Supporting Information (1)

Extracted ion chromatograms, FT-ICR MS spectra and Isotopic fine structures of key compounds discriminating Korean and Brazilian propolis, proposed in Table 2
Compound #1 in Table 2

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.79</td>
<td>161.060</td>
</tr>
</tbody>
</table>

- **a) Extracted Ion Chromatogram**
- **b) Spectrum**
- **c) Isotopic Fine Structure**

Experimental

Theoretical

C10H9O2
Compound #2 in Table 2

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.26</td>
<td>209.081</td>
</tr>
</tbody>
</table>

a) Extracted Ion Chromatogram

b) Spectrum

K_1-B,5_02_377.d: +MS, 8.07-8.35min #175-181

209.080846
1+ 191.070268
1+ 231.062812

210.084212
1+ 211.085082
1+ 211.087545

211.086
1+ 211.085124
1+ 211.087577

3) Isotopic Fine Structure

C11H13O4

Experimental

Theoretical
Compound #3 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

K_1-8,5_02_377.d: +MS, 16.70-16.79min #363-365

Theoretical
C15H19O4

Experimental
Compound #4 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

Theoretical

C17H15O6
Compound #5 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

K_1-8.5_02_377.d: +MS, 12.80-12.94min #278-281

Experimental

Theoretical

C16H13O7
Compound #6 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical

C18H17O6
Compound #7 in Table 2

- **a) Extracted Ion Chromatogram**
- **b) Spectrum**
- **c) Isotopic Fine Structure**

**Experimental**

**Theoretical**

C20H20NO4
Compound #8 in Table 2

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.45</td>
<td>343.118</td>
</tr>
</tbody>
</table>

**a) Extracted Ion Chromatogram**

**b) Spectrum**

**c) Isotopic Fine Structure**

Experimental

C19H18O6
Compound #9 in Table 2

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.49</td>
<td>285.112</td>
</tr>
</tbody>
</table>

### a) Extracted Ion Chromatogram

![Extracted Ion Chromatogram](image)

### b) Spectrum

![Spectrum](image)

### c) Isotopic Fine Structure

![Isotopic Fine Structure](image)

Experimental

Theoretical

C17H17O4
Compound #10 in Table 2

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.48</td>
<td>285.075</td>
</tr>
</tbody>
</table>

a) Extracted Ion Chromatogram

b) Spectrum

K_1-B,5_02_377.d: +MS, 12.39-12.53min #269-272

M = 285.075819
M+1 = 286.079179
M+2 = 287.080078

Experimental

Theoretical
C16H12O5
Compound #11 in Table 2

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.43</td>
<td>295.227</td>
</tr>
</tbody>
</table>

- **a) Extracted Ion Chromatogram**
  - Compound #11 (m/z 295.227)
  - Experimental: K_1-B,5_02_377.d: +MS, 18.40-18.44min #400-401

- **b) Spectrum**
  - Mass peaks: 295.227024
  - Isotopes: 611.429165

- **c) Isotopic Fine Structure**
  - 

**Theoretical Compound**

C18H31O3

Experimental compound

Theoretical compound
Compound #12 in Table 2

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.43</td>
<td>255.065</td>
</tr>
</tbody>
</table>

**a) Extracted Ion Chromatogram**

**b) Spectrum**

**c) Isotopic Fine Structure**

**Experimental**

**Theoretical**

C15H11O4
Compound #13 in Table 2

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.98</td>
<td>357.133</td>
</tr>
</tbody>
</table>

**a) Extracted Ion Chromatogram**

**b) Spectrum**

**c) Isotopic Fine Structure**

Theoretical

C20H21O6

Experimental
Compound #14 in Table 2

RT | m/z
---|---
10.66 | 269.081

Experimental

Theoretical
C16H13O4
Compound #15 in Table 2

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.69</td>
<td>269.081</td>
</tr>
</tbody>
</table>

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical

C16H13O4
Compound #16 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical

C16H13O7
Compound #17 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical

C15H13O5
Compound #18 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical
C15H14O4
Compound #19 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.30</td>
<td>268.264</td>
</tr>
</tbody>
</table>

Experimental

C17H34NO
Compound #20 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical

C20H40NO
Compound #21 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.25</td>
<td>301.071</td>
</tr>
</tbody>
</table>

c) Isotopic Fine Structure

Experimental

C16H13O6
Compound #22 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

Experimental

Theoretical

C17H15O7
Compound #23 in Table 2

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.26</td>
<td>215.107</td>
</tr>
</tbody>
</table>

a) Extracted Ion Chromatogram

b) Spectrum

Experimental

Theoretical

C14H15O2
Compound #24 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

Experimental

Theoretical C14H15O3
Compound #25 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

