

Supplementary Material for: Diversity and Toxicity of the Genus *Coolia* Meunier in Brazil, and Detection of 44-methyl Gambierone in *Coolia tropicalis*

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Table S1. List of compounds extracted from the Personal Compound Database and Library (PCDL, Agilent Mass Hunter software), created by Phycotoxins Laboratory (IFREMER, France) and used for *Coolia* spp. screening.

| Name | Molecular Formula | Mass (Da) | CAS |
|-----------------------------|--|-------------|-------------|
| Cooliatoxin metabolite 1 | C ₅₆ H ₇₈ O ₁₈ S ₂ | 1102.46296 | |
| Cooliatoxin metabolite 2 | C ₅₇ H ₈₀ O ₁₈ S ₂ | 1116.47861 | |
| Cooliatoxin metabolite 3 | C ₅₇ H ₇₈ O ₁₉ S ₂ | 1130.45787 | |
| Cooliatoxin metabolite 4 | C ₅₇ H ₈₄ O ₁₈ S ₂ | 1120.50991 | |
| Cooliatoxin metabolite 5 | C ₅₈ H ₈₆ O ₁₈ S ₂ | 1134.52556 | |
| Cooliatin | C ₁₅ H ₂₂ NaO ₄ | 289.14158 | |
| desulfo-YTX (cooliatoxin) | C ₅₅ H ₈₂ O ₁₈ S | 1062.52219 | 255041-59-9 |
| YTX | C ₅₅ H ₈₂ O ₂₁ S ₂ | 1142.479 | 112514-54-2 |
| Homo-YTX | C ₅₆ H ₈₄ O ₂₁ S ₂ | 1156.49465 | 196309-94-1 |
| 45-OH-YTX | C ₅₅ H ₈₂ O ₂₂ S ₂ | 1158.47392 | 124863-39-4 |
| 45-OH-Homo-YTX | C ₅₆ H ₈₄ O ₂₂ S ₂ | 1172.48957 | 196309-97-4 |
| COOH-YTX | C ₅₅ H ₈₂ O ₂₃ S ₂ | 1174.46883 | 262842-91-1 |
| COOH Homo YTX | C ₅₆ H ₈₄ O ₂₃ S ₂ | 1188.48448 | 292850-13-6 |
| Heptanor-41-oxo-Homo-YTX | C ₄₉ H ₇₄ O ₂₁ S ₂ | 1062.4164 | 346631-41-2 |
| 40-epi-Heptanor-41-oxo-YTX | C ₄₈ H ₇₂ O ₂₁ S ₂ | 1048.40075 | 803745-66-6 |
| YTX enone | C ₄₈ H ₇₂ O ₂₁ S ₂ | 1048.40075 | 803745-67-7 |
| Heptanor-41-oxo-YTX | C ₄₈ H ₇₂ O ₂₁ S ₂ | 1048.40075 | 448238-76-4 |
