

Supplementary material

Chemical profile and antioxidant capacity of propolis from *Tetragonula*, *Lepidotrigona*, *Lisotrigona* and *Homotrigona* stingless bee species in Vietnam

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|-----------------------|-----|------|------|-----|-----|------|-----|------|------|---|-----|------|------|------|---|-----|---|-----|-----|-----|-----|-----|-----|-----|---|--|
| Cardanol C13:1 | 0 | 0.5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| Cardanol C15:0 | 0 | 0.4 | 0.1 | 3.5 | 0.3 | 0 | 0 | 0.2 | 0.1 | 0 | 0.1 | 0.1 | 0.3 | Tr. | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.1 | 0 | |
| Cardanol C15:1 | 0 | 1.8 | 0.2 | 3.9 | 0.3 | 0 | Tr. | 0.3 | 0.3 | 0 | 0 | 0 | 0.3 | 0 | 0 | 0 | 0 | 0 | 0.1 | 0 | 0 | 0 | 0 | 0.1 | 0 | |
| Cardanol C17:0 | 0.1 | 0 | 0.1 | 0 | 0 | 0.3 | 0 | 0.4 | 0 | 0 | 0.1 | 0.1 | 0.7 | 0.1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| Cardanol C17:1 | 0.4 | 0 | 0.9 | 0 | 0 | 0 | 0.1 | 2.4 | 0.4 | 0 | 0.4 | 0.6 | 3.3 | 0.1 | 0 | 0.1 | 0 | 0.1 | 0.2 | 0.1 | 0 | 0.2 | 0 | 0 | 0 | |
| Cardanol C17:3 | 0 | 0.4 | 0 | 0 | 0 | 0 | 0 | 0.4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| Cardanol C19:1 | 0.4 | 1.1 | 0.8 | 0 | 0 | 0.4 | 0 | 1.8 | 0.6 | 0 | 0.4 | 0.3 | 1.7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Resorcinols (cardols) | 7.2 | 26.4 | 34.2 | 1.3 | 1.2 | 17.7 | 1.3 | 34.1 | 20.4 | 0 | 7.8 | 13.5 | 37.1 | 13.2 | 0 | 2.1 | 0 | 4.1 | 0.6 | 0.4 | 0.1 | 0.2 | 2.1 | 0 | 0 | |
| Resorcinol C15:0 | 0.4 | 1.6 | 1.5 | 0 | Tr. | 0 | 0 | 1.1 | 0.9 | 0 | 0.4 | 0.6 | 1.4 | 1.2 | 0 | 0.2 | 0 | 0.2 | 0 | Tr. | 0 | 0 | 0.1 | 0 | 0 | |
| Resorcinol C15:1 | 0.2 | 3 | 2.3 | 0 | 0 | 0 | 0 | 1.3 | 1.1 | 0 | 0.4 | 0.4 | 1.3 | 4.4 | 0 | 0.2 | 0 | 0.1 | 0 | 0 | 0 | 0 | 0.1 | 0 | 0 | |
| Resorcinol C17:0 | 0.5 | 2.6 | 0 | 1.3 | 0.2 | 1 | 0.4 | 2 | 1.5 | 0 | 0.2 | 0.7 | 1.6 | 0 | 0 | 0.1 | 0 | 0.2 | 0 | 0 | Tr. | 0.1 | 0.1 | 0 | 0 | |
| Resorcinols C17:1 | 4.5 | 12.1 | 22.5 | 0 | 0 | 12.3 | 0 | 22.4 | 10.8 | 0 | 5.7 | 10.7 | 25.7 | 6.8 | 0 | 1.1 | 0 | 2.6 | 0.6 | 0.4 | 0.1 | 0.1 | 1.6 | 7r. | 0 | |
| Resorcinols C17:3 | 1.6 | 2.6 | 0.8 | 0 | 0 | 0.5 | 0 | 1.1 | 0.6 | 0 | 0 | 0 | 1.8 | 0 | 0 | 0 | 0 | 0.2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| Resorcinol C19:0 | 0 | 4.5 | 0.5 | 0 | 0 | 0 | 0 | 0.2 | 0.2 | 0 | 0 | 0 | 0.1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| Resorcinols C19:1 | 0 | 0 | 6.6 | 0 | 1 | 3.9 | 0.9 | 6 | 5.3 | 0 | 1.1 | 1.1 | 5.2 | 0.8 | 0 | 0.5 | 0 | 0.8 | 0 | 0 | 0 | 0 | 0.2 | 0 | 0 | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Anacardic acids | 3.7 | 7.1 | 16.2 | 1.6 | 4.3 | 3.5 | 2.6 | 7.3 | 15.4 | 0 | 2.7 | 8.7 | 9 | 0.5 | 0 | 0.4 | 0 | 0.9 | 0.3 | 0.7 | 0.1 | 0.2 | 0.2 | 0.1 | 0 | |
| Anacardic acid C15:0 | 0.1 | 0 | 3 | 1.6 | 0 | 0 | 0 | 0 | Tr. | 0 | 0 | 0 | 0 | 0.1 | 0 | Tr. | 0 | 0 | 0 | 0 | Tr. | 0.1 | 0 | Tr. | 0 | |
| Anacardic acids C15:1 | 0.9 | 0.5 | 1 | 0 | 3.4 | 0.4 | 1.9 | 0 | 5.8 | 0 | 0 | 0.5 | 0 | 0.1 | 0 | 0 | 0 | 0.1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| Anacardic acids C17:1 | 0 | 3.6 | 7.1 | 0 | 0.5 | 3.1 | 0.3 | 3.8 | 4.5 | 0 | 1.3 | 4.8 | 4.2 | 0.3 | 0 | 0.4 | 0 | 0 | 0.2 | 0.2 | 0.1 | 0.1 | 0.2 | 0.1 | 0 | |
| Anacardic acid C17:3 | 0 | 0 | 0.2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |

