Supplementary Material

Exploratory analysis of commercial olive-based dietary supplements using untargeted and targeted metabolomics

Mar Garcia-Aloy ¹, Nelli Groff ¹, Domenico Masuero ¹, Mauro Nisi ², Antonio Franco ³, Furio Battelini ², Urska Vrhovsek ¹ and Fulvio Mattivi ¹, ⁴,*

¹ Metabolomics Unit, Food Quality and Nutrition Department, Research and Innovation Centre Fondazione Edmund Mach, San Michele all’Adige, Italy
² Agraria Riva del Garda S.C.A., Riva del Garda, Italy
³ Ethifenol S.R.L., Bergamo, Italy
⁴ Department of Cellular, Computational and Integrative Biology - CIBIO, University of Trento, San Michele all’Adige, Italy
Table S1. Unknown compounds detected in study samples.

| C     | Compound                  | Formula       | RT  | Ions                                                                 |
|-------|---------------------------|---------------|-----|----------------------------------------------------------------------|
| C203  | Unknown 001 (glucoside)   | C_{27}H_{50}O_{17}N_{2}     | 78  | 294.1551 [M+H]^+                                                      |
| C204  | Unknown 002 (glucoside)   | C_{40}H_{50}O_{17}N_{2}     | 82  | 323.1704 [M+H]^+                                                      |
| C205  | Unknown 003 (glucoside)   | C_{27}H_{38}O_{17}N_{2}     | 96  | 347.0982 [M+H+HCOOH]^+                                               |
| C206  | Unknown 004 glucoside     | C_{30}H_{38}O_{17}N_{2}     | 257 | 377.1453 [M+H+HCOOH]; 333.1546 [M+H]; 350.1812 [M+NH4]^+; 153.091 [M+H-hexose-H2O]^+ |
| C207  | Unknown 004               | C_{27}H_{38}O_{17}N_{2}     | 282 | 171.1015 [M+H]^+; 172.1049 ^13C[M+H]^+; 188.1283 [M+NH4]^+; 153.091 [M+H-H2O]; 111.0803 [M+H-C6H5O2]^+ |
| C208  | Unknown 005 (glucoside)   | C_{40}H_{50}O_{17}N_{2}     | 278 | 467.1769 [M+H+HCOOH]; 468.1803 ^13C[M+H+HCOOH]; 423.1862 [M+H]^+; 440.2126 [M+NH4]^+; 441.2163 ^13C[M+NH4]^+; 261.1335 [M+H-hexose]; 243.1228 [M+H-hexose-H2O]^+ |
| C209  | Unknown 006 (glucoside)   | C_{40}H_{50}O_{17}N_{2}     | 316 | 403.1794 [M+H-H]; 422.2386 [M+NH4]^+                                |
| C210  | Unknown 007 (glucoside)   | C_{40}H_{50}O_{17}N_{2}     | 346 | 523.1808 [M+H]^+                                                      |
| C211  | Unknown 008 (glucoside) (I) | C_{27}H_{38}O_{17}N_{2}   | 369 | 521.1665 [M+H]; 567.1719 [M+H+HCOOH]                                   |
| C212  | Unknown 008 (glucoside) (II) | C_{27}H_{38}O_{17}N_{2} | 366 | 553.1599 [M+H-H]                                                      |
| C213  | Unknown 009 (glucoside)   | C_{27}H_{38}O_{17}N_{2}     | 398 | 691.2243 [M+H-H]                                                      |
| C214  | Unknown 010 (glucoside)   | C_{27}H_{38}O_{17}N_{2}     | 403 | 583.2032 [M+H-H]; 585.2085 [M+H+HCOOH]; 602.2443 [M+NH4]^+; 603.2477 ^13C[M+NH4]^+; 423.165 [M+H-hexose]; 377.1233 [M+H-Hexose-H2O-C6H5O2]; 378.1265 ^13C[M-H-Hexose-H2O-C6H5O2]; 225.0758 [+]; 359.1127 [+]; 539.1758 [+]; 13C[M+H]^+ |
| C215  | Unknown 011 glucoside     | C_{27}H_{38}O_{17}N_{2}     | 521 | 421.1506 [M+H-H]; 422.1539 ^13C[M-H]^+                               |
| C216  | Unknown 011               | C_{27}H_{38}O_{17}N_{2}     | 414 | 729.2974 [M-H]                                                      |
| C217  | Unknown 012 (glucoside)   | C_{27}H_{38}O_{17}N_{2}     | 81  | 268.1181 [M+H]^+                                                      |
| C218  | Unknown 013 (I)           | C_{27}H_{38}O_{17}N_{2}     | 174 | 268.1181 [M+H]^+                                                      |
| C219  | Unknown 013 (II)          | C_{27}H_{38}O_{17}N_{2}     | 112 | 233.1031 [M+H+HCOOH]; 189.1122 [M+H]; 206.1388 [M+NH4]^+             |
| C220  | Unknown 014 (I)           | C_{27}H_{38}O_{17}N_{2}     | 143 | 233.103 [M+H+HCOOH]; 189.1122 [M+H]; 234.1702 [M+C3H2N]^+           |
| C221  | Unknown 014 (II)          | C_{27}H_{38}O_{17}N_{2}     | 169 | 187.0977 [M-H]                                                      |
| C222  | Unknown 014 (III)         | C_{27}H_{38}O_{17}N_{2}     | 205 | 187.0975 [M-H]                                                      |
| C223  | Unknown 014 (IV)          | C_{27}H_{38}O_{17}N_{2}     | 218 | 185.0819 [M-H]                                                      |
| C224  | Unknown 015 (I)           | C_{27}H_{38}O_{17}N_{2}     | 301 | 185.082 [M-H]; 187.0965 [M-H]^+                                     |
| C225  | Unknown 015 (II)          | C_{27}H_{38}O_{17}N_{2}     | 263 | 461.1665 [M+H-HCOOH]; 434.2021 [M+NH4]^+                             |
| C226  | Unknown 016 (I)           | C_{27}H_{38}O_{17}N_{2}     | 308 | 461.1664 [M+H+HCOOH]; 462.1696 ^13C[M+H+HCOOH]; 434.2019 [M+NH4]^+; 435.2054 ^13C[M+NH4]^+ |
| C  | Compound         | Formula | RT   | Ions                                      | LI |
|----|------------------|---------|------|-------------------------------------------|----|
| 228| Unknown 017 (I)  | CₙHₘOₙ   | 288  | 583.2032 [M-H+HCOOH]                     | IV |
| 229| Unknown 017 (II) | CₙHₘOₙ   | 407  | 539.2126 [M+H]                           | IV |
| 230| Unknown 018 (I)  | CₙHₘOₙ   | 338  | 551.2709 [M-H+HCOOH]                     | IV |
| 231| Unknown 018 (II) | CₙHₘOₙ   | 344  | 551.2709 [M-H+HCOOH]; 524.3065 [M+NH₄⁺] | IV |
| 232| Unknown 019 (I)  | CₙHₘOₙ   | 356  | 365.1596 [M+H]                           | IV |
| 233| Unknown 019 (II) | CₙHₘOₙ   | 374  | 365.1597 [M+H]                           | IV |
| 234| Unknown 020 (I)  | CₙHₘOₙ   | 360  | 197.1172 [M+H]                           | IV |
| 235| Unknown 020 (II) | CₙHₘOₙ   | 370  | 197.1173 [M+H]                           | IV |
| 236| Unknown 021 (I)  | CₙHₘOₙ   | 360  | 579.2083 [M-H]; 293.103 [frag]           | IV |
| 237| Unknown 021 (II) | CₙHₘOₙ   | 372  | 579.2083 [M-H]                           | IV |
| 238| Unknown 022 (I)  | CₙHₘOₙ   | 361  | 307.1542 [M+H]                           | IV |
| 239| Unknown 022 (II) | CₙHₘOₙ   | 497  | 307.1542 [M+H]                           | IV |
| 240| Unknown 023 (I)  | CₙHₘOₙ   | 411  | 349.165 [M+H]                            | IV |
| 241| Unknown 023 (II) | CₙHₘOₙ   | 539  | 349.1647 [M+H]; 417.1885 [*]             | IV |
| 242| Unknown 024 (I)  | CₙHₘOₙ   | 455  | 485.1817 [M+H]                           | IV |
| 243| Unknown 024 (II) | CₙHₘOₙ   | 461  | 485.1819 [M+H]                           | IV |
