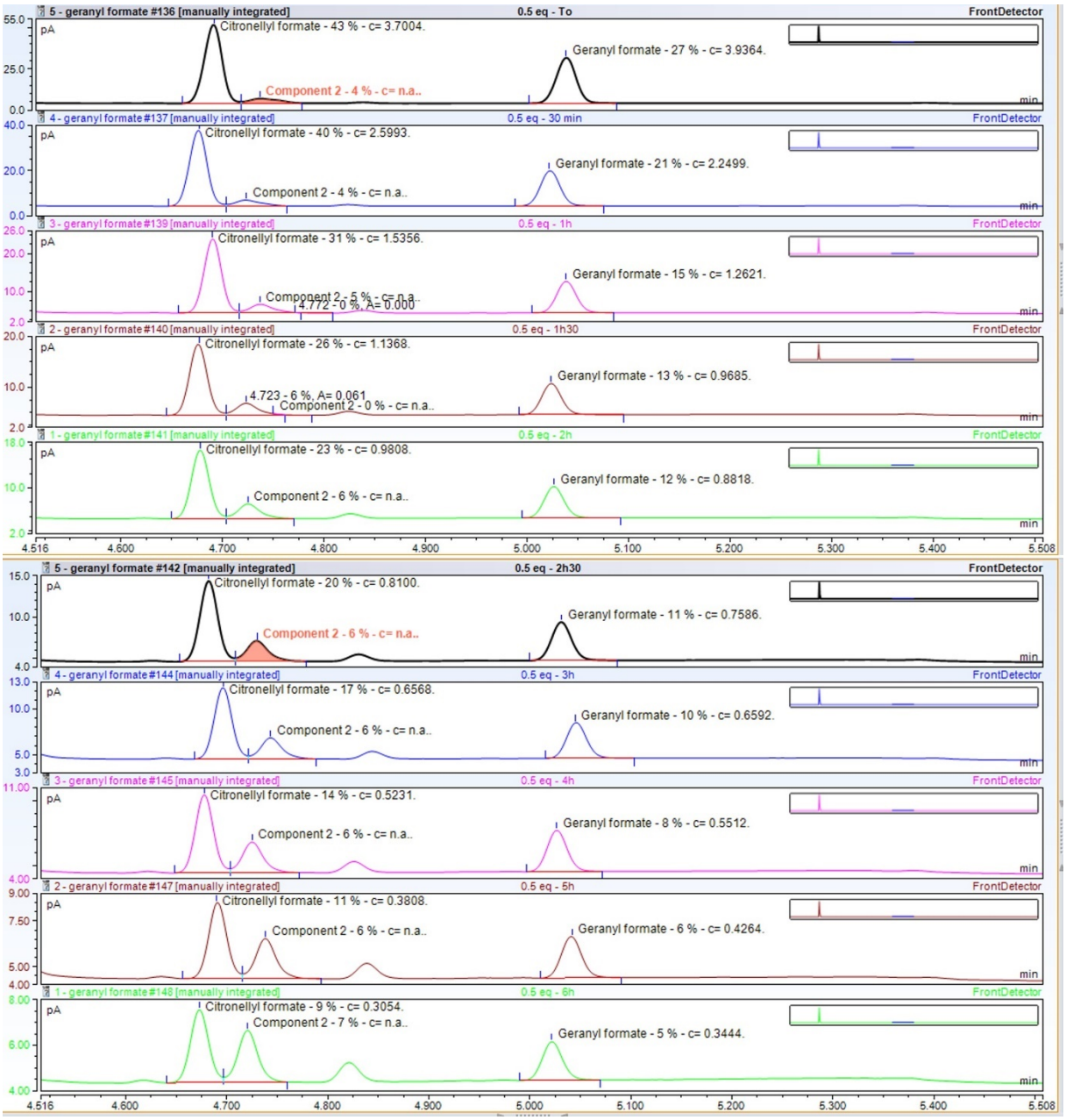



**Figure 10: GC-FID monitoring of the conversion of citronellyl and geranyl formates without catalyst in EtOH**

### 3.2 Monitoring of citronellyl formate and geranyl formate conversion by GC-FID in transesterification reaction of *Pelargonium graveolens* essential oil by ethanol

The monitoring of the conversion of citronellyl formate and geranyl formate with ecocatalyst at 0.5 equivalent of K was reported in Figure 8.