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|--|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-----------|-------------|-------------|-------------|-------------|-------------|-----------|-------------|-------------|-------------|-------------|-------------|
| Anacardic acid C19:0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.2 | 0 | 0 | 0.7 | 0.2 | 2.4 | 0 | 0 | 0 | 0 | 0.4 | 0.1 | 0 | 0 | 0 | 0 | 0 | 0 |
| Anacardic acid C19:1 | 2.7 | 3 | 4.9 | 0 | 0.4 | 0 | 0.4 | 3.3 | 5.1 | 0 | 0.7 | 3.2 | 2.4 | 0 | 0 | 0 | 0 | 0.4 | 0 | 0.5 | 0 | 0 | 0 | 0 | 0 |
| Triterpenes | 35.6 | 22.8 | 28.9 | 33.0 | 28.9 | 32.2 | 28.9 | 26.1 | 33.1 | 14.3 | 31.6 | 31.9 | 18.4 | 22 | 50.8 | 39.3 | 45.6 | 33.6 | 28.8 | 24 | 28.2 | 20.5 | 31.6 | 16.4 | 56.2 |
| (13 <i>E</i> ,17 <i>E</i>)-Polydopa-7,13,17,21-tetraen-3 β -ol ^b | 0 | 0 | 0.1 | 0 | 0.8 | 0 | 0 | 0 | 0 | 11.2 | 0 | 0 | 0 | 0 | 0 | 0.3 | 0 | 0 | 0 | 0 | 0 | 0.6 | 0 | 0 | 0 |
| Lanosterol ^c | 1.8 | 2 | 0.2 | 0 | 0 | 0.5 | 0.6 | 0.3 | 0.9 | 0 | 0 | 0 | 0.4 | 2.9 | 0.4 | 0.8 | 0 | 0.4 | 0.2 | 0 | 0 | 0 | 0 | 0 | 0 |
| Lanosterol (3- <i>epi</i>) ^c | 3 | 2.7 | 0 | 0 | 0 | 0 | 0 | 0.4 | 0.2 | 0 | 0 | 0.6 | 0 | 3.1 | 0 | 0.3 | 0 | 0.6 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| α -Amyrine | 3.3 | 0 | 2.7 | 0.8 | 1.5 | 2.8 | 2.9 | 1.7 | 3.2 | 0.9 | 2.8 | 2.5 | 2.1 | 2.8 | 6.8 | 4.5 | 1.2 | 7.4 | 1.1 | 0 | 5.6 | 3.9 | 0 | 2 | 0.7 |
| β -Amyrine | 5.2 | 2.2 | 2.2 | 0.9 | 1.0 | 3.2 | 3.8 | 1.4 | 2.7 | 0.4 | 4.4 | 3.0 | 2.4 | 4.3 | 9.0 | 9.5 | 2.1 | 3.3 | 0 | 5.1 | 8.7 | 2.6 | 7.2 | 1.4 | 0.5 |
| α -Amyrenone | 2.2 | 0 | 0 | 0 | 0 | 0.7 | 0.9 | 0.5 | 0 | 0 | 3.0 | 0 | 0 | 0 | 0 | 1.7 | 0 | 0 | 2.1 | 4.5 | 3.9 | 3.4 | 3.1 | 0 | 0 |
| β -Amyrenone | 3.1 | 0 | 0 | 0 | 0 | 0.7 | 1.2 | 0.6 | 0.1 | 0 | 1.1 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 2.8 | 2.9 | 0 | 1.6 | 0.9 | 0 |
| Ursolic acid | 0 | 0 | 0 | 1 | 3.2 | 2.1 | 2.8 | 0 | 0.8 | 0 | 0 | 0 | 0 | 0 | 4.9 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Oleanolic acid | 0 | 0 | 0 | 0 | 0 | 0 | 0.4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.9 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.1 |
| Ursonic acid | 0 | 0 | 0 | 2.7 | 2.7 | 2.9 | 2.5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4.9 | 0 | 1 | 1.9 | 0 | 0 | 0 | 0 | 0 | 2.7 | 3.8 |
| Moronic acid | 0 | 0 | 0 | 3.5 | 2.4 | 0.9 | 1.1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Oleanonic acid | 0.1 | 0 | 0 | 0 | 0 | 0 | 0.2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.9 | 1 | 2.6 | 1.3 | 0 | 0 | 0 | 0 | 0 | 1.8 | 1.9 |
| Lantanolic acid ^b | 0 | 0 | 1.2 | 11.5 | 3.4 | 0 | 2.8 | 0 | 1.5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Uvaol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.5 | 0 | 0.4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.1 |
| Erythrodiol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.2 | 0 | 0.8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.6 |
| Ursolic aldehyde | 0 | 0 | 0 | 0.1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3.0 | 1.1 | 3.2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2.2 |
| Oleanolic aldehyde | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4.6 | 0 | 8.8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3.4 |