| 244| Unknown 025 (I)  | CₙHₘOₙ   | 496  | 227.1288 [M-H]                           | IV |
| 245| Unknown 025 (II) | CₙHₘOₙ   | 548  | 227.1289 [M-H]                           | IV |
| 246| Unknown 026 (I)  | CₙHₘOₙ   | 616  | 577.2687 [M-H]                           | IV |
| 247| Unknown 026 (II) | CₙHₘOₙ   | 623  | 577.2688 [M-H]; 578.272 ³C[M-H]; 596.3098 [M+NH₄⁺] | IV |
| 248| Unknown 027      |         | 273  | 272.9589 [M-H]; 158.9786 [frag]; 288.9363 [-] | V  |
| 249| Unknown 028      |         | 101  | 102.0338 [M+H]; 81.5204 [frag]; 90.5258 [frag]; 84.9596 [*]; 86.9926 [*]; 94.045 [*]; 102.9702 [*]; 105.0032 [*]; 110.0086 [*]; 112.0062 [*]; 125.9862 [*]; 128.0192 [*]; 151.0353 [*]; 152.0364 [*]; 153.0329 [*]; 156.0142 [*]; 167.0129 [*]; 171.9918 [*]; 214.9179 [*]; 216.9511 [*]; 223.9893 [*]; 239.9668 [*]; 255.9446 [*]; 265.016 [-] | V  |
| 250| Unknown 029      |         | 297  | 296.8823 [M-H]; 128.9598 [frag]; 212.9211 [frag] | V  |
| 251| Unknown 030      |         | 291  | 292.8456 [M+H⁺]; 122.9244 frag[*]; 124.9225 frag[*]; 206.886 frag[*]; 290.8475 [*] | V  |
| 252| Unknown 031      |         | 103  | 104.1069 [M+H⁺]                         | V  |
| 253| Unknown 032      |         | 289  | 290.0761 [M+H⁺]                         | V  |
| 254| Unknown 033      | CₙHₘNₙOₙ | 53   | 295.1142 [M+H⁺]; 252.1082 [*]; 266.1237 [*] | IV |
| C | Compound          | Formula       | RT | Ions                                           | LI |
|---|------------------|---------------|----|------------------------------------------------|----|
| C255 | Unknown 034 | C₇H₈O₂ | 54  | 116.0705 [M+NH₄]⁺ | IV |
| C256 | Unknown 035 | C₇H₈O₃ | 54  | 191.0773 [M-H]  | IV |
| C257 | Unknown 036 | C₇H₈O₄ | 54  | 231.0267 [M+H-H₂O]⁺ | IV |
| C258 | Unknown 037 | C₇H₈O₅ | 55  | 317.0552 [M-H]; 125.0013 [-] | IV |
| C259 | Unknown 038 | H₂PO₄ | 55  | 96.9699 [M-H]; 98.9840 [M+H]⁺ | IV |
| C260 | Unknown 039 | C₇H₈O₆ | 56  | 355.0884 [M-H]  | IV |
| C261 | Unknown 040 | C₇H₈O₇ | 56  | 118.0862 [M+NH₄]⁺ | IV |
| C262 | Unknown 041 | C₇H₈O₈ | 58  | 439.0774 [M-H]  | IV |
| C263 | Unknown 042 | C₇H₈O₉ | 62  | 305.1346 [M+Na]⁺; 305.1346 [M+Na]⁺ | IV |
| C264 | Unknown 043 | C₇H₈O₈ | 74  | 512.1974 [M+NH₄]⁺ | IV |
| C265 | Unknown 044 | C₇H₈O₉ | 75  | 350.1449 [M+NH₄]⁺ | IV |
| C266 | Unknown 045 | C₇H₈O₁₀ | 76  | 333.1191 [M-H]; 352.1605 [M+NH₄]⁺ | IV |
| C267 | Unknown 046 | C₇H₈O₁₁ | 76  | 147.0300 [M-H]  | IV |
| C268 | Unknown 047 | C₇H₈O₁₂ | 77  | 115.0039 [M-H]  | IV |
| C269 | Unknown 048 | C₇H₈O₁₃ | 82  | 224.1283 [M+NH₄]⁺ | IV |
| C270 | Unknown 049 | C₇H₈O₁₄ | 84  | 363.1295 [M-H+HCOOH]; 319.1391 [M+H]⁺ | IV |
| C271 | Unknown 050 | C₇H₈O₁₅ | 85  | 217.0717 [M-H]  | IV |
| C272 | Unknown 051 | C₇H₈O₁₆ | 88  | 365.1454 [M-H+HCOOH]; 321.1547 [M+H]; 338.1813 [M+NH₄]⁺ | IV |
| C273 | Unknown 052 | C₇H₈NO₃ | 91  | 420.1653 [M+H]⁺ | IV |
| C274 | Unknown 053 | C₇H₈NO₄ | 94  | 295.1033 [M-H]; 314.1449 [M+NH₄]⁺ | IV |
| C275 | Unknown 054 | C₇H₈NO₅ | 95  | 529.2139 [M-H]  | IV |
| C276 | Unknown 055 | C₇H₈NO₆ | 109 | 252.1231 [M+NH₄]⁺ | IV |
| C277 | Unknown 056 | C₇H₈NO₇ | 110 | 333.0825 [M-H+HCOOH]; 306.1186 [M+NH₄]⁺ | IV |
| C278 | Unknown 057 | C₇H₈NO₈ | 112 | 234.1702 [M+NH₄]⁺ | IV |
| C279 | Unknown 058 | C₇H₈NO₉ | 128 | 175.1329 [M+H]⁺ | IV |
| C280 | Unknown 059 | C₇H₈NO₁₀ | 132 | 310.0931 [M-H]; 312.108 [M+H]⁺ | IV |
| C281 | Unknown 060 | C₇H₈NO₁₁ | 135 | 275.0771 [M-H]  | IV |
| C282 | Unknown 061 | C₇H₈O₁₂ | 152 | 161.0455 [M-H]  | IV |
| C283 | Unknown 062 | C₇H₈O₁₃ | 154 | 147.0664 [M-H]  | IV |
| C  | Compound  | Formula   | RT  | Ions                              | LI |
|----|-----------|-----------|-----|-----------------------------------|----|
| C284 | Unknown 063 | C28H34NO3 | 166 | 282.1338 [M+H]+                  | IV |
| C285 | Unknown 064 | C28H34O3 | 168 | 381.1404 [M-H]-                  | IV |
| C286 | Unknown 065 | C28H34NO7 | 170 | 326.1238 [M+H]+                  | IV |
| C287 | Unknown 066 | C28H34O3 | 172 | 149.0251 [M-H]-                  | IV |
| C288 | Unknown 067 | C28H34O3 | 197 | 375.1294 [M-H]-                  | IV |
| C289 | Unknown 068 | C28H34O3 | 207 | 755.2981 [M-H]; 447.1145 [-]    | IV |
| C290 | Unknown 069 | C28H34O3 | 209 | 145.0859 [M+H]+                  | IV |
| C291 | Unknown 070 | C28H34O3 | 213 | 181.0506 [M-H]; 200.0918 [M+NH4]+ | IV |
| C292 | Unknown 071 | C28H34O3 | 218 | 331.1391 [M-H]-; 348.1656 [M+NH4]+ | IV |
| C293 | Unknown 072 | C28H34O3 | 225 | 114.0912 [M+NH4]+                | IV |
| C294 | Unknown 073 | C28H34O3 | 234 | 196.0969 [M+NH4]+                | IV |
| C295 | Unknown 074 | C28H34O3 | 238 | 252.1595 [M+NH4]+                | IV |
| C296 | Unknown 075 | C28H34O3 | 241 | 175.0613 [M-H]-                  | IV |
| C297 | Unknown 076 | C28H34O3 | 241 | 229.0719  [M-H]                  | IV |
| C298 | Unknown 077 | C28H34O3 | 243 | 431.156 [M-H]; 477.1613 [M-H+HCOOH]; 450.1969 [M+NH4]+ | IV |
| C299 | Unknown 078 | C28H34O3 | 246 | 375.1296 [M-H+HCOOH]; 348.1656 [M+NH4]+ | IV |
| C300 | Unknown 079 | C28H34O3 | 247 | 266.1388 [M+NH4]+                | IV |
| C301 | Unknown 080 | C28H34O3 | 248 | 130.1589 [M+NH4]+                | IV |
| C302 | Unknown 081 | C28H34O3 | 255 | 344.1341 [M+NH4]+                | IV |
| C303 | Unknown 082 | C28H34O3 | 259 | 390.176 [M+NH4]+; 193.086 [*]    | IV |
| C304 | Unknown 083 | C28H34O3 | 271 | 611.1826 [M-H]-                  | IV |
| C305 | Unknown 084 | C28H34O3 | 271 | 153.0909 [M-H]-                  | IV |
| C306 | Unknown 085 | C28H34O3 | 275 | 318.1701 [M+NH4]-                | IV |
| C307 | Unknown 086 | C28H34O3 | 275 | 447.1508 [M-H+HCOOH]; 420.1865 [M+NH4]+; 421.19 13C[M+NH4]+ | IV |
| C308 | Unknown 087 | C28H34O3 | 275 | 305.0699 [M-H]-                  | IV |
| C309 | Unknown 088 | C28H34O3 | 276 | 519.1718 [M-H]-                  | IV |
| C310 | Unknown 089 | C28H34O3 | 285 | 185.1172 [M-H]-                  | IV |
| C311 | Unknown 090 | C28H34O3 | 310 | 424.1812 [M+NH4]+                | IV |
| C312 | Unknown 091 | C28H34O3 | 312 | 302.1599 [M+NH4]+; 422.1657 [*] | IV |
| C   | Compound     | Formula   | RT | Ions                                      | LI |
|-----|--------------|-----------|----|-------------------------------------------|----|
| C313| Unknown 092  | C₃₁H₃₀O₉ | 313| 401.1817 [M-H]; 420.2229 [M+NH₄]⁺        | IV |