| 40-epi-Heptanor-nor-YTX | C ₄₅ H ₆₇ O ₂₀ S ₂ | 991.366711 | |
| Heptanor-nor-YTX enone | C ₄₅ H ₆₇ O ₂₀ S ₂ | 991.366711 | |
| Heptanor-41-nor-oxo-YTX | C ₄₅ H ₆₇ O ₂₀ S ₂ | 991.366711 | |
| 32-O-triarabinosyl-HomoYTX | C ₇₁ H ₁₀₇ O ₃₃ S ₂ | 1551.613602 | |
| 32-O-diarabinosyl-HomoYTX | C ₆₆ H ₉₉ O ₂₉ S ₂ | 1419.571344 | |
| 32-O-triarabinosyl-YTX | C ₇₀ H ₁₀₅ O ₃₃ S ₂ | 1537.597952 | |
| 9-Me-41-Homo-YTX amide | C ₆₁ H ₉₄ NO ₂₅ S ₂ | 1304.555634 | |
| 32-O-arabinosyl-YTX | C ₆₀ H ₈₉ O ₂₅ S ₂ | 1273.513435 | |
| 44,45-diOH-41-Homo-YTX | C ₅₆ H ₈₅ O ₂₃ S ₂ | 1189.492305 | |
| 44,45-diOH-Homo-YTX | C ₅₆ H ₈₅ O ₂₃ S ₂ | 1189.492305 | |
| 44,55-diOH-YTX | C ₅₅ H ₈₄ O ₂₃ S ₂ | 1176.48448 | 862783-86-6 |
| 9-Me-41-Homo-YTX | C ₅₇ H ₈₅ O ₂₁ S ₂ | 1169.502476 | |
| 41-Homo-YTX | C ₅₆ H ₈₄ O ₂₁ S ₂ | 1156.49465 | |
| Trinor-YTX | C ₅₂ H ₇₈ O ₂₁ S ₂ | 1102.4477 | 181365-95-7 |
| nor-YTX | C ₅₂ H ₇₇ O ₂₀ S ₂ | 1085.444961 | |
| 32-O-diarabinosyl-YTX | C ₆₅ H ₉₇ O ₂₉ S ₂ | 1405.555694 | |
| 41-Homo-YTX amide | C ₆₀ H ₉₂ NO ₂₅ S ₂ | 1290.539984 | |
| 32-O-arabinosyl-HomoYTX | C ₆₁ H ₉₁ O ₂₅ S ₂ | 1287.529085 | |
| 9-Me-44,45-diOH-41-Homo-YTX | C ₅₇ H ₈₇ O ₂₃ S ₂ | 1203.507956 | |
| MTX | C ₁₆₄ H ₂₅₈ O ₆₈ S ₂ | 3379.61719 | 59392-53-9 |
| Maitotoxin sodium | C ₁₆₄ H ₂₅₆ Na ₂ O ₆₈ S ₂ | 3423.58108 | 59392-53-9 |
| MTX4 | C ₁₅₇ H ₂₄₁ NO ₆₈ S ₂ | 3292.48724 | |
| Gambierone | C ₅₁ H ₇₆ O ₁₉ S | 1024.47015 | |
| 44-methylgambierone (MTX3) | C ₅₂ H ₇₈ O ₁₉ S | 1038.4858 | |
| Gambieroxide | C ₆₀ H ₉₀ O ₂₂ S | 1194.56445 | |
| Gambieric acid A | C ₅₉ H ₉₂ O ₁₆ | 1056.63854 | 138434-64-7 |