[illegible]

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|---|----------|----------|------------|-------------|-------------|------------|------------|----------|------------|------------|----------|----------|----------|-------------|----------|------------|----------|-------------|-------------|------------|------------|-------------|----------|----------|----------|
| Triterpene hydroxy acid (M ⁺ =598) | 2.4 | 0 | 0 | 1.9 | 1.4 | 1.7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| Triterpenic acid (M ⁺ =616) | 0 | 0 | 0 | 0.4 | 3.0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.1 | 0 | 0 | 0 | 0.1 | 0 | 0 | 0 |
| Xanthones | 0 | 0 | 4.8 | 28.9 | 23.3 | 1.5 | 6.5 | 0 | 2.5 | 47 | 0 | 0 | 0 | 20.5 | 0 | 2.8 | 0 | 0 | 0 | 0 | 8.1 | 38.6 | 0 | 0 | 0 |
| 4-Geranyl-1,3,5-trihydroxyxanthone ^b | 0 | 0 | 0.7 | 4.2 | 2.7 | 0 | 0.6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| α-Mangostin ^b | 0 | 0 | 1.4 | 4 | 2.7 | 0.9 | 1.4 | 0 | 0.5 | 7.6 | 0 | 0 | 0 | 4.6 | 0 | 0.5 | 0 | 0 | 0 | 0 | 0 | 6.3 | 0 | 0 | 0 |
| Dihydromangostanine ^b | 0 | 0 | 0.8 | 0 | 4.1 | 0 | 1.7 | 0 | 1 | 0.3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3.0 | 0 | 0 | 0 | 0 |
| Cochinchinone A ^b | 0 | 0 | 1.1 | 15.8 | 7.1 | 0.6 | 1.7 | 0 | 1 | 36.3 | 0 | 0 | 0 | 4.2 | 0 | 0.5 | 0 | 0 | 0 | 0 | 4.1 | 20.7 | 0 | 0 | 0 |
| Cratoxylumxanthone B ^b | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.2 | 0 | 0 | 0 | 0.3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4.7 | 0 | 0 | 0 |
| Cochinchinone K ^b | 0 | 0 | 0.8 | 3.5 | 3.6 | 0 | 0.7 | 0 | 0 | 2.6 | 0 | 0 | 0 | 1.7 | 0 | 0 | 0 | 0 | 0 | 0 | 1.0 | 6.9 | 0 | 0 | 0 |
| Xanthone (M ⁺ =536) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 9.7 | 0 | 1.8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Xanthone (M ⁺ =554) | 0 | 0 | 0 | 1.4 | 3.1 | 0 | 0.4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Tocotrienols | 0 | 0 | 0 | 0.2 | 0.3 | 0 | 0 | 0 | 0 | 1.8 | 0 | 0 | 0 | 0.8 | 0 | 0.1 | 0 | 0 | 0 | 0 | 1.1 | 0 | 0 | 0 | 0 |