| C314| Unknown 093  | C₃₁H₃₀O₉ | 313| 412.2178 [M+NH₄]⁺                        | IV |
| C315| Unknown 094  | C₃₁H₃₀O₉ | 314| 439.1822 [M-H]                           | IV |
| C316| Unknown 095  | C₃₁H₃₀O₉ | 314| 454.2281 [M+NH₄]⁺                       | IV |
| C317| Unknown 096  | C₃₁H₃₀O₉ | 315| 183.1016 [M+H]                           | IV |
| C318| Unknown 097  | C₃₁H₃₀O₉ | 319| 551.1772 [M-H]                           | IV |
| C319| Unknown 098  | C₃₁H₃₀O₉ | 319| 446.1808 [M+NH₄]⁺                       | IV |
| C320| Unknown 099  | C₃₁H₃₀O₉ | 321| 557.2453 [M-H+HCOOH]; 513.2541 [M+H]⁺  | IV |
| C321| Unknown 100  | C₃₁H₃₀O₉ | 325| 155.1066 [M+H]                           | IV |
| C322| Unknown 101  | C₃₁H₃₀O₉ | 328| 253.0719 [M-H]                           | IV |
| C323| Unknown 102  | C₃₁H₃₀O₉ | 331| 241.1072 [M+H]                           | IV |
| C324| Unknown 103  | C₃₁H₃₀O₉ | 337| 197.082 [dialdehydic elenolic ester decarboxymethyl - H] | IV |
| C325| Unknown 104  | C₃₁H₃₀O₉ | 340| 775.2301 [M-H]                           | IV |
| C326| Unknown 105  | C₃₁H₃₀O₉ | 344| 477.1388 [M+H]                           | IV |
| C327| Unknown 106  | C₃₁H₃₀O₉ | 345| 625.2036 [M-H]                           | IV |
| C328| Unknown 107  | C₃₁H₃₀O₉ | 346| 543.2081 [M-H]; 562.2494 [M+NH₄]⁺      | IV |
| C329| Unknown 108  | C₃₁H₃₀O₉ | 347| 533.2028 [M-H]                           | IV |
| C330| Unknown 109  | C₃₁H₃₀O₉ | 347| 317.103 [M-H]                            | IV |
| C331| Unknown 110  | C₃₁H₃₀O₉ | 353| 354.1335 [M+NH₄]⁺                       | IV |
| C332| Unknown 111  | C₃₁H₃₀O₉ | 355| 401.1595 [M+H]; 598.2492 [+*]            | IV |
| C333| Unknown 112  | C₃₁H₃₀O₉ | 362| 291.1229 [M+H]                           | IV |
| C334| Unknown 113  | C₃₁H₃₀O₉ | 364| 461.1453 [M-H]                           | IV |
| C335| Unknown 114  | C₃₁H₃₀O₉ | 365| 623.1982 [M-H+HCOOH]; 596.2333 [M+NH₄]⁺ | IV |
| C336| Unknown 115  | C₃₁H₃₀O₉ | 372| 781.2561 [M-H]                           | IV |
| C337| Unknown 116  | C₃₁H₃₀O₉ | 372| 491.156 [M-H]; 493.1701 [M+H]⁺; 339.1076 [+*] | IV |
| C338| Unknown 117  | C₃₁H₃₀O₉ | 373| 789.2457 [M-H]                           | IV |
| C339| Unknown 118  | C₃₁H₃₀O₉ | 374| 623.2346 [M-H]; 381.1556 [frag]         | IV |
| C340| Unknown 119  | C₃₁H₃₀O₉ | 381| 484.2177 [M+NH₄]⁺                       | IV |
| C341| Unknown 120  | C₃₁H₃₀O₉ | 381| 541.1822 [M-H]; 560.2239 [M+NH₄]⁺      | IV |
| C  | Compound            | Formula     | RT | Ions                                | LI |
|----|---------------------|-------------|----|-------------------------------------|----|
| C342 | Unknown 121      | C3H3O5      | 388| 539.118 [M+H]+                      | IV |
| C343 | Unknown 122      | C3H4O4      | 388| 655.2401 [M-H]                      | IV |
| C344 | Unknown 123      | C3H5O5      | 388| 717.1461 [M-H]; 718.1492 [C-MH]; 719.1518 (2)C[M-H]; 736.1864 [M+NH4]; 737.19 [3C+NH4]+ | IV |
| C345 | Unknown 124      | C3H5NO5     | 390| 700.269 [M-H]                       | IV |
| C346 | Unknown 125      | C3H4O3      | 397| 713.2446 [M+H]+                     | IV |
| C347 | Unknown 126      | C3H3O4      | 397| 221.1901 [M+H]+; 441.2458 [*]       | IV |
| C348 | Unknown 127      | C3H5O4      | 397| 463.2549 [M-H+HCOOH]; 419.264 [M-H]+ | IV |
| C349 | Unknown 128      | C3H5O3      | 402| 793.2923 [M-H]                      | IV |
| C350 | Unknown 129      | C3H5O3      | 405| 601.2134 [M-H]; 602.2168 [3C-MH]    | IV |
| C351 | Unknown 140      | C3H6O3      | 409| 789.2613 [M-H]                      | IV |
| C352 | Unknown 141      | C3H6O4      | 409| 428.1918 [M-NH4]+; 456.2227 [*]     | IV |
| C353 | Unknown 142      | C3H6O4      | 424| 289.1463 [M+H]+                     | IV |
| C354 | Unknown 143      | C3H5NO7     | 430| 390.1548 [M+H]+                     | IV |
| C355 | Unknown 144      | C3H6O4      | 442| 321.1341 [M-H-H2O-C3H4O]           | IV |
| C356 | Unknown 145      | C3H6O4      | 444| 397.1495 [M-H]+                     | IV |
| C357 | Unknown 146      | C3H6O4      | 450| 393.1192 [M-H]                      | IV |
| C358 | Unknown 147      | C3H5O4      | 450| 213.1122 [M+H]+                     | IV |
| C359 | Unknown 148      | C3H6O4      | 463| 349.1294 [M-H-CH3OH]                | IV |
| C360 | Unknown 149      | C3H4O4      | 470| 577.2867 [M-H+HCOOH]; 533.2953 [M-H]+ | IV |
| C361 | Unknown 150      | C3H6O4      | 472| 471.166 [M-H]; 490.2068 [M-NH4]+    | IV |
| C362 | Unknown 151      | C3H5O7     | 483| 319.1187 [DOA-H]                    | IV |
| C363 | Unknown 152      | C3H5O5     | 485| 331.2492 [M-H]; 333.2638 [M+H]+    | IV |
| C364 | Unknown 153      | C3H5O7     | 495| 609.234 [M-H]                       | IV |
| C365 | Unknown 154      | C3H5O7     | 509| 591.1466 [M+H]+                     | IV |
| C366 | Unknown 155      | C3H5O7     | 508| 379.1763 [M-H]                      | IV |
| C367 | Unknown 156      | C3H5O7     | 509| 287.2226 [M-H]; 289.2374 [M+H]+    | IV |
| C368 | Unknown 157      | C3H5O7     | 516| 271.1178 [M+H]+; 239.0915 [M+H+CH3OH]+ | IV |
| C369 | Unknown 158      | C3H5O7     | 520| 319.1543 [M+H]+                     | IV |
| C370 | Unknown 159      | C3H5O7     | 521| 181.1223 [M+H]+                     | IV |
| C Compound       | Formula | RT   | Ions                                                                 |
|-----------------|---------|------|----------------------------------------------------------------------|
| C371 Unknown 160| C₃₇₁H₃₇O₈| 521  | 377.1234 [M+H]⁺; 440.1917 [+] / 445.1469 [+]                           |
| C372 Unknown 161| C₃₁H₂₀O₈| 529  | 345.1708 [M-H]⁻                                                        |
| C373 Unknown 162| C₃₁H₂₆O₅| 546  | 485.2181 [M-H]⁻                                                        |
| C374 Unknown 163| C₃₁H₃₄O₈| 575  | 721.2654 [M-H]⁻                                                        |
| C375 Unknown 164| C₃₁H₄₀O₂| 588  | 330.3368 [M+NH₄]⁺                                                     |
| C376 Unknown 165| C₃₁H₳₄O₂| 594  | 356.3524 [M+NH₄]⁺                                                     |
| C377 Unknown 166| C₃₁H₂₆N₂O₆| 622 | 566.3462 [M-H+HCOOH]⁻ / 522.3554 [M+H]⁻                                |
| C378 Unknown 167| C₃₁H₴₄O₇| 709  | 555.2842 [M-H]⁻ / 556.2875 [M-H⁺] / 574.3257 [M+NH₄]⁺                |

LI: IV
Table S2. MS/MS fragments of detected compounds by LTQ-Orbitrap.