Experimental

Theoretical

C14H17O3
Compound #26 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

Experimental

Theoretical

C14H17O4
Compound #27 in Table 2

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.96</td>
<td>271.097</td>
</tr>
</tbody>
</table>

a) Extracted Ion Chromatogram

Experimental

Theoretical

C16H15O4
Compound #28 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

B_1-8,3_02_367.d: +MS, 18.72-18.85min #406-409

<table>
<thead>
<tr>
<th>Compound #28 in Table 2</th>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>18.78</td>
<td>273.258</td>
</tr>
</tbody>
</table>

C20H33

Experimental

Theoretical
Compound #29 in Table 2

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.59</td>
<td>301.180</td>
</tr>
</tbody>
</table>

a) Extracted Ion Chromatogram

b) Spectrum

Experimental

Theoretical

C19H25O3
Compound #30 in Table 2

<table>
<thead>
<tr>
<th>RT</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.48</td>
<td>311.128</td>
</tr>
</tbody>
</table>

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical

C19H19O4
Compound #31 in Table 2

**a) Extracted Ion Chromatogram**

**b) Spectrum**

**c) Isotopic Fine Structure**

---

### Experimental

**RT**

<table>
<thead>
<tr>
<th>17.81</th>
</tr>
</thead>
</table>

### Theoretical

C20H33O3

<table>
<thead>
<tr>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>321.2423</td>
</tr>
</tbody>
</table>
Compound #32 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

C20H27O6
Compound #33 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical

C22H31O6
Compound #34 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

C25H25O12

Experimental

Theoretical

C25H25O12
Compound #35 in Table 2

a) Extracted Ion Chromatogram

b) Spectrum

Experimental

Theoretical

C32H47O6

b) Spectrum

- Experimental
- Theoretical

C32H47O6
Supporting Information (2)

Extracted ion chromatograms, FT-ICR MS spectra and isotopic fine structures of key compounds discriminating Korean and Chinese propolis, proposed in Table 3
Compound #1 in Table 3

- **a) Extracted Ion Chromatogram**

- **b) Spectrum**

- **c) Isotopic Fine Structure**

Experimental

C17H15O4
Compound #2 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical
C19H25O2
Compound #3 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

m/z 315.195539

K_1-85_02_377.d: +MS, 17.76-17.90 min #386-389

m/z 655.397596

m/z 315.196

m/z 316.198923

m/z 317.199837

Time [min]

Experimental

Theoretical

C20H27O3
Compound #4 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical

C20H19NO4
Compound #5 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

K_1-8.5_02_377.d: +MS, 15.42-15.79min #335-343

Experimental

Theoretical

C24H19O6
Compound #6 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical

C24H21O7
Compound #7 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

K_1-8,5_02_377.d: +MS, 18.49-18.77 min #402-408

389.11933
746.92615
973.67795

Experimental

C30H45O3

Theoretical
Compound #8 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

K_1-8.5_02_377.d: +MS, 18.58-18.63 min #404-405

Experimental

Theoretical

C30H51O4
Compound #9 in Table 3

- **a) Extracted Ion Chromatogram**
- **b) Spectrum**
- **c) Isotopic Fine Structure**

**Experimental**

**Theoretical**

C31H53O4
Compound #10 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical

C30H51O5
Compound #11 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

K_1-8,5,02_377.d: +MS, 18.22-18.58min #396-404

K_1-9,5,02_377.d: +MS, 18.22-18.58min #396-404

M 501.321356
M+1 502.324426
M+2 503.327788

M 501.321066
M+1 502.3249126
M+2 503.3279589

C30H45O6

Experimental

Theoretical
Compound #12 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

K_1-8.5_02_377.d: +MS, 18.54-19.04min #403-414

Experimental

Theoretical

C30H47O6
Compound #13 in Table 3

- a) Extracted Ion Chromatogram
- b) Spectrum
- c) Isotopic Fine Structure

<table>
<thead>
<tr>
<th>min</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.50</td>
<td>563.168</td>
</tr>
</tbody>
</table>

Experimental C28H32ClO10

Theoretical
Compound #14 in Table 3

Experimental

<table>
<thead>
<tr>
<th>min</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.79</td>
<td>161.060</td>
</tr>
</tbody>
</table>