| d-Tocotrienol | 0 | 0 | Tr. | 0.2 | 0.2 | 0 | Tr. | 0 | 0 | 0.9 | 0 | 0 | 0 | 0.6 | 0 | 0.1 | 0 | 0 | 0 | 0 | Tr. | 0.8 | 0 | 0 | 0 |
| β/γ-Tocotrienol | 0 | 0 | 0 | 0 | 0.1 | 0 | 0 | 0 | 0 | 0.9 | 0 | 0 | 0 | 0.2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.3 | 0 | 0 | 0 |
| Unknowns | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 11.2 | 19.7 | 6.0 | 0 | 0 | 0 | 0 | 0 |
| Unknown 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5.7 | 8.1 | 0 | 0 | 0 | 0 | 0 | 0 |
| Unknown 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2.2 | 5.6 | 0 | 0 | 0 | 0 | 0 | 0 |
| Unknown 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.5 | 5.7 | 2.4 | 0 | 0 | 0 | 0 | 0 |

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| Unknown 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.8 | 5.9 | 3.6 | 0 | 0 | 0 | 0 | 0 |
|-----------|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|-----|-----|-----|---|---|---|---|---|

^a The detailed information (bee species, geographical location and time of collection) for the propolis samples from V-1 to V-25 is presented in Table 1; ^b Identified by reference compounds; ^c Intercheangable compounds. *T.i.* – *Tetragonula iridipennis*; *L.v.*- *Lepidotrigona ventralis*; *T.l.* – *Tetragonula laeviceps*; *L.c.* – *Lisotrigona carpenteri*; *H.a.* – *Homotrigona apicalis*; *L.t.* – *Lepidotrigona terminata*. Tr. – traces (< 0.05 %TIC).

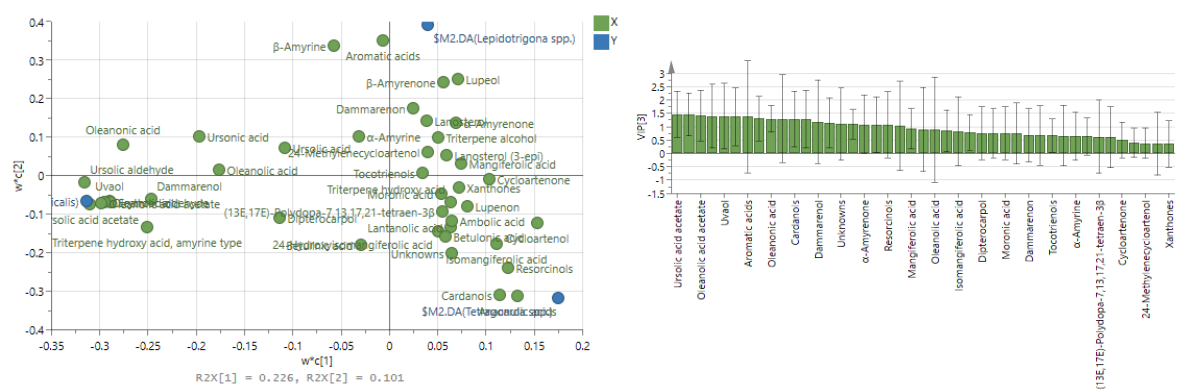


Figure S1. Loading plot and variable's contribution in the projection (VIP) of PLS-DA model for classification of 24 propolis samples based on 43 variables in accordance with the three stingless bee genera *Tetragonula*, *Lepidotrigona* and *Homotrigona*.