| C     | Compound                  | MS² and pseudo-MSⁿ spectra                                                                 |
|-------|---------------------------|-------------------------------------------------------------------------------------------|
| C001  | Gluconic acid             | 195.0511 [M-H]: 129.0195 (100), 177.0405 (12)                                              |
| C002  | Quinic acid               | 191.0564 [M-H]: 85.0299 (38), 93.0350 (24), 109.0299 (11), 111.0456 (14), 127.0405 (31), 173.0459 (19), 191.0564 (100) |
| C003  | Malic acid                | 133.0146 [M-H]: 115.0040 (100)                                                            |
| C004  | Isocitric acid            | 191.0200 [M-H]: 111.0090 (100), 173.0093 (10)                                             |
| C005  | Citric acid               | 191.0199 [M-H]: 111.0090 (100), 173.0093 (11)                                             |
| C006  | Succinic acid             | 117.0197 [M-H]: 73.0299 (76), 99.0091 (25), 117.0196 (100)                                |
| C007  | Sugar alcohol             | 181.072 [M-H]: 59.0143 (22), 71.0143 (23), 85.0299 (10), 89.0248 (36), 101.0248 (100), 113.0248 (23), 119.0353 (13), 131.0353 (16), 143.0352 (10), 163.0614 (78), 181.0721 (42) |
|       |                           | 183.0865 [M+H]+: 69.0333 (19), 129.0544 (34), 147.0651 (82), 165.0755 (100)                |
| C008  | Pentose acid              | 165.041 [M-H]: 75.0991 (13), 87.0991 (10), 99.0091 (16), 101.0247 (23), 105.0196 (76), 129.0196 (45), 147.0301 (100) |
| C009  | Hexose                    | 179.0565 [M-H]: 75.0990 (16), 81.0349 (14), 99.0091 (20), 143.0351 (100), 161.0457 (44) |
|       |                           | 225.062 [M-H+HCOOH]: 89.0247 (19), 161.0458 (11), 179.0562 (100)                         |
| C010  | Di-hexose                 | 341.1094 [M-H]: 101.0246 (24), 161.0457 (100), 179.0565 (25)                              |
|       |                           | 387.1148 [M-H+HCOOH]: 161.0457 (43), 179.0562 (14), 341.1088 (100)                        |
|       |                           | 360.1505 [M+NH₄]+: 163.0600 (13), 325.1128 (100)                                          |
| C011  | Tri-hexose                | 549.1677 [M-H+HCOOH]: 161.0457 (12), 341.1087 (40), 443.1406 (10), 503.1619 (100)       |
|       |                           | 522.2082 [M+NH₄]+: 325.1129 (100), 487.1655 (67), 505.1773 (15)                           |
| C012  | Tetra-hexose              | 711.2203 [M+H+HCOOH]: 665.2143 (100)                                                     |
| C013  | Glycerol                  | 93.0500 [M-H]: 57.0333 (78), 75.0439 (100)                                               |
| C014  | Trihydroxy-octadecadienoic acid | 327.2179 [M-H]: 171.1028 (100), 201.1132 (12), 211.1340 (27), 221.1183 (11), 229.1447 (51), 239.1289 (11), 291.1966 (44), 309.2072 (16) |
| C015  | Trihydroxyoctadecenoic acid (I) | 329.2338 [M-H]: 171.1028 (28), 201.1132 (100), 293.2122 (23), 311.2225 (46)            |
|       |                           | 331.2481 [M-H]: 277.2164 (26), 295.2267 (100), 313.2375 (53)                              |
| C016  | Trihydroxyoctadecenoic acid (II) | 329.2337 [M-H]: 171.1028 (100), 211.1340 (70), 229.1446 (92), 293.2122 (31), 311.2228 (38) |
| C017  | Apigenin glucoside (I)    | 431.0991 [M-H]: 311.0560 (100), 341.0668 (28)                                             |
|       |                           | 433.1129 [M+H]+: 313.0708 (22), 337.0707 (15), 367.0814 (38), 379.0811 (11), 397.0917 (31), 415.1020 (100) |
| C   | Compound                                      | MS² and pseudo-MS² spectra                   |
|-----|-----------------------------------------------|----------------------------------------------|
| C018| Apigenin glucoside (II)                       | 431.0991 [M-H]: 268.0378 (12), 269.0456 (100) |
|     |                                               | 433.113 [M+H]: 271.0691 (100)                 |
| C019| Apigenin rutinoside (I)                       | 577.1566 [M-H]: 293.0455 (28), 413.0877 (100) |
|     |                                               | 579.1716 [M+H]: 271.0601 (4), 415.1022 (18), 433.1126 (100) |
| C020| Apigenin rutinoside (II)                      | 577.1566 [M-H]: 269.0455 (100)                 |
|     |                                               | 579.1714 [M+H]: 271.0691 (18), 433.1130 (100) |
| C021| Apigenin rhamnosyl acetyl-glucoside (I)       | 621.1814 [M+H]: 271.0604 (8), 313.0710 (11), 415.1023 (15), 433.1128 (100) |
| C022| Apigenin rhamnosyl acetyl-glucoside (II)      | 619.1674 [M-H]: 293.0451 (32), 413.0876 (100), 455.0993 (14), 559.1456 (28), 577.1561 (11) |
|     |                                               | 621.1816 [M+H]: 271.0599 (5), 313.0709 (14), 415.1023 (17), 433.1127 (100) |
| C023| Apigenin rhamnosyl acetyl-glucoside (III)     | 619.1672 [M-H]: 293.0456 (36), 413.0879 (100) |
|     |                                               | 621.1815 [M+H]: 271.0602 (6), 415.1023 (14), 433.1128 (100) |
| C024| Apin                                           | 563.1413 [M-H]: 353.0666 (43), 383.0773 (52), 443.0985 (100), 473.1090 (75), 503.1194 (20), 545.1298 (16) |
| C025| Methoxy-apigenin glucoside                    | 461.1096 [M-H]: 284.0323 (11), 298.0481 (14), 299.0560 (100), 446.0853 (74) |
|     |                                               | 463.124 [M+H]: 301.0705 (100)                 |
| C026| Luteolin                                      | 285.0405 [M-H]: 133.0297 (16), 149.0246 (10), 151.0037 (47), 175.0401 (100), 197.0608 (21), 198.0321 (11), 199.0400 (86), 201.0194 (23), 213.0558 (24), 217.0505 (66), 223.0401 (14), 241.0507 (95), 243.0298 (56), 257.0457 (18), 267.0292 (12), 285.0416 (2) |
|     |                                               | 287.0553 [M+H]: 153.0182 (45), 177.0675 (100), 287.0560 (4) |
| C027| Luteolin glucoside (I)                       | 447.0936 [M-H]: 285.0405 (100)                 |
|     |                                               | 449.1085 [M+H]: 287.0550 (100)                 |
|     |                                               | 287.055 [M+H-hexose]: 135.0439 (13), 153.0181 (95), 161.0229 (10), 177.0674 (100), 287.0561 (4) |
| C028| Luteolin glucoside (II)                      | 447.0934 [M-H]: 285.0404 (100)                 |
|     |                                               | 449.1082 [M+H]: 287.0551 (100)                 |
| C029| Luteolin rutinoside                           | 593.1517 [M-H]: 285.0402 (100)                 |
|     |                                               | 595.1654 [M+H]: 287.0545 (12), 449.1082 (100) |
| C030| Quercetin glucoside                           | 463.0881 [M-H]: 300.0277 (33), 301.0353 (100) |
|     |                                               | 465.1025 [M+H]: 303.0500 (100)                 |
|     |                                               | 303.05 [M+H-hexose]: 137.0229 (19), 153.0187 (20), 165.0182 (63), 229.0495 (92), 247.0602 (30), 257.0443 (100), 285.0388 (51) |
| C031| Quercetin rutinoside                          | 609.1467 [M-H]: 300.0276 (34), 301.0353 (100) |
|     |                                               | 611.1611 [M+H]: 303.0501 (100), 465.1025 (30) |
| C   | Compound                      | MS² and pseudo-MS² spectra                                                                 |
|-----|-------------------------------|---------------------------------------------------------------------------------------------|
| C032| Caffeic acid hexoside         | 341.0882 [M-H]: 135.0454 (11), 179.0351 (100), 251.0559 (14), 281.0668 (20)                 |
| C033| Caffeic acid rutinoside       | 487.1464 [M-H]: 179.0350 (100)                                                             |
| C034| Caffeic acid ethyl ester      | 207.0664 [M-H]: 135.0452 (23), 161.0246 (18), 179.0350 (100)                               |
| C035| Caffeoyl-threonic acid (I)    | 297.0616 [M-H]: 135.0301 (100), 135.0457 (2), 179.0350 (19)                                |
| C036| Caffeoyl-threonic acid (II)   | 297.0617 [M-H]: 135.0301 (100), 135.0458 (2), 179.0351 (21)                                |
| C037| Calceolarioside B             | 477.1411 [M-H]: 161.0246 (100), 315.1085 (19)                                             |
| C038| Rosmarinic acid               | 359.0777 [M-H]: 161.0246 (100), 179.0350 (23), 197.0456 (25)                               |
| C039| Coumaroylquinic acid          | 337.0931 [M-H]: 191.0560 (100)                                                             |
| C040| Cinnamic acid hexoside        | 309.0984 [M-H]: 111.0454 (47), 113.0247 (11), 129.0559 (12), 173.0457 (41), 223.0613 (27), 247.0976 (100), 291.0872 (43) |
| C041| Neochlorogenic acid           | 353.088 [M-H]: 191.0562 (100)                                                             |
| C042| Chlorogenic acid              | 353.088 [M-H]: 191.0562 (100)                                                             |
| C043| Verbascoside                  | 623.1985 [M-H]: 315.1083 (2), 461.1662 (100)                                              |
| C044| Isoverbascoside               | 623.1991 [M-H]: 315.1085 (2), 461.1662 (100)                                              |
