Supporting Information
for
Tunable microwave-assisted method for the solvent-free and catalyst-free peracetylation of natural products
Manuela Oliverio*1,2, Paola Costanzo1, Monica Nardi3, Carla Calandruccio1, Raffaele Salerno2, and Antonio Procopio1,2

Address: 1Department of Health Science, University Magna Graecia of Catanzaro, Viale Europa, Loc. Germaneto, 88100 Catanzaro, Italy, 2InterRegional Center for Food Safety and Health, University Magna Graecia of Catanzaro, Viale Europa, Loc. Germaneto, 88100 Catanzaro, Italy and 3Department of Chemistry, Università della Calabria, Cubo 12C, 87036-Arcavacata di Rende (CS), Italy

Email: Manuela Oliverio - m.oliverio@unicz.it.
*Corresponding author

Scaled oleuropein peracetylation procedure, GC–MS, LC–HRMS, 1H and 13C NMR spectra of new compounds, as well as calculation for green chemistry metrics
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Experimental

Scale-up MW-assisted peracetylation of oleuropein

For scale up reaction 8 positions of the XF100 rotor were occupied with 100 mL PTFE-TFM vessel, loaded in a ceramic pressure jacket sealed with a dedicated PTFE-TFM cap with integrated relief valve and safety disk, fixed in a PEK seal holder.

Oleuropein (1 g) was left to react under MW heating with dry acetic anhydride (10 mL) in a 100 mL vial (rotor XF-100), equipped with a magnetic stirrer in the presence of molecular sieves (10% w/w). The microwave oven, equipped with IR sensor for external temperature control has been set with the power program provided as described in Table S1.

![Figure S1: Temperature profiles in Scale-up and lab scale reactions](image)

Table S1: P-controlled MW program (Synthos 3000, equipped with XF-100 rotor) for the scaled peracetylation of oleuropein

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>P (W)</th>
<th>T (°C)(^{a})</th>
<th>IR limit (°C)</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>0→5</td>
<td>0→350</td>
<td>0→110</td>
<td>105</td>
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</tr>
<tr>
<td>5→10</td>
<td>350</td>
<td>110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10→12</td>
<td>350→400</td>
<td>110→120</td>
<td></td>
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</tr>
<tr>
<td>12→62</td>
<td>400</td>
<td>120</td>
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<tr>
<td>62→65</td>
<td>0</td>
<td>120→50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)Calculated as follows: \(T_{\text{internal}} = 1.214 \times T_{\text{IR}}\)
N-acetyl anthranilic acid (1a) Yellow powder; Yield 100%; $^1$H NMR and $^{13}$C NMR data were compared with those reported in a spectra Database [1].

Acetyl Salicylic acid (2a) White powder; Yield 100%; $^1$H-NMR and $^{13}$C-NMR data were compared with those reported in a spectra Database [1].

O-acetyl cholesterol (3a) White powder; Yield 62%; MS (70 eV, IE): m/z (%) = 368 [M$^+$-CH$_2$COO] (100), 353 [M$^+$-CH$_2$COOCH$_3$] (30), 247 [M$^+$-CH$_2$COOCH$_3$-C$_9$H$_{13}$] (30), 147 [C$_{11}$H$_{15}$$^+$] (100), 133 [C$_{11}$H$_{15}$$^+$-CH$_2$] (45), 119 [C$_{11}$H$_{15}$$^+$-2xCH$_2$] (50), 105 [C$_{11}$H$_{15}$$^+$-3xCH$_2$] (70), 91 [C$_{11}$H$_{15}$$^+$-4xCH$_2$] (60); $^1$H NMR (300MHz, CDCl$_3$, 25°C, TMS) $\delta$: 5.40-5.35 (br d, J=4.8 Hz, 1H, H$_A$), 4.67-4.54 (m, 1H, H$_B$), 2.36-2.28 (br d, J=7.7 Hz, 2H, H$_C$), 2.04 (s, 3H, H$_D$), 2.02-0.83 (m, 38H), 0.67 (s, 3H, H$_E$); $^{13}$C NMR (300MHz, CDCl$_3$, 25°C, TMS) $\delta$: 170.2, 140.2, 122.7, 57.2, 56.8, 50.7, 42.8, 40.2, 39.8, 38.5, 37.4, 37.0, 36.6, 36.0, 32.4, 32.2, 28.3, 28.2, 28.1, 24.5, 24.2, 22.8, 22.6, 21.4, 21.2, 19.4, 19.0, 12.1, 10.3.

Peracetylated Hydroxytyrosol (4a) Yellow Oil; Yield 100%; $^1$H-NMR and $^{13}$C-NMR data were compared with those reported in literature [2].