Theoretical

C10H9O2
Compound #15 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

K_1-B_5_02_377.d: +MS, 12.57-12.71 min #273-276

Experimental

Theoretical

C18H17O6
Compound #16 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical
C16H13O5
Compound #17 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

K₁-B,5₂₀₂₇₇.d: +MS, 14.13-14.32min #307-311

Experimental

C₁₄H₁₇O₄

Theoretical
Compound #18 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical

C16H13O5
Compound #19 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

C19H19O6
Compound #20 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

K_1-8_5_02_377.d: +MS, 15.33-15.56min #333-338

M+1
M+2

M

m/z

315.086664

651.148500

491.099841

316.089994

317.093354

315.087

Experimental

Theoretical

C17H15O6
Compound #21 in Table 3

Experimental

Theoretical
C11H13O4
Compound #22 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

K_1-B.5_02_377.d: +MS, 12.80-13.03min #278-283

Experimental

Theoretical

C16H13O7
Compound #23 in Table 3

- **a) Extracted Ion Chromatogram**
- **b) Spectrum**
- **c) Isotopic Fine Structure**

**Experimental**

<table>
<thead>
<tr>
<th>min</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.97</td>
<td>285.076</td>
</tr>
</tbody>
</table>

**Theoretical**

C16H13O5
Compound #24 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

K_1-8,5_02_377.d: +MS, 17.90-18.03min #389-392

M 357.133467
M+1 358.136620
M+2 359.139974

M+2 359.139974

M 357.133265
M+1 358.136620
M+2 359.140161

m/z

Experimental

Theoretical

C20H21O6
Compound #25 in Table 3

a) Extracted Ion Chromatogram

Experimental

b) Spectrum

Theoretical

C15H13O4
Compound #26 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

C18H34O4
Compound #27 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

C_1-8,4_02_372.d: +MS, 16.88-17.02min #367-370

C_1-8,4_02_372.d: +MS, 16.88-17.02min #367-370

333.203733 1+
643.418428

1+
643.418428

m/z 644.42

644.421800 1+
644.414795 1+
644.421120 1+

1+
645.425203

645.424481

C36H61O8

Experimental

Theoretical

m/z 643.419

min

16.94

m/z

643.419
Compound #28 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental
C15H11O5
Compound #29 in Table 3

(a) Extracted Ion Chromatogram

(b) Spectrum

(c) Isotopic Fine Structure

Experimental

Theoretical

C18H35O3
**Compound #30 in Table 3**

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

<table>
<thead>
<tr>
<th>Experimental</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C18H33O3</strong></td>
<td><strong>C18H33O3</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>min</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.68</td>
<td>297.243</td>
</tr>
</tbody>
</table>
Compound #31 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

C20H40NO
Compound #32 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

<table>
<thead>
<tr>
<th>min</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.51</td>
<td>323.258</td>
</tr>
</tbody>
</table>
Compound #33 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

Experimental

Theoretical

C20H35O4
Compound #34 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical

C26H23O8
Compound #35 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical

C20H37O3
Compound #36 in Table 3

**a) Extracted Ion Chromatogram**

**b) Spectrum**

**c) Isotopic Fine Structure**

---

**Experimental**

**Theoretical**

C20H37O4
Compound #37 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical

C26H39O3
Compound #38 in Table 3

a) Extracted Ion Chromatogram

Experimental
C_1-B,4_02_372.d: EIC 606.546000±0.001 +All MS

b) Spectrum

Experimental
C_1-B,4_02_372.d: +MS, 19.63-19.72min #427-429

Theoretical
C38H72NO4

Experimental
M

Theoretical
M+1

Experimental
M+2
Compound #39 in Table 3

(a) Extracted Ion Chromatogram

(b) Spectrum

(c) Isotopic Fine Structure

Experimental

Theoretical

C16H15O5
Compound #40 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

M

321.242472

1+

C1-B,4_02_372.d: +MS, 18.17-18.26min #395-397

M+1

322.245776

1+

M+2

323.249131

1+

Experimental

Theoretical

C20H33O3
Compound #41 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

C_1-B,4_02_372.d: +MS, 17.71-17.85min #385-388

Experimental

Theoretical

C20H39O4
Compound #42 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

C23H17O6
Compound #43 in Table 3

a) Extracted Ion Chromatogram

b) Spectrum

c) Isotopic Fine Structure

Experimental

Theoretical
C24H21O7