| C045| Hydroxy-verbascoside          | 639.1937 [M-H]: 459.1509 (10), 487.1463 (3), 529.1565 (14), 621.1830 (100)                |
| C046| Methyl-hydroxy-verbascoside (I)| 653.2092 [M-H]: 459.1509 (3), 621.1825 (100)                                             |
| C048| Dimethyl-hydroxy-verbascoside | 667.225 [M-H]: 459.1504 (5), 621.1823 (100)                                              |
| C049| 3,4-Dihydroxyphenylglycol     | 169.051 [M-H]: 151.0402 (100)                                                             |
|     |                               | 151.0405 [M-H-H-O]: 123.0454 (100)                                                         |
|     |                               | 171.0652 [M+H]: 139.0387 (100)                                                            |
| C050| Hydroxytyrosol                | 153.0562 [M-H]: 123.0455 (100), 153.0560 (23)                                             |
| C051| Hydroxytyrosol glucoside (I)  | 153.056 [M-H-hexose]: 85.0299 (11), 89.0246 (69), 101.0246 (69), 113.0246 (100), 135.0452 (21), 153.0558 (41) |
|     |                               | 317.1237 [M+H]: 137.0595 (100), 221.0799 (13), 299.1125 (20)                              |
| C   | Compound                                        | MS² and pseudo-MSⁿ spectra                                                                 |
|-----|------------------------------------------------|------------------------------------------------------------------------------------------|
| C052| Hydroxytyrosol glucoside (II)                   | 315.1085 [M-H]: 123.0455 (10), 135.0453 (34), 153.0559 (100)                            |
|     |                                                | 334.1499 [M-NH₄⁺]: 137.0596 (79), 155.0702 (10), 155.0718 (1), 251.0914 (10), 263.0916 (46), 261.1020 (35), 299.1178 (22), 317.1232 (100) |
| C053| Hydroxytyrosol rutinoside                       | 461.1666 [M-H]: 135.0453 (48), 297.0981 (15), 315.1085 (100)                          |
|     |                                                | 153.0562 [M-H-rutinoside]: 123.0454 (100)                                                |
|     |                                                | 480.2082 [M-NH₄⁺]: 247.0969 (13), 265.1072 (20), 275.0971 (13), 301.1287 (37), 309.1181 (49), 463.1811 (100) |
| C054| Dimer of hydroxytyrosol (I)                     | 305.1034 [M-H]: 123.0454 (2), 135.0455 (1), 153.0560 (10), 245.0823 (2), 275.0925 (100), 287.0925 (6) |
| C055| Dimer of hydroxytyrosol (II)                    | 305.1032 [M-H]: 245.0820 (21), 275.0923 (100), 287.0924 (7)                           |
| C056| Dimer of hydroxytyrosol (III)                   | 305.1033 [M-H]: 245.0821 (7), 275.0925 (100), 287.0925 (52)                          |
| C057| Dimer of hydroxytyrosol (IV)                    | 305.1032 [M-H]: 123.0454 (16), 151.0403 (41), 153.0559 (100)                         |
|     |                                                | 324.1446 [M-NH₄⁺]: 137.0595 (52), 153.0546 (100), 155.0701 (19), 271.0962 (20), 289.1062 (40), 307.1181 (16) |
| C059| Lactone (ester with hydroxytyrosol) (I)         | 321.1348 [M-H]: 185.0819 (100)                                                          |
| C060| Lactone (ester with hydroxytyrosol) (II)        | 321.1346 [M-H]: 111.0454 (14), 111.0818 (34), 185.0819 (100), 303.1238 (13)           |
|     |                                                | 323.1493 [M-H⁺]: 201.0918 (15), 219.1025 (26), 261.1124 (100), 279.1229 (78)        |
| C061| Lactone (ester with hydroxytyrosol) (III)       | 321.1348 [M-H]: 185.0820 (100)                                                          |
|     |                                                | 323.1498 [M-H⁺]: 137.0603 (31), 153.0905 (22), 169.0866 (100)                        |
| C062| Lactone (ester with hydroxytyrosol) (IV)        | 321.1346 [M-H]: 185.0819 (100)                                                          |
|     |                                                | 323.1493 [M-H⁺]: 137.0594 (100)                                                        |
| C063| Lactone glucoside (ester with hydroxytyrosol) (I)| 483.1877 [M-H]: 211.1130 (30), 241.1236 (25), 285.1133 (100), 303.1242 (10), 465.1769 (84) |
|     |                                                | 485.2014 [M-H⁺]: 269.1170 (57), 287.1276 (100), 305.1383 (24), 323.1485 (16)        |
| C064| Lactone glucoside (ester with hydroxytyrosol) (II)| 483.1876 [M-H]: 347.1348 (100)                                                        |
| C065| Tyrosol glucoside                               | 299.1144 [M-H]: 89.0247 (66), 101.0247 (70), 113.0247 (100), 119.0353 (42), 119.0505 (20), 125.0247 (11), 131.0353 (23), 143.0351 (81), 161.0457 (33), 179.0563 (64) |
|     |                                                | 318.1555 [M-NH₄⁺]: 121.0646 (11), 187.0754 (66), 205.0858 (74), 229.0860 (49), 247.0965 (80), 265.1070 (100), 301.1285 (42) |
| C066| Homogentisic acid                               | 167.0832 [M-H]: 123.0454 (100)                                                         |
| C068| Oleuropein isomer (I)                           | 539.1772 [M-H]: 179.0561 (17), 179.0723 (4), 223.0613 (100), 333.0825 (15), 377.1234 (6), 403.1247 (54) |
| C069| Oleuropein                                     | 539.1773 [M-H]: 275.0571 (16), 275.0927 (72), 307.0826 (90), 345.0988 (15), 377.1249 (100) |
|     |                                                | 377.1245 [M-H-hexose]: 275.0923 (86), 307.0821 (100), 345.0982 (19)                   |
| C    | Compound                        | MS<sup>2</sup> and pseudo-MS<sup>n</sup> spectra                                                   |
|------|---------------------------------|--------------------------------------------------------------------------------------------------|
|      |                                 | 558.2184 [M+NH<sub>4</sub>]<sup>+</sup>: 361.1282 (100), 379.1367 (24)                              |
|      |                                 | 361.1284 [M+H-hexose-H<sub>2</sub>O]<sup>+</sup>: 137.0595 (100), 165.0546 (17), 329.1018 (18)  |
|      | Oleuropein isomer (II)          | 539.1774 [M-H]: 275.0562 (14), 275.0924 (74), 307.0822 (91), 327.0876 (13), 345.0983 (19), 377.1243 (100) |
|      | Oleuropein isomer (III)         | 539.1774 [M-H]: 275.0562 (23), 275.0923 (63), 307.0821 (100), 345.0982 (10), 377.1243 (45), 403.1248 (21) |
|      |                                 | 379.1388 [M+H-hexose]: 137.0595 (72), 165.0545 (15), 225.0758 (36), 243.0863 (12), 347.1125 (39), 361.1282 (100) |
|      | Oleuropein isomer (IV)          | 539.1773 [M-H]: 275.0557 (9), 275.0922 (59), 307.0820 (72), 345.0985 (100)                           |
|      | Oleuropein glucoside (I)        | 701.2301 [M-H]: 315.1082 (100), 437.1441 (19), 469.1352 (46), 539.1766 (26)                         |
|      | Oleuropein glucoside (II)       | 701.2306 [M-H]: 539.1768 (100)                                                                   |
|      |                                 | 720.2707 [M+NH<sub>4</sub>]<sup>+</sup>: 347.1128 (11), 361.1285 (44), 379.1387 (100), 541.1918 (44) |
|      | Oleuropein glucoside (III)      | 701.2299 [M-H]: 275.0559 (29), 275.0921 (75), 307.0819 (100), 345.0978 (16), 377.1239 (85), 539.1776 (6), 565.1769 (46), 669.2029 (11) |
|      | Oleuropein aglycone (I)         | 377.1246 [M-H]: 241.0718 (100), 275.0925 (2), 307.0819 (2), 345.0985 (1)                         |
|      |                                 | 424.1969 [M+CH<sub>2</sub>NH<sub>2</sub>]<sup>+</sup>: 137.0594 (15), 361.1281 (100)              |
|      |                                 | 361.1283 [M+H-H<sub>2</sub>O]<sup>+</sup>: 137.0595 (100), 165.0547 (15), 329.1023 (15)         |
|      | Oleuropein aglycone (II)        | 377.1247 [M-H]: 275.0554 (2), 275.0923 (86), 307.0821 (100), 345.0981 (18)                         |
|      |                                 | 379.1389 [M-H]: 137.0595 (100), 225.0756 (71), 347.1124 (25), 361.1279 (30)                      |
|      | Oleuropein aglycone (III)       | 377.1247 [M-H]: 275.0555 (2), 275.0924 (84), 307.0822 (100), 345.0983 (18)                         |
|      |                                 | 379.1389 [M-H]: 137.0595 (100), 225.0760 (25), 347.1124 (24), 361.1276 (20)                       |
|      | Oleuropein aglycone (IV)        | 377.1248 [M-H]: 275.0554 (2), 275.0924 (86), 307.0822 (100), 345.0982 (18)                         |
|      |                                 | 379.1389 [M-H]: 137.0595 (100), 225.0758 (46), 243.0861 (12), 347.1123 (42)                       |
|      | Hydroxy-oleuropein              | 555.1725 [M-H]: 223.0613 (16), 291.0512 (1), 291.0871 (12), 323.0771 (16), 393.1193 (31), 403.1248 (48), 537.1612 (100) |
|      | Methyl-oleuropein aglycone (I)  | 391.1403 [M-H]: 151.0765 (100)                                                                     |
|      | Methyl-oleuropein aglycone (II) | 391.1403 [M-H]: 223.0612 (7), 255.0875 (100)                                                      |
|      | Methyl-oleuropein aglycone (III)| 391.1401 [M-H]: 211.0976 (19), 223.0612 (4), 255.0874 (100), 359.1137 (10)                      |
|      | Hydroxy-methyl-oleuropein       | 569.1882 [M-H]: 223.0613 (11), 403.1247 (75), 407.1348 (13), 537.1611 (100)                       |