5 - geranyl formate #136 [manually integrated]
0.5 eq - To
FrontDetector
pA
Citronellyl formate - 43 % - c= 3.7004.
Geranyl formate - 27 % - c= 3.9364.
Component 2 - 4 % - c= n.a..
min
4 - geranyl formate #137 [manually integrated]
0.5 eq - 30 min
FrontDetector
Citronellyl formate - 40 % - c= 2.5993.
Geranyl formate - 21 % - c= 2.2499.
Component 2 - 4 % - c= n.a..
3 - geranyl formate #139 [manually integrated]
0.5 eq - 1h
FrontDetector
Citronellyl formate - 31 % - c= 1.5356.
Geranyl formate - 15 % - c= 1.2621.
Component 2 - 5 % - c= n.a..
4.772 - 0 %, A= 0.000
2 - geranyl formate #140 [manually integrated]
0.5 eq - 1h30
FrontDetector
Citronellyl formate - 26 % - c= 1.1368.
Geranyl formate - 13 % - c= 0.9685.
4.723 - 6 %, A= 0.061
Component 2 - 0 % - c= n.a..
1 - geranyl formate #141 [manually integrated]
0.5 eq - 2h
FrontDetector
Citronellyl formate - 23 % - c= 0.9808.
Geranyl formate - 12 % - c= 0.8818.
Component 2 - 6 % - c= n.a..
4.516
4.600
4.700
4.800
4.900
5.000
5.100
5.200
5.300
5.400
5.508
5 - geranyl formate #142 [manually integrated]
0.5 eq - 2h30
FrontDetector
pA
Citronellyl formate - 20 % - c= 0.8100.
Geranyl formate - 11 % - c= 0.7586.
Component 2 - 6 % - c= n.a..
min
4 - geranyl formate #144 [manually integrated]
0.5 eq - 3h
FrontDetector
Citronellyl formate - 17 % - c= 0.6568.
Geranyl formate - 10 % - c= 0.6592.
Component 2 - 6 % - c= n.a..
3 - geranyl formate #145 [manually integrated]
0.5 eq - 4h
FrontDetector
Citronellyl formate - 14 % - c= 0.5231.
Geranyl formate - 8 % - c= 0.5512.
Component 2 - 6 % - c= n.a..
2 - geranyl formate #147 [manually integrated]
0.5 eq - 5h
FrontDetector
Citronellyl formate - 11 % - c= 0.3808.
Component 2 - 6 % - c= n.a..
Geranyl formate - 6 % - c= 0.4264.
1 - geranyl formate #148 [manually integrated]
0.5 eq - 6h
FrontDetector
Citronellyl formate - 9 % - c= 0.3054.
Component 2 - 7 % - c= n.a..
Geranyl formate - 5 % - c= 0.3444.
4.516
4.600
4.700
4.800
4.900
5.000
5.100
5.200
5.300
5.400
5.508