O-acetyl citronellol (6a) Yellow Oil; Yield 100%; MS (70 eV, IE): m/z (%) = 198 [M$^+$] (1), 138 [M$^+$-CH$_2$CO$_2$H] (40), 123 [C$_{10}$H$_{15}$$^+$-CH$_3$] (60), 109 [C$_9$H$_{15}$$^+$-CH$_2$] (30), 95 [C$_9$H$_{15}$$^+$-2xCH$_2$] (98), 81 [C$_9$H$_{15}$$^+$-3xCH$_3$] (100), 69 [C$_9$H$_{15}$$^+$-C$_9$H$_6$] (98); $^1$H NMR (300MHz, CDCl$_3$, 25°C, TMS) $\delta$: 5.14-5.04 (br t, J$_{CD}$=6 Hz, 1H, H$_C$), 4.18-4.02 (m, 2H, H$_E$), 2.04 (s, 3H, H$_D$), 2.04-1.87 (m, 2H, H$_B$), 1.68 (s, 3H, H$_A$), 1.60 (s, 3H, H$_A$); 13C NMR (300MHz, CDCl$_3$, 25°C, TMS) $\delta$: 171.7, 135.6, 129.9, 82.4, 64.9, 63.2, 39.9, 35.8, 35.6, 35.3, 35.2, 33.8, 30.2, 30.0, 29.8, 26.7, 26.6, 25.2, 24.6, 21.3, 19.8, 19.7, 19.0.

O-acetyl paracetamol (7a) White powder; Yield 93%; MS (70 eV, IE): m/z (%) = 193 [M$^+$] (10), 151 [M$^+$-CH$_2$C=O] (50), 109 [C$_9$H$_{15}$$^+$-CH$_2$] (30), 105 [C$_9$H$_{15}$$^+$-2xCH$_2$] (45), 81 [C$_9$H$_{15}$$^+$-3xCH$_3$] (100), 69 [C$_9$H$_{15}$$^+$-C$_9$H$_6$] (98); $^1$H NMR (300MHz, CDCl$_3$, 25°C, TMS) $\delta$: 7.62-7.52 (br s, 1H, NH), 7.51-7.43 (d, J$_{ortho}$=8.8 Hz, 2H, H$_C$), 6.96-7.06 (d, J$_{ortho}$=8.8 Hz, 2H, H$_D$), 2.29 (s, 3H, H$_E$), 2.18 (s, 3H, H$_A$); 13C NMR (300MHz, CDCl$_3$, 25°C, TMS) $\delta$: 170.0, 168.6, 147.2, 135.9, 122.3, 122.1, 24.8, 21.4.

N-Boc-O-acetyl tyrosine methyl ester (8a) White powder; Yield 95%; MS (70 eV, IE): m/z (%) = 337 [M$^+$] (1), 264 [M$^+$-Or-But] (10), 219 [M$^+$-2xCOOCH$_3$] (15), 178 [M$^+$-COCH$_3$-NH$_2$COO-But] (100), 107 [CH$_3$POO$^-$] (45); $^1$H NMR (300MHz, CDCl$_3$, 25°C, TMS) $\delta$: 7.13 (s, 2H, H$_G$), 7.03 (s, 2H, H$_F$), 5.1-4.8 (br s, 1H, NH), 4.7-4.3 (br s, 1H$_D$), 3.71 (s, 3H, H$_A$), 3.2-2.8 (br s, 2H, H$_E$), 2.29 (s, 3H, H$_C$), 1.42 (s, 3H, H$_B$); 13C NMR (300MHz, CDCl$_3$, 25°C, TMS) $\delta$: 172.5, 169.7, 155.4, 150.0, 134.0, 130.6, 121.9, 80.3, 54.7, 52.6, 38.0, 28.6, 21.4.

O-acetyl myrtenol (10a) Yellow Oil; Yield 100%; MS (70 eV, IE): m/z (%) = 152 [M$^+$-CH$_2$COH] (1), 119 [M$^+$-CH$_2$COH-CH$_3$] (40), 91 [119$^+$-CH$_2$=CH$_2$] (100); $^1$H NMR (300MHz, CDCl$_3$, 25°C, TMS) $\delta$: 5.59 (m, 1H, H$_C$), 4.51-4.36 (m, 2H, H$_D$), 2.45-2.08 (m, 5H, H$_E$); 2.05 (s, 3H, H$_A$), 1.29 (s, 1H, H$_H$), 1.21-1.16 (d, J$_{EF}$=8.7 Hz, 1H, H$_F$), 0.84 (s, 3H, H$_H$); 13C NMR (300MHz, CDCl$_3$, 25°C, TMS) $\delta$: 171.4, 143.3, 121.8, 67.4, 43.9, 41.1, 38.4, 21.8, 31.6, 26.5, 21.3.
Peracetylated Methyl-α-D-glucopyranoside (11a) White powder; Yield 70%; $^1$H-NMR and $^{13}$C-NMR data were compared with those reported in literature [3].