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| Gambieric acid B | C ₆₀ H ₉₄ O ₁₆ | 1070.65419 | 141363-65-7 |
| Gambieric acid C | C ₆₅ H ₁₀₀ O ₁₉ | 1184.68588 | 138458-89-6 |
| Gambieric acid D | C ₆₆ H ₁₀₂ O ₁₉ | 1198.70153 | 141363-66-8 |
| Gambierol | C ₄₃ H ₆₄ O ₁₁ | 756.44486 | |
| P-CTX 1 | C ₆₀ H ₈₆ O ₁₉ | 1110.57634 | 11050-21-8 |
| P-CTX 2 (52-epi-54-deoxy-P-CTX1) | C ₆₀ H ₈₆ O ₁₈ | 1094.58142 | 142185-85-1 |
| P-CTX 3 (54-deoxy P-CTX1) | C ₆₀ H ₈₆ O ₁₈ | 1094.58142 | 139641-09-6 |
| P-CTX 3C | C ₅₇ H ₈₂ O ₁₆ | 1022.56029 | 148471-85-6 |
| P-CTX 3B | C ₅₇ H ₈₂ O ₁₆ | 1022.56029 | 263336-58-9 |
| P-CTX 4B | C ₆₀ H ₈₄ O ₁₆ | 1060.57594 | 123676-76-6 |
| P-CTX 4A | C ₆₀ H ₈₄ O ₁₆ | 1060.57594 | 66231-73-0 |
| 50-OH P-CTX 3 | C ₆₀ H ₈₆ O ₁₉ | 1110.57634 | 263336-54-5 |
| 52-epi P-CTX 1 | C ₆₀ H ₈₆ O ₁₉ | 1110.57634 | 189013-49-8 |
| 54-Epi P-CTX 1 | C ₆₀ H ₈₆ O ₁₉ | 1110.57634 | 287732-40-5 |
| 52,54- Diepi P-CTX 1 | C ₆₀ H ₈₆ O ₁₉ | 1110.57634 | 287732-42-7 |
| M-seco P-CTX 4A | C ₆₀ H ₈₆ O ₁₇ | 1078.5865 | 287412-00-4 |
| M-seco 2,3dihydro, 2-OH-49-O-Me-P-CTX 3C | C ₅₈ H ₈₈ O ₁₈ | 1072.59707 | 374624-43-8 |
| 2,3-dihydro, 2,3,51-triOH P-CTX 3C | C ₅₇ H ₈₄ O ₁₉ | 1072.56069 | 263336-63-6 |
| A-seco-2,3 dihydro,51-OH P-CTX 3C | C ₅₇ H ₈₆ O ₁₈ | 1058.58142 | 263336-64-7 |
| 2,3 diOH P-CTX 3C | C ₅₇ H ₈₄ O ₁₈ | 1056.56577 | 263336-62-5 |
| M-seco 49-O-Me-P-CTX 3C | C ₅₈ H ₈₆ O ₁₇ | 1054.58651 | 287411-99-8 |
| 2,3- dihydro, 2-oxo,51-OH P-CTX 3C | C ₅₇ H ₈₂ O ₁₈ | 1054.55012 | 287732-77-8 |
| 2,3- dihydro, 3-oxo, 51-OH P-CTX 3C | C ₅₇ H ₈₂ O ₁₈ | 1054.55012 | 263336-61-4 |
| 2,3- dihydro-2-OH P-CTX 3C | C ₅₇ H ₈₄ O ₁₇ | 1040.57086 | 287732-78-9 |
| M-seco P-CTX 3C | C ₅₇ H ₈₄ O ₁₇ | 1040.57086 | 287411-98-7 |
| 2,3- dihydro-3-OH P-CTX-3C | C ₅₇ H ₈₄ O ₁₇ | 1040.57085 | 263336-60-3 |
| 51-OH P-CTX 3C | C ₅₇ H ₈₂ O ₁₇ | 1038.55521 | 263336-59-0 |
| 3-OH,7-oxo P-CTX | C ₆₀ H ₈₈ O ₂₁ | 1144.58181 | 263336-57-8 |
| 4- OH, 7-oxo P-CTX | C ₆₀ H ₈₈ O ₂₁ | 1144.58181 | 287732-85-8 |
| 7-Oxo P-CTX | C ₆₀ H ₈₆ O ₂₀ | 1126.57125 | 263336-55-6 |
| C-CTX 1 | C ₆₂ H ₉₂ O ₁₉ | 1140.62329 | 193363-37-0 |
| C-CTX 2 | C ₆₂ H ₉₂ O ₁₉ | 1140.62329 | 193363-38-1 |
| I-CTX 1 | C ₆₂ H ₉₂ O ₁₉ | 1140.62329 | |
| I-CTX 2 | C ₆₂ H ₉₂ O ₁₉ | 1140.62329 | |
| I-CTX 3 | C ₆₂ H ₉₂ O ₂₀ | 1156.6182 | |
| I-CTX 4 | C ₆₂ H ₉₂ O ₂₀ | 1156.6182 | |
| I-CTX 5 | C ₆₂ H ₉₀ O ₁₉ | 1138.60763 | |
| I-CTX 6 | C ₆₂ H ₉₀ O ₂₀ | 1154.60255 | |