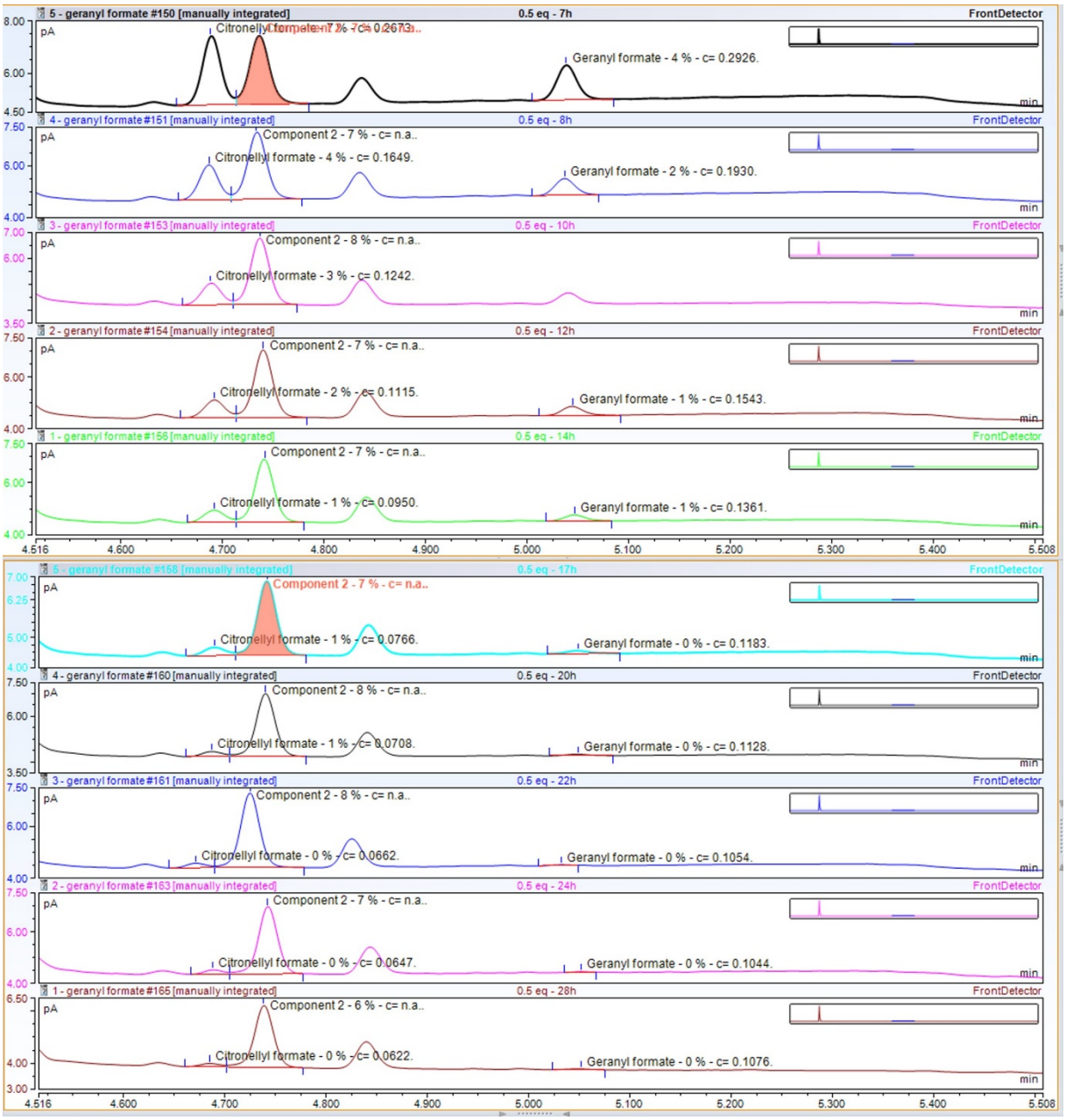



**Figure 11: GC-FID monitoring of the conversion of citronellyl and geranyl formates by 0.5 eq. K of Eco1-E-FA-JA in EtOH**

The entire chromatograms at initial time and after 8 h of reaction are depicted in Figure 11. The other compounds which are contained in *P. graveolens* were not affected by the reaction and no byproducts were identified.