|      | Demethyloleuropein              | 525.162 [M-H]: 165.0588 (21), 195.0663 (100), 249.0767 (12), 301.1081 (23), 319.1187 (28), 363.1088 (14), 389.1089 (44), 481.1721 (62) |
|      | DOA (I)                         | 319.119 [M-H]: 123.0454 (8), 135.0454 (1), 153.0599 (49), 165.0588 (4), 257.1185 (19), 259.0976 (81), 275.1289 (100) |
|      |                                 | 321.1334 [M+H]: 137.0594 (2), 249.0755 (23), 285.1120 (14), 303.1227 (100)                       |
|      | DOA (II)                        | 321.1336 [M+H]: 137.0595 (100), 303.1230 (16)                                                     |
| C   | Compound                          | MS² and pseudo-MSⁿ spectra                                                                 |
|-----|-----------------------------------|--------------------------------------------------------------------------------------------|
| C088| DOA (III)                         | C088 DOA (III) 319.1193 [M-H]: 123.0454 (10), 135.0454 (1), 153.0559 (51), 165.0558 (4), 257.1185 (16), 259.0977 (74), 275.1289 (100) |
|     |                                  | 321.1334 [M+H]: 137.0596 (6), 167.0699 (1), 249.0759 (13), 285.1124 (12), 303.1230 (100) |
| C089| DOA (IV)                          | C089 DOA (IV) 319.1191 [M-H]: 165.0558 (21), 195.0662 (100), 301.1081 (12) |
|     |                                  | 321.1356 [M+H]: 137.0594 (16), 261.1127 (13), 285.1132 (11), 303.1230 (100) |
| C090| DOA (V)                           | C090 DOA (V) 319.1191 [M-H]: 139.0767 (21), 183.0663 (100) |
|     |                                  | 321.1336 [M+H]: 137.0595 (100), 303.1230 (14) |
| C091| DOA (VI)                          | C091 DOA (VI) 319.1191 [M-H]: 139.0767 (8), 183.0663 (100) |
|     |                                  | 321.1335 [M+H]: 137.0595 (100), 303.1230 (14) |
| C092| DOA linked to hydroxytyrosol (I) | C092 DOA linked to hydroxytyrosol (I) 455.1719 [M-H]: 205.0872 (17), 257.1183 (35), 275.1294 (13), 301.1083 (25), 319.1188 (100), 385.1291 (33), 425.1603 (20), 437.1607 (51) |
|     |                                  | 457.1864 [M+H]: 137.0596 (17), 303.1231 (53), 321.1329 (10), 385.1284 (29), 439.1755 (100) |
| C093| DOA linked to hydroxytyrosol (II)| C093 DOA linked to hydroxytyrosol (II) 455.1715 [M-H]: 153.0560 (24), 257.1191 (14), 259.0973 (17), 275.0926 (18), 275.1294 (19), 301.1073 (11), 319.1187 (85), 385.1291 (100), 437.1602 (20) |
|     |                                  | 457.1864 [M+H]: 137.0596 (17), 303.1231 (53), 321.1329 (10), 385.1284 (29), 439.1755 (100) |
| C094| DOA linked to hydroxytyrosol (III)| C094 DOA linked to hydroxytyrosol (III) 455.1714 [M-H]: 153.0559 (25), 259.0975 (16), 275.0929 (18), 275.1282 (15), 319.1186 (77), 385.1292 (100), 437.1606 (13) |
|     |                                  | 457.1869 [M+H]: 137.0597 (20), 303.1233 (55), 385.1283 (32), 439.1756 (100) |
| C095| Hydroxy-DOA                       | C095 Hydroxy-DOA 335.114 [M-H]: 199.0613 (100) |
|     |                                  | 337.1284 [M+H]: 137.0595 (32), 277.1063 (17), 301.1082 (13), 319.1176 (100) |
| C096| Hydrated-DOA (I)                  | C096 Hydrated-DOA (I) 337.1295 [M-H]: 201.0769 (100) |
|     |                                  | 339.1444 [M+H]: 137.0595 (100), 309.1331 (13) |
| C097| Hydrated-DOA (II)                 | C097 Hydrated-DOA (II) 337.1296 [M-H]: 201.0769 (100) |
|     |                                  | 337.1296 [M+H]: 137.0595 (32), 277.1063 (17), 301.1082 (13), 319.1176 (100) |
| C098| Hydrated-DOA (III)                | C098 Hydrated-DOA (III) 337.1296 [M-H]: 123.0453 (27), 153.0558 (100), 165.0557 (48), 183.0662 (19), 199.0616 (11), 319.1186 (48) |
|     |                                  | 337.1296 [M+H]: 137.0595 (32), 277.1063 (17), 301.1082 (13), 319.1176 (100) |
| C099| Hydrated-DOA linked to hydroxytyrosol (I) | C099 Hydrated-DOA linked to hydroxytyrosol (I) 473.1823 [M-H]: 153.0558 (26), 249.0768 (14), 257.1185 (14), 275.1292 (11), 319.1186 (69), 403.1402 (74), 413.1608 (19), 455.1713 (100) |
|     |                                  | 492.2228 [M+NH₄]: 165.0546 (17), 321.1330 (100), 457.1866 (15) |
| C100| Hydrated-DOA linked to hydroxytyrosol (II) | C100 Hydrated-DOA linked to hydroxytyrosol (II) 473.1822 [M-H]: 201.0768 (16), 337.1293 (100) |
|     |                                  | 492.2228 [M+NH₄]: 165.0546 (17), 321.1330 (100), 457.1866 (15) |
| C101| Hydrated-DOA linked to hydroxytyrosol (III) | C101 Hydrated-DOA linked to hydroxytyrosol (III) 473.1819 [M-H]: 337.1293 (100) |
|     |                                  | 473.1819 [M+H]: 201.0768 (16), 337.1293 (100) |
| C102| Hydrated-DOA linked to hydroxytyrosol glucoside | C102 Hydrated-DOA linked to hydroxytyrosol glucoside 635.2351 [M-H]: 195.0662 (83), 301.1079 (13), 319.1186 (100), 473.1815 (45), 545.2031 (18), 575.2122 (20) |
|     |                                  | 654.2756 [M+NH₄]: 303.1227 (30), 321.1336 (51), 457.1861 (40), 475.1960 (100), 619.2387 (19) |
| C103| Methyl-DOA                        | C103 Methyl-DOA 333.1346 [M-H]: 153.0921 (16), 197.0819 (100) |
|     |                                  | 335.1488 [M+H]: 137.0595 (100), 190.9978 (57), 317.1375 (13) |
| C104| Acetal of DOA (I)                 | C104 Acetal of DOA (I) 365.1607 [M-H]: 183.0663 (44), 229.1081 (100), 319.1182 (46) |
| C  | Compound                                 | MS² and pseudo-MS⁵ spectra                                                                 |
|----|------------------------------------------|---------------------------------------------------------------------------------------------|
| C105 | Acetal of DOA (II)                       | 229.1084 [M-H-hydroxytyrosol]: 121.0662 (37), 137.0610 (14), 153.0922 (100), 185.1183 (64), 201.1131 (11) |
| C106 | Acetal of DOA (III)                      | 365.1608 [M-H]: 229.1082 (100)                                                            |
| C107 | Acetal of DOA (IV)                       | 365.161 [M-H]: 195.0664 (30), 229.1083 (100), 319.1190 (11)                                |
|     |                                          | 384.2021 [M+NH₄]: 121.0656 (19), 133.1012 (22), 133.1233 (30), 195.1016 (56), 213.1124 (100) |
| C108 | Acetal of DOA linked to hydroxytyrosol    | 501.2132 [M-H]: 365.1605 (100)                                                            |
| C109 | Ligrostoside (I)                        | 523.1829 [M-H]: 259.0978 (35), 291.0873 (56), 361.1296 (100)                              |
|     |                                          | 361.1299 [M-H-hexose]: 259.0976 (75), 291.0871 (100)                                      |
|     |                                          | 542.2246 [M+NH₄]: 225.0758 (29), 387.1285 (37), 507.1857 (100)                           |
| C110 | Ligrostoside (II)                       | 523.1829 [M-H]: 259.0975 (16), 291.0871 (26), 361.1292 (29), 421.1501 (37), 453.1401 (100) |
|     |                                          | 525.1974 [M+H]: 225.0751 (16), 347.1142 (10), 475.1619 (34), 507.1837 (100)              |
| C111 | Ligrostoside glucoside                  | 685.2349 [M-H]: 299.1137 (13), 421.1501 (24), 453.1401 (65), 523.1822 (100)              |
|     |                                          | 704.2764 [M+NH₄]: 369.1182 (37), 475.1596 (14), 489.1758 (99), 507.1858 (100)            |
| C112 | Ligrostoside aglycone                   | 361.1299 [M-H]: 259.0976 (73), 291.0871 (100)                                            |
|     |                                          | 363.1443 [M+H]: 121.0646 (100), 225.0762 (22), 331.1182 (17)                              |
| C113 | Decarboxymethyl ligrostoside aglycone   | 349.1295 [M-H+HCOOH]: 139.0766 (11), 169.0871 (18), 213.0768 (100)                       |
|     |                                          | 305.1389 [M-H]: 137.0595 (19), 169.0859 (100)                                            |
| C114 | Hydroxy-decarboxymethyl-ligrostoside aglycone | 319.1189 [M-H]: 111.0090 (40), 121.0298 (16), 153.0560 (10), 181.0507 (100), 199.0612 (16) |
|     |                                          | 321.1335 [M-H]: 121.0646 (100), 137.0595 (24), 151.0755 (15), 303.1229 (15)              |
| C115 | Oleoside                                | 389.1097 [M-H]: 121.0297 (12), 121.0662 (25), 165.0558 (73), 183.0663 (100), 209.0459 (14), 227.0562 (81), 345.1200 (4) |
|     |                                          | 391.1238 [M-H]: 211.0601 (60), 229.0707 (100)                                            |
| C116 | Secologanoside                          | 389.1096 [M-H]: 121.0662 (15), 165.0559 (20), 183.0664 (6), 209.0457 (32), 345.1193 (100) |
|     |                                          | 408.1502 [M+NH₄]: 211.0599 (40), 229.0706 (100)                                          |
| C117 | Oleoside aglycone                       | 227.0564 [M-H]: 139.0767 (100), 165.0558 (100), 183.0663 (51)                            |
|     |                                          | 229.0709 [M-H]: 193.0494 (13), 211.0600 (100)                                            |
| C118 | Caffeoyl-oleoside                       | 551.1409 [M-H]: 179.0351 (11), 251.0562 (16), 281.0668 (24), 341.0879 (30), 345.1193 (10), 389.1092 (24), 507.1508 (100), 533.1305 (18) |