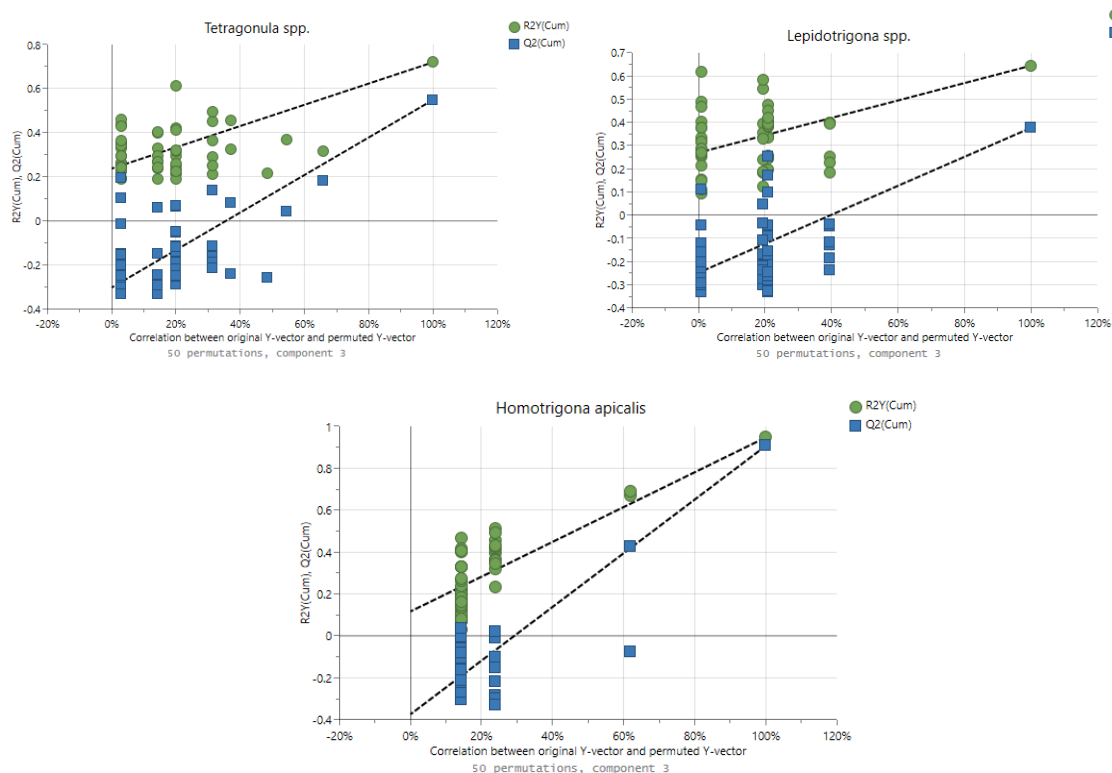


Figure S2. Permutation tests for the three predefined classes in PLS-DA model for classification of 24 propolis samples based on 14 variables.

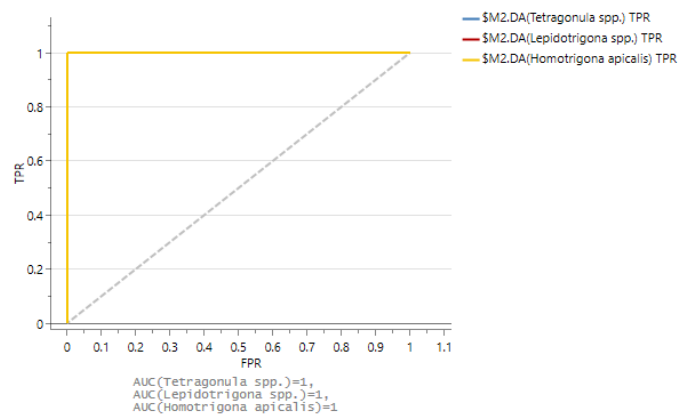


Figure S3. ROC analysis for *Tetragonula*, *Lepidotrigona* and *Homotrigona* stingless bee propolis.