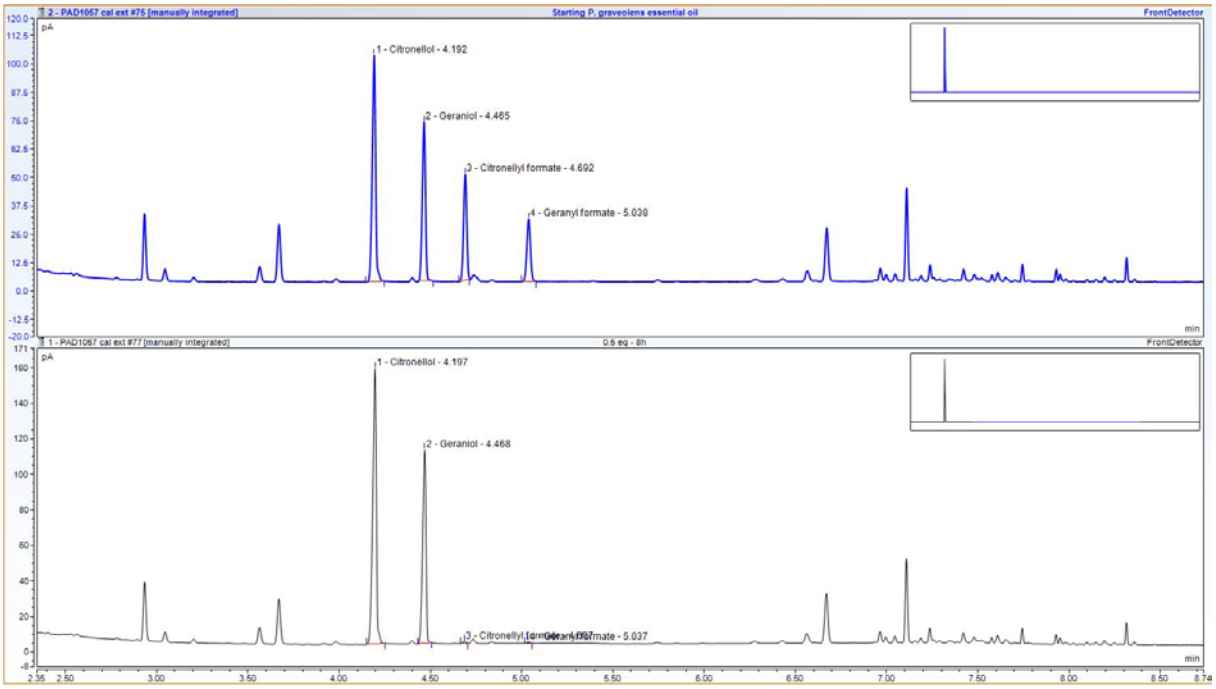



**Figure 12 : Entire chromatogram at initial time and after 8 h of transesterification reaction by EtOH**

### 3.3 GC-FID analyses of transesterification reaction of *P. graveolens* EO with MeOH.

The entire chromatograms at t = 0 h and t = 4 h of reaction are depicted in Figure 11 and the zoom on the area of interest is reported in Figure 12. The other compounds which are contained in *P. graveolens* were not affected by the reaction and no byproducts were identified.