|     |                                          | 553.1561 [M+H]: 163.0390 (85), 181.0498 (26), 211.0601 (11), 325.0922 (100), 535.1448 (88) |
| C119 | Caffeoyl-oleoside glucoside             | 713.194 [M-H]: 323.0771 (13), 345.1180 (2), 443.1196 (20), 489.1402 (28), 507.1507 (69), 533.1305 (67), 551.1406 (100), 669.2031 (12) |
| C  | Compound                                           | MS² and pseudo-MS² spectra                                                                 |
|----|----------------------------------------------------|------------------------------------------------------------------------------------------|
| C120 | Coumaroyl-oleoside                                 | 535.1465 [M-H]: 235.0615 (12), 265.0718 (20), 345.1193 (16), 389.1092 (22), 491.1559 (100) |
|     |                                                   | 537.1609 [M+H]: 147.0439 (40), 165.0546 (26), 291.0859 (13), 309.0971 (100), 519.1494 (76) |
| C121 | Dimethyl-hydroxy-octenoyloxy-secologanoside (I)    | 557.2247 [M-H]: 183.0662 (45), 185.1183 (68), 199.1341 (25), 209.0455 (18), 227.0562 (41), 227.1287 (37), 257.1393 (12), 371.0980 (100), 389.1086 (28) |
|     |                                                   | 537.1609 [M+H]: 147.0439 (40), 165.0546 (26), 291.0859 (13), 309.0971 (100), 519.1494 (76) |
| C122 | Dimethyl-hydroxy-octenoyloxy-secologanoside (II)   | 557.2251 [M-H]: 185.1183 (13), 199.1340 (13), 227.1290 (16), 345.1192 (29), 513.2345 (100) |
|     |                                                   | 557.2247 [M+H]: 183.0662 (45), 185.1183 (68), 199.1341 (25), 209.0455 (18), 227.0562 (41), 227.1287 (37), 257.1393 (12), 371.0980 (100), 389.1086 (28) |
| C123 | Elenolic acid (II)                                 | 241.0723 [M-H]: 95.0506 (60), 101.0247 (29), 121.0299 (18), 127.0403 (82), 139.0402 (100), 165.0558 (29), 197.0822 (11), 209.0456 (14) |
|     |                                                   | 243.0867 [M+H]: 165.0546 (22), 207.0652 (17), 211.0600 (20), 225.0758 (100) |
| C124 | Elenolic acid (III)                                | 241.0723 [M-H]: 95.0505 (1), 127.0404 (1), 139.0403 (1), 165.0558 (100) |
|     |                                                   | 243.0866 [M+H]: 193.0494 (11), 207.0651 (17), 211.0600 (22), 225.0758 (100) |
| C125 | Elenolic acid (IV)                                 | 241.0721 [M-H]: 95.0506 (58), 101.0247 (32), 121.0299 (21), 127.0403 (82), 139.0402 (100), 165.0558 (32), 197.0822 (11), 209.0456 (15) |
|     |                                                   | 243.0865 [M+H]: 139.0388 (14), 165.0545 (16), 211.0600 (100), 225.0758 (13) |
| C126 | Elenolic acid (V)                                  | 241.0721 [M-H]: 95.0506 (58), 101.0247 (32), 121.0299 (21), 127.0403 (82), 139.0402 (100), 165.0558 (32), 209.0457 (16) |
|     |                                                   | 243.0864 [M+H]: 211.0600 (100), 225.0757 (94) |
| C127 | Elenolic acid glucoside (I)                        | 403.1252 [M-H]: 179.0561 (30), 179.0720 (2), 223.0612 (100), 333.0825 (15), 359.1348 (14), 371.0981 (18) |
|     |                                                   | 403.1251 [M-H]: 181.0507 (4), 213.0769 (4), 225.0406 (14) |
| C128 | Elenolic acid glucoside (II)                       | 403.1253 [M-H]: 179.0562 (26), 179.0721 (7), 223.0613 (59), 371.0984 (100) |
| C129 | Elenolic acid diglucoside                          | 611.1834 [M+HCOOH]: 403.1246 (100) |
|     |                                                   | 403.1251 [M-H]: 179.0560 (27), 223.0612 (100), 333.0815 (12), 359.1339 (16), 371.0981 (17) |
| C130 | Desoxy-elenolic acid                               | 225.0771 [M-H]: 89.0247 (100) |
|     |                                                   | 227.0916 [M+H]: 109.0280 (26), 141.0544 (62), 155.0702 (25), 177.0543 (12), 183.0654 (11), 185.0807 (62), 195.0650 (30), 209.0807 (100) |
| C131 | Hydroxy-elenolic acid (I)                          | 257.0699 [M-H]: 137.0610 (100), 181.0507 (4), 213.0769 (4), 225.0406 (14) |
|     |                                                   | 259.0818 [M+H]: 227.0549 (100), 241.0708 (58) |
| C132 | Hydroxy-elenolic acid (II)                         | 257.0671 [M-H]: 137.0610 (65), 181.0507 (100), 213.0769 (81), 225.0406 (11) |
|     |                                                   | 259.0815 [M+H]: 227.0551 (61), 241.0706 (100) |
| C133 | Decarboxy-hydroxy-elenolic acid (I)                 | 213.077 [M-H]: 151.0777 (0), 169.0871 (100) |
|     |                                                   | 215.0917 [M+H]: 155.0704 (17), 197.0810 (100) |
| C134 | Decarboxy-hydroxy-elenolic acid (II)                | 213.0773 [M-H]: 107.0869 (52), 139.0767 (50), 151.0766 (3), 169.0872 (100) |
|     |                                                   | 215.0915 [M+H]: 197.0806 (100) |
| C  | Compound                                                                 | MS² and pseudo-MS² spectra                                                                                                                                                                                                 |
|----|---------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| C136 | Decarboxy-hydroxy-elenolic acid (III)                                     | 213.0771 [M-H]: 139.0767 (4), 151.0766 (100), 169.0871 (10), 183.0664 (29), 195.0665 (11)  
|     |                                                                          | 215.0917 [M+H]: 155.0702 (100), 197.0807 (26)                                                                                                                                                                               |
| C137 | Decarboxy-hydroxy-elenolic acid (IV)                                      | 213.0772 [M-H]: 107.0869 (14), 139.0767 (25), 151.0766 (100), 169.0872 (12), 183.0664 (70), 195.0664 (19)  
|     |                                                                          | 215.0914 [M+H]: 155.0701 (100), 197.0807 (29)                                                                                                                                                                               |
| C138 | Decarboxy-hydroxy-elenolic acid (V)                                       | 213.0771 [M-H]: 139.0763 (1), 151.0766 (100), 169.0878 (1)  
|     |                                                                          | 215.0917 [M+H]: 155.0702 (100), 197.0808 (24)                                                                                                                                                                               |
| C139 | Decarboxy-hydroxy-elenolic acid (VI)                                      | 213.0772 [M-H]: 139.0767 (9), 151.0765 (100), 169.0871 (75), 183.0663 (70), 195.0664 (19)  
|     |                                                                          | 215.0914 [M+H]: 155.0702 (100), 197.0808 (36)                                                                                                                                                                               |
| C142 | Decarboxy-hydroxy-elenolic acid linked to hydroxytyrosol (III)          | 349.1296 [M-H]: 213.0769 (100), 331.1190 (19)  
|     |                                                                          | 213.0772 [M-H-hydroxytyrosol]: 151.0765 (100), 169.0870 (12), 183.0663 (33), 195.0663 (13)  
|     |                                                                          | 351.1442 [M+H]: 137.0596 (100)                                                                                                                                                                                           |
| C143 | Decarboxy-hydroxy-elenolic acid linked to hydroxytyrosol (IV)           | 349.1295 [M-H]: 151.0765 (41), 213.0769 (14), 331.1188 (100)  
|     |                                                                          | 213.0771 [M-H-hydroxytyrosol]: 151.0765 (100), 195.0663 (12)  
|     |                                                                          | 351.1442 [M+H]: 137.0596 (100), 333.1335 (46)                                                                                                                                                                           |
| C144 | Decarboxy-hydroxy-elenolic acid linked to hydroxytyrosol (V)            | 349.1297 [M-H]: 151.0765 (25), 213.0769 (20), 331.1189 (100)  
|     |                                                                          | 351.1436 [M+H]: 137.0594 (100), 215.0913 (36)                                                                                                                                                                           |
| C145 | Methyl-elenolic acid (I)                                                | 255.0877 [M-H]: 95.0505 (73), 115.0403 (37), 121.0298 (24), 139.0402 (98), 141.0559 (100), 165.0557 (36), 209.0456 (23)  
|     |                                                                          | 257.102 [M+H]: 211.0600 (100), 239.0913 (89)                                                                                                                                                                           |