Table S2. Misclassification table for PLS-DA model for classification of 24 propolis samples based on 14 variables propolis in accordance with the three genera *Tetragonula*, *Lepidotrigona* and *Homotrigona*.

| | Members | Correct | <i>Tetragonula</i> spp. | <i>Lepidotrigona</i> spp. | <i>Homotrigona</i> <i>apicalis</i> |
|------------------------------------|---------|---------|----------------------------|------------------------------|---------------------------------------|
| <i>Tetragonula</i> spp. | 14 | 100% | 14 | 0 | 0 |
| <i>Lepidotrigona</i> spp. | 7 | 85.71% | 1 | 6 | 0 |
| <i>Homotrigona</i> <i>apicalis</i> | 3 | 100% | 0 | 0 | 3 |
| Total | 24 | 95.83% | 15 | 6 | 3 |
| Fisher's prob. | 6.4e-08 | | | | |

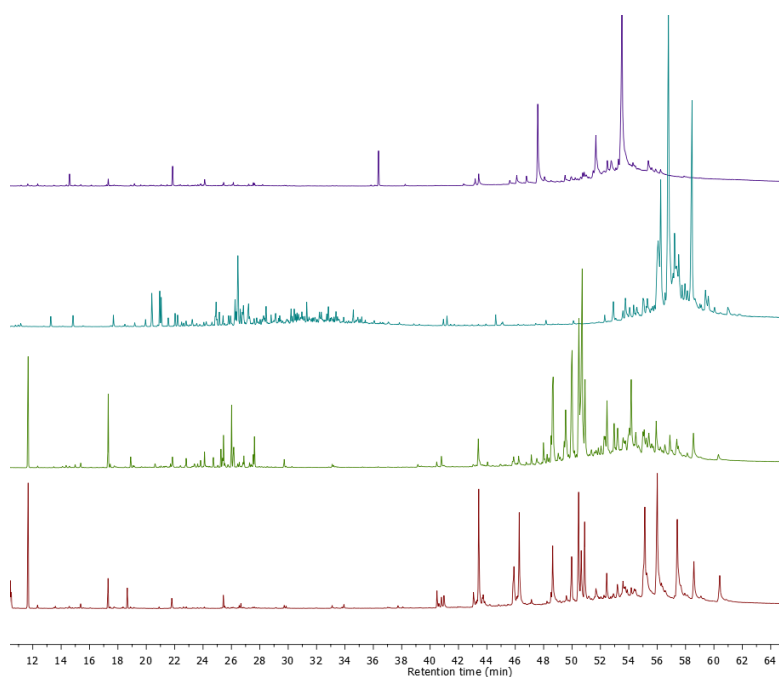


Figure S4. GC chromatograms of selected samples. From bottom to top: propolis from *Tetragonula iridipennis* (V-12), *Lepidotrigona terminata* (V-16), *Homotrigona apicalis* (V-17) and *Lisotrigona carpenteri* (V-10).

Table S3. Pearson correlation (r) between groups of phenolic constituents and DPPH and FRAP values.

| Correlation among variables | DPPH | FRAP |
|---|---------|---------|
| Phenolic acids | 0.623** | 0.786** |
| Cardanols | 0.032 | -0.064 |
| Resorcinols | -0.287 | -0.313 |
| Anacardic acids | -0.175 | -0.231 |
| Xanthoness | 0.538** | 0.302 |
| Phenolic acids + cardanols + resorcinols + anacardic acids + xanthoness | 0.220 | 0.315 |
| Phenolic acids + xanthoness | 0.624** | 0.417* |

*Correlation is significant at the 0.05 level (two-tailed). ** Correlation is significant at the 0.01 level (two-tailed).