Table S2. List of MRM transitions (*m/z*) used in ESI- to detect YTXs on system B (API 4000QTrap).

| Compound | MRM transitions (<i>m/z</i>) | CE (eV) | CXP (eV) |
|----------------|--------------------------------|---------|----------|
| YTX | 1141.4 > 1061.6 | -48 | -17 |
| | 1141.4 > 855.6 | -98 | -19 |
| Homo YTX | 1155.6 > 1075.6 | -48 | -17 |
| | 1155.6 > 869.4 | -98 | -19 |
| 45-OH YTX | 1157.5 > 1077.5 | -48 | -17 |
| | 1157.5 > 855.5 | -98 | -19 |
| 45-OH homo YTX | 1171.5 > 1091.5 | -48 | -17 |
| | 1171.5 > 869.4 | -98 | -19 |
| COOH YTX | 1173.5 > 1093.5 | -48 | -17 |
| | 1173.5 > 855.5 | -98 | -19 |
| Homo COOH YTX | 1187.5 > 1107.5 | -48 | -17 |
| | 1187.5 > 869.4 | -98 | -19 |

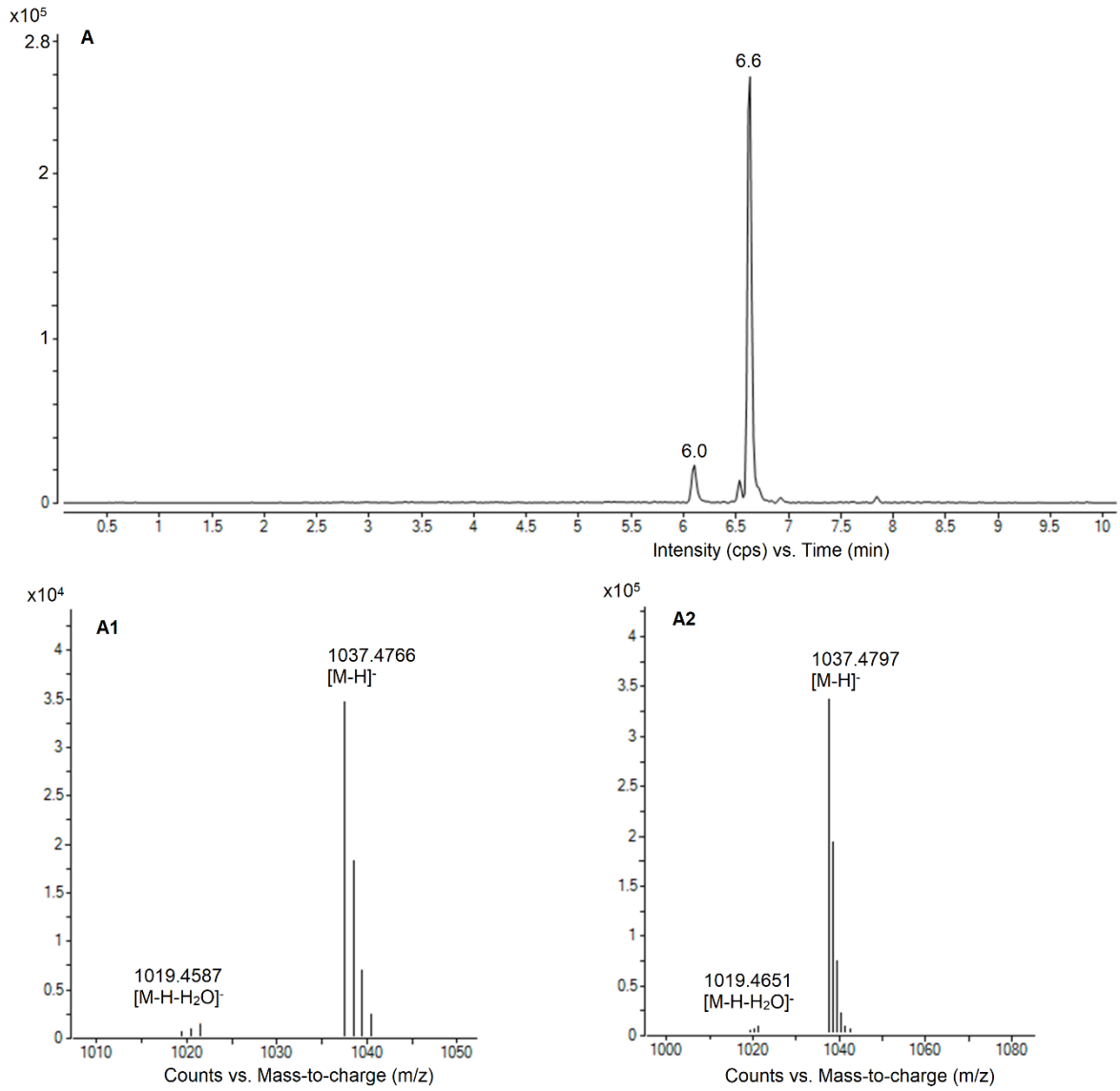


Figure S1. (A) LC-HRMS chromatogram of *C. tropicalis* extract and high resolution full scan mass spectra acquired in negative mode on the apex of peaks at (A1) 6.0 min for 44-methyl gambierone isomer and (A2) at 6.6 min for 44-methyl gambierone.