Triacetyl Uridine (12a) Yellow Oil; Yield 92%; HRMS: [M+Na$^+$] m/z 393.0902 (theoretical [M+Na$^+$] m/z 393.0904); $^1$H NMR (300MHz, CDCl$_3$, 25°C, TMS) δ: 7.43-7.38 (d, $J_{A,B}$=8.2 Hz, 1H, H$_A$), 6.08-6.02 (d, $J_{C,D}$=4.8 Hz, 1H, H$_C$), 5.83-5.77 (d, $J_{A,B}$=8.2 Hz, 1H, H$_B$), 5.38-5.29 (m, 2H, H$_G$), 4.36-4.30 (m, 3H, H$_{D,E,F}$), 2.15 (s, 3H, H$_H$), 2.14 (s, 3H, H$_I$), 2.11 (s, 3H, H$_L$); $^{13}$C NMR (300MHz, CDCl$_3$, 25°C, TMS) δ: 170.1, 169.5, 162.4, 150.4, 139.5, 103.6, 88.3, 80.5, 73.1, 70.7, 63.3 20.7, 20.4 20.3.

Peracetylated Oleuropein (14a) Yellow powder; Yield 100%; MS, $^1$H-NMR e $^{13}$C-NMR data were compared with those reported in literature [2].

Peracetylated β-D-lactose (15a) White powder; Yield 50%; $^1$H-NMR and $^{13}$C-NMR data were compared with those reported in literature [4].
Green chemistry metrics
Atom Economy (AE) and Reaction Mass Efficiency (RME) were used to evaluate the greenness of the procedure, calculated according to the report of Constable et al.[5]:

Atom economy (AE) = \( \frac{\text{FW all reaction products}}{\text{FW all reaction reagents}} \times 100 \)

Reaction Mass Efficiency (RME) = \( \frac{\text{Mass of all reaction products}}{\text{Mass of all reaction reagents}} \times 100 \)

The general reaction took into account was:

\[
\text{R-(OH)}_n + n \text{Ac}_2\text{O} \rightarrow \text{R-(OAc)}_n + n \text{AcOH}
\]

Were \( n \) is the stoichiometric coefficient between reagents.

The calculations are reported in Table S2.

### Table S2

<table>
<thead>
<tr>
<th>FW reag tot (FW AA X stoch)</th>
<th>FW perac phenol</th>
<th>AE</th>
<th>yield</th>
<th>RME</th>
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<tr>
<td>1630</td>
<td>1030</td>
<td>63</td>
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<td>28,35</td>
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</table>

For the calculation of mass intensity and mass productivity, the work-up used in the general reaction was considered as a part of the full process. In this case the general reaction equation is composed by the following three steps:
Peracetylated phenol, EtOAc and NaOAc were considered as useful products, while phenol, excess of acetic anhydride, EtOH and NaHCO₃ were included in the total mass calculation respectively as reagents, solvent and reaction auxiliaries, and used in the following equations:

\[ \text{Mass Intensity (MI)} = \frac{\text{Mass of all chemicals used}}{\text{Mass of all reaction products}} \]

\[ \text{Mass Productivity (MP)} = \frac{1}{\text{Mass Intensity}} \times 100 \]

Table S3 summarizes the calculations of the previous parameters.

**Table S3**

<table>
<thead>
<tr>
<th>Phenol mass</th>
<th>ecc AA mass (reag + solv)</th>
<th>auxiliary mass</th>
<th>perac phenol mass</th>
<th>EtOAc mass</th>
<th>NaOAc mass</th>
<th>MI</th>
<th>MP</th>
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</thead>
<tbody>
<tr>
<td>13,7</td>
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<td>17.9</td>
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<tr>
<td>13,8</td>
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<td>18</td>
<td>871.2</td>
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</tbody>
</table>
GC-EIMS spectra

Sample 3a
Sample 5a

\[
\begin{align*}
\text{H}_3\text{CO} & \quad \text{OAc} \\
\text{AcO} & \quad \text{OAc} \\
\text{5a} & 
\end{align*}
\]
Sample 6a
Sample 7a
Sample 8a

\[
\begin{align*}
\text{AcO} & \quad \text{H} \quad \text{N} \quad \text{Boc} \\
\text{HN} & \quad \text{OMe} \\
\end{align*}
\]

Data File: peracet_3_1-10
Operator: ITQ
Acquisition Date: 02/27/15 12:04:59 PM
Run Time (min): 26.50
Instrument Method: C:\Meilirur\METODY\Glicerol\ecocontrol_400
Current Processing Method: N/A