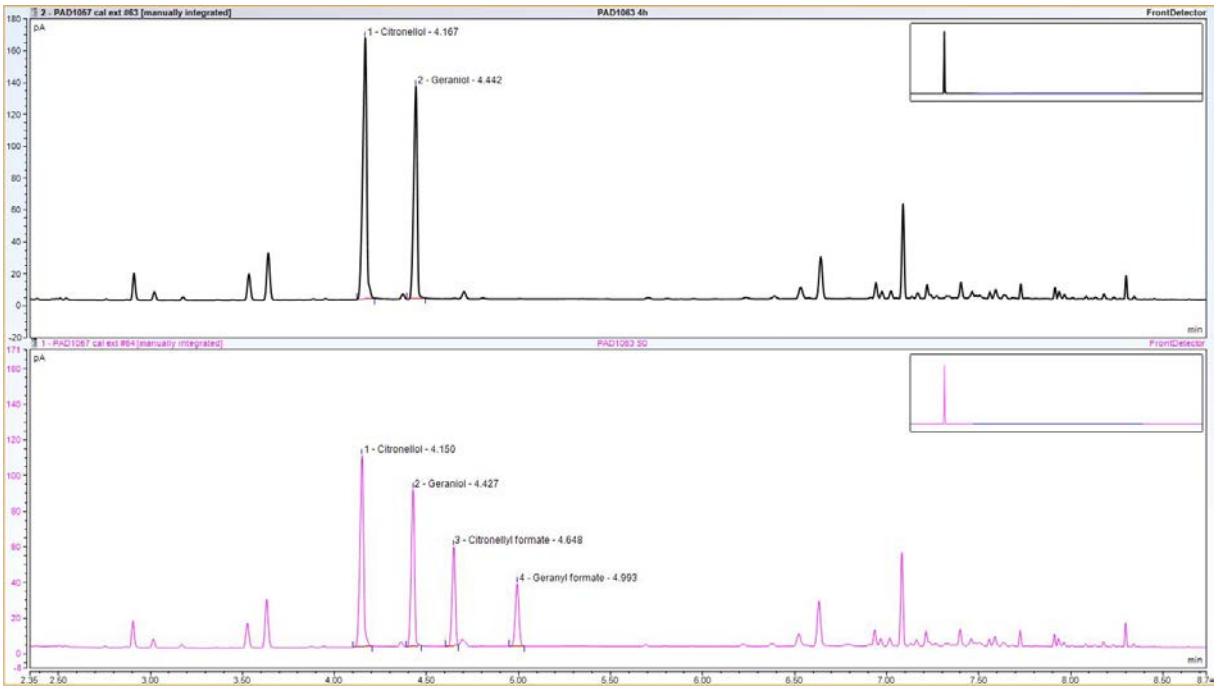



**Figure 13 : Entire GC-FID chromatograms of the reaction at initial time and after 4 h of reaction**

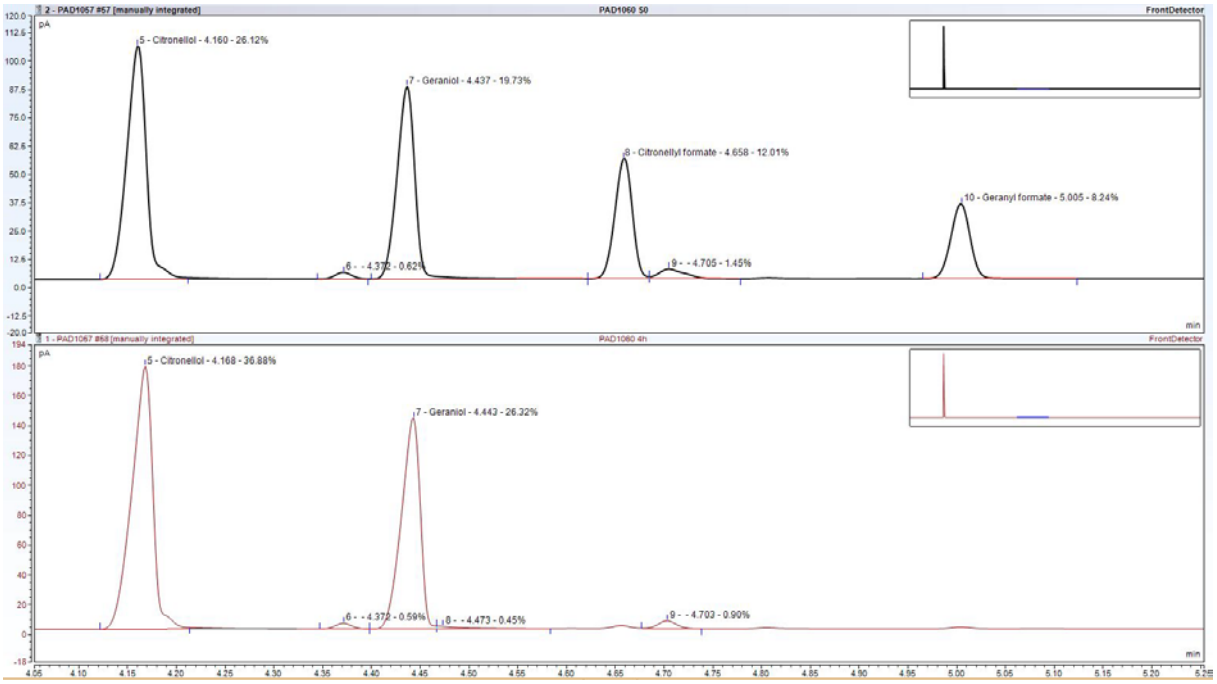



**Figure 14: Zoom on the area of interest.**

### 3.4 GC-FID analyses of transesterification reaction of P. graveolens EO with EtOH and 4 mol% $Ti(OiPr)_4$ as a catalyst.