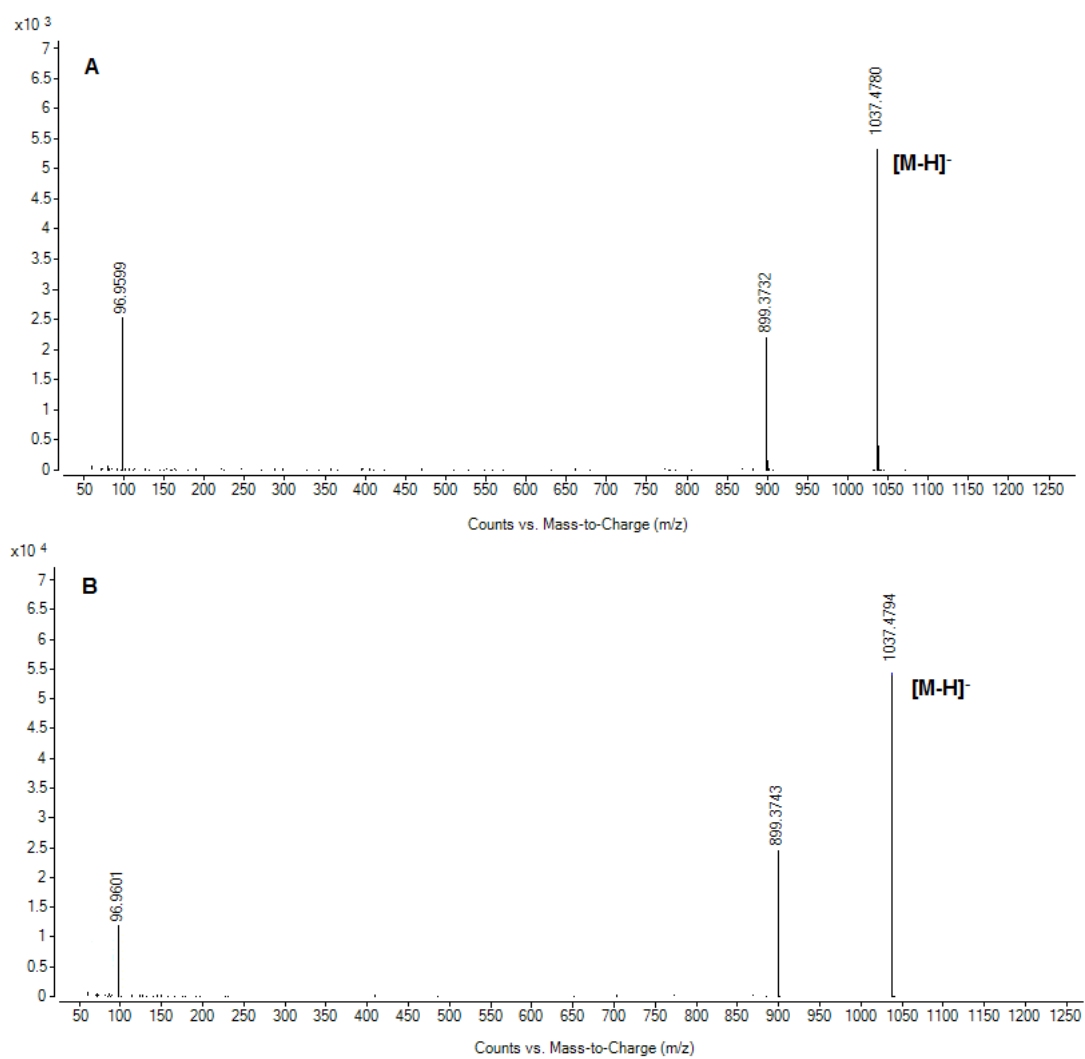


Figure S2. HRMS/MS spectra of $[M-H]^-$ (m/z 1037.4785) for (A) 44-methyl gambierone isomer at 6.0 min and for (B) 44-methyl gambierone at 6.6 min, resulting from an average of three collision energies (40, 65 and 90 eV).