RT: 0.00 - 58.50

\[
\begin{align*}
\text{mz} & \quad 20.46 \\
\end{align*}
\]

\[
\begin{align*}
\text{mz} & \quad 175.1 \\
\end{align*}
\]

\[
\begin{align*}
\text{mz} & \quad 182.1 \\
\end{align*}
\]

\[
\begin{align*}
\text{mz} & \quad 216.8 \\
\end{align*}
\]
Sample 9a

**Peracetylated albutamol**

**Di-O-acetylated salbutamol**

**Mono-O-acetylated salbutamol**
Sample 10a

\[
\text{AcO}
\]

RT: 0.00 - 30.53

Relative Abundance

Mass spectra for Sample 10a.
LC/HRMS spectra

Sample 12a

LCHRMS (m/z) spectrum of peracetylated uridine (isolated product) in total ion current (TIC, entry A) and extract ion current (XIC, B [M + H]+). C ([M + Na]+).
HRMS ($m/z$, [M + Na]$^+$; [M + H]$^+$ accuracy (ppm)) spectra of peracetylated uridine:

Peracetylated uridine: experimental value [M + Na]$^+$ $m/z$ 393.0902 (theoretical [M + Na]$^+$ $m/z$ 393.0904), and [M + H]$^+$ $m/z$ 371.1083 (theoretical [M + H]$^+$ $m/z$ 371.1085).
Sample 13a

LCHRMS (m/z, [M + Na]⁺ and [M – H]⁻ only for entry F) spectrum of O-acetylated quercetin (reaction mix) in total ion current (TIC, entry A) and extract ion CURRENT (XIC, entry B–F) relative to main acetylated forms: tetra-O-acetylated quercetin (8% of the mix, entry B), di-O-acetylated-quercetin (60% of the mix, entry C), tri-O-acetylated quercetin (7% of the mix, entry D), mono-O-acetylated quercetin (25% of the mix, entry E). The conversion was estimated around 96%, because of the presence of 6% of unreacted quercetin (entry F).
HRMS (m/z, [M+Na]+; accuracy (ppm)) spectra of O-acetylated Quercetin:

Sample 16a

LCHRMS ($m/z$, [M + Na]$^+$) spectrum of $O$-acetylated $\alpha$-ederin (reaction mix) in total ion current (TIC, entry A) and extract ion current (XIC, entry B,C) relative to main acetylated-forms: Esa-$O$-acetylated $\alpha$-ederin (85% of the mix, entry B), penta-$O$-acetylated $\alpha$-ederin (15% of the mix, entry C).
HRMS (m/z, [M + Na]⁺; R = operative resolution; accuracy (ppm)) spectra of O-acetylated α-ederin:


Sample 17a

LCHRMS (m/z, [M + Na]+) of spectrum of O-acetylated rutin (isolated product) in extract ion (XIC) of Peracetylated-rutin.
HRMS $m/z, [M + Na]^+; R = \text{operative resolution; accuracy (ppm)}$ spectra of peracetylated rutin:

$^1$H NMR spectra

Sample 3a
Sample 5a
Sample 6a
Sample 7a

![Chemical Structure]

*** Current Data Parameters ***
NAME : ac1
EXPNO : 1
PROCNO: 1
Sample 8a
Sample 9a
Sample 10a

*** Current Data Parameters ***
NAME : ac15
EXPNO : 1
PROCNO : 1
Samples

\[
\begin{align*}
&L - \text{carboxyl} \\
&G - \text{ester} \\
&\text{A} - \text{amide} \\
&\text{B} - \text{amide} \\
&\text{HE} - \text{hydroxyl} \\
&\text{HF} - \text{hydroxyl} \\
&\text{HC} - \text{hydroxyl} \\
&\text{D} - \text{ester} \\
&\text{H} - \text{ester}
\end{align*}
\]

*** Current Data Parameters ***

NAME : ac21
EXPNO : 1
PROCNO : 1

S30
Sample 13a

(mix, characterization of the major product)
Sample 17a
$^{13}$C NMR spectra

Sample 3a
Sample 6a
Sample 7a

![Chemical Structure](image)

*** Current Data Parameters ***
- NAME : ac1c13
- EXPNO : 1
- PROCNO : 1

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169.9907
168.6208
147.1893
135.8989
122.3192
121.1608
77.7829
77.3600
76.9371
24.8432
21.4230
(ppm)

---

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
**Sample 8a**

![Chemical Structure](image)

***Current Data Parameters***

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**NMR Spectra**

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S38
Sample 9a

![Chemical Structure]

*** Current Data Parameters ***
NAME : ac13c13
EXPNO : 1
PROCNO : 1
**Current Data Parameters**

NAME: ac15c13

EXPNO: 1

PROCNO: 1
Sample 12a

*** Current Data Parameters ***
NAME : ac21c13
EXPNO : 1
PROCNO : 1
Sample 13a

*(mix, characterization of the major product)*
Sample 17a

References

1. SDBS Web: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 02/03/2015)