The Figure 15 showed the GC-FID analyses of the starting EO and the crude of the reaction mixture after 8 h of reaction with $Ti(OiPr)_4$ (4 mol%) and EtOH. The conversions of CF and GF were measured at respectively 42 and 58%.

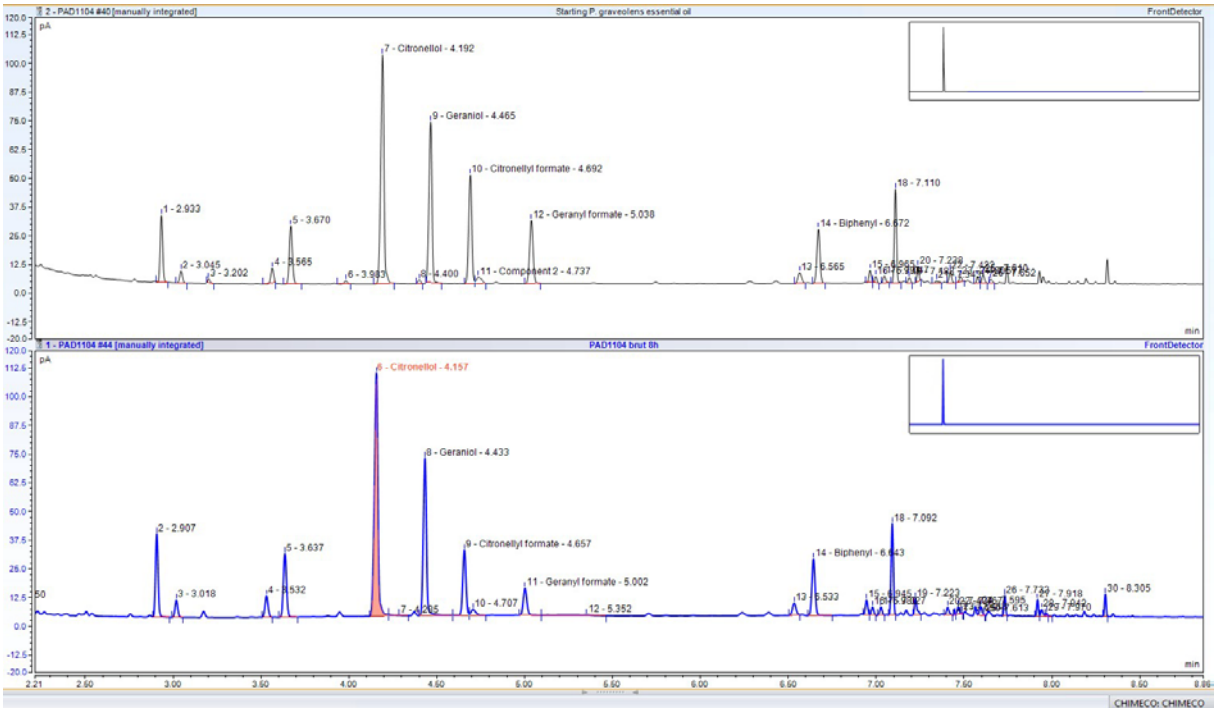



**Figure 15 : GC-FID analysis of reaction of transesterification with Ti(OiPr)4**