| C146 | Methyl-elenolic acid (II)                                               | 257.1022 [M+H]: 225.0758 (100)                                                                                                                                                                                             |
| C147 | Aldehydic form of decarboxymethyl elenolic acid (I)                     | 217.1074 [M+H]: 121.0646 (32), 169.0860 (12), 187.0961 (19), 199.0963 (100)                                                                                                                                              |
| C148 | Aldehydic form of decarboxymethyl elenolic acid (II)                    | 217.1071 [M+H]: 121.0644 (45), 169.0858 (38), 187.0962 (97), 199.0962 (100)                                                                                                                                              |
| C149 | Aldehydic form of decarboxymethyl elenolic acid (III)                   | 215.0928 [M-H]: 139.0767 (22), 183.0664 (100)  
|     |                                                                          | 217.1073 [M+H]: 199.0965 (100)                                                                                                                                                                                           |
| C150 | Aldehydic form of decarboxymethyl elenolic acid glucoside               | 377.1459 [M-H]: 153.0923 (24), 197.0820 (100)  
|     |                                                                          | 379.1602 [M+H]: 199.0965 (100), 217.1075 (19)                                                                                                                                                                           |
| C151 | Elenolic acid dialdehyde epimer linked to hydroxytyrosol glucoside     | 541.1929 [M-H]: 225.0768 (10), 361.1294 (100)  
|     |                                                                          | 363.144 [M+H-hexose-H₂O]: 137.0596 (100)                                                                                                                                                                               |
| C   | Compound                                                                 | MS² and pseudo-MSⁿ spectra                                                                 |
|-----|-------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| C152| Elenolic acid dialdehyde epimer linked to hydroxytyrosol (I)            | 379.1403 [M-H]: 151.0401 (23), 199.0612 (100), 333.0979 (27)                               |
| C153| Elenolic acid dialdehyde epimer linked to hydroxytyrosol (II)           | 379.1405 [M-H]: 211.0614 (27), 243.0876 (100)                                           |
|     |                                                                         | 381.154 [M-H]: 137.0594 (48), 227.0913 (16), 245.1015 (10), 349.1281 (100)               |
| C154| Hydrated product of methyl-decarboxy-hydroxy-elenolic acid (I)          | 245.1035 [M-H]: 107.0869 (20), 151.0765 (16), 169.0871 (35), 183.0663 (31), 213.0769 (100), 215.0924 (24), 227.0926 (13) |
| C155| Hydrated product of methyl-decarboxy-hydroxy-elenolic acid (II)         | 245.1032 [M-H]: 111.0818 (29), 155.0715 (14), 201.1132 (100)                             |
| C156| Hydrated product of methyl-decarboxy-hydroxy-elenolic acid (III)        | 245.1032 [M-H]: 111.0818 (37), 155.0716 (24), 201.1133 (100), 227.0926 (12)              |
| C158| Cannizzaro-like product of elenolic acid dialdehyde (II)                | 259.0826 [M-H]: 95.0505 (61), 101.0246 (15), 113.0611 (97), 127.0403 (16), 139.0402 (11), 165.0558 (14), 215.0563 (24), 227.0562 (11), 241.0718 (100) |
| C159| DEDA (I)                                                                | 183.0664 [M-H]: 95.0868 (23), 139.0768 (100)                                           |
|     |                                                                         | 185.081 [M-H]: 121.0645 (60), 125.0594 (31), 149.0595 (7), 167.0701 (100)               |
| C160| DEDA (II)                                                               | 183.0666 [M-H]: 59.0142 (28), 95.0872 (5), 139.0765 (17), 165.0559 (100)                |
| C161| DEDA (III)                                                              | 183.0665 [M-H]: 95.0870 (7), 139.0767 (100)                                           |
|     |                                                                         | 185.0809 [M-H]: 95.0854 (26), 121.0647 (4), 123.0440 (15), 149.0597 (9), 167.0703 (100), 185.0809 (13) |
| C162| DEDA (IV)                                                               | 183.0665 [M-H]: 95.0870 (41), 139.0767 (100), 183.0664 (14)                             |
|     |                                                                         | 185.081 [M-H]: 121.0646 (100), 149.0598 (0), 167.0703 (5)                               |
| C163| Hydroxy-DEDA                                                            | 199.0614 [M-H]: 111.0091 (26), 111.0818 (100), 155.0715 (83), 181.0507 (32)             |
|     |                                                                         | 201.0761 [M-H]: 165.0545 (44), 183.0650 (100)                                         |
| C164| DEDA hydrated (I)                                                       | 201.077 [M-H]: 95.0869 (19), 113.0611 (15), 157.0871 (31), 183.0663 (20)               |
| C166| DEDA hydrated (III)                                                    | 201.0771 [M-H]: 139.0766 (35), 157.0872 (100), 183.0664 (24)                            |
|     |                                                                         | 220.118 [M+NH₄⁺]: 90.0547 (46), 184.0968 (29), 202.1073 (100)                          |
| C167| DEDA hydrated (IV)                                                     | 201.0772 [M-H]: 139.0767 (39), 157.0872 (100), 183.0664 (27)                           |
| C168| DEDA ester (I)                                                          | 197.0822 [M-H]: 151.0402 (100)                                                        |
| C169| DEDA ester (II)                                                        | 197.0822 [M-H]: 153.0922 (100)                                                         |
| C170| DEDA ester (III)                                                       | 197.082 [M-H]: 109.1024 (20), 153.0921 (100)                                          |
| C  | Compound                          | MS² and pseudo-MS² spectra                                                                 |
|----|-----------------------------------|---------------------------------------------------------------------------------------------|
| C171 | DEDA alditol (I)                  | 347.1352 [M-H]: 139.0768 (18), 163.0613 (13), 181.0719 (100), 183.0665 (1), 277.0924 (10)     |
|     |                                   | 349.1495 [M-H]: 121.0645 (16), 185.0811 (26), 313.1286 (58), 331.1393 (100)                  |
|     |                                   | 366.1758 [M+NH₄]: 331.1391 (100)                                                           |
| C172 | DEDA alditol (II)                 | 347.1352 [M-H]: 123.0454 (16), 139.0767 (58), 163.0613 (29), 165.0558 (13), 181.0719 (100), 183.0662 (4), 277.0928 (16), 329.1240 (22) |
| C173 | DEDA alditol (III)                | 347.1352 [M-H]: 123.0452 (10), 139.0767 (56), 163.0613 (19), 165.0558 (54), 181.0719 (100), 183.0664 (21), 277.0930 (31), 329.1247 (17) |
|     |                                   | 349.1501 [M-H]: 121.0648 (34), 185.0809 (24), 313.1286 (56), 331.1392 (100)                  |
| C174 | DEDA alditol (IV)                 | 347.1352 [M-H]: 139.0768 (46), 163.0608 (26), 165.0558 (26), 181.0717 (100), 183.0667 (47), 277.0924 (17), 329.1237 (22) |
|     |                                   | 349.1497 [M+H]: 121.0646 (33), 185.0808 (24), 313.1283 (54), 331.1388 (100)                  |
| C175 | DEDA alditol (V)                  | 366.1758 [M-H]: 123.0452 (16), 139.0767 (58), 163.0613 (29), 165.0558 (13), 181.0719 (100), 183.0662 (4), 277.0928 (16), 329.1240 (22) |
|     |                                   | 349.1501 [M-H]: 121.0648 (34), 185.0809 (24), 313.1286 (56), 331.1392 (100)                  |
| C176 | Loganin                          | 435.1511 [M-H+HCOOH]: 313.1294 (100), 357.1194 (54), 375.1299 (15)                         |
|     |                                   | 391.1603 [M-H]: 133.0647 (5), 151.0748 (6), 169.0857 (5), 211.0964 (100), 229.1071 (27)    |
|     |                                   | 229.1074 [M+H-hexose]: 155.0703 (23), 169.0859 (100), 179.0701 (1), 197.0809 (11), 211.0964 (34) |
| C177 | Loganin aglycone (I)             | 229.1073 [M-H]: 151.0751 (5), 155.0702 (20), 169.0858 (21), 179.0703 (3), 197.0808 (8), 211.0965 (100) |
|     |                                   | 211.0968 [M-H+H₂O]: 133.0647 (31), 137.0596 (44), 151.0753 (100), 155.0704 (1), 169.0859 (5), 179.0703 (75), 181.0859 (14), 183.1016 (15), 193.0859 (51), 197.0811 (1) |
| C178 | Loganin aglycone (II)             | 229.1072 [M-H]: 155.0701 (66), 169.0858 (100), 197.0805 (17), 211.0964 (41)                |
|     |                                   | 211.0968 [M-H+H₂O]: 133.0648 (37), 151.0752 (39), 161.0596 (26), 169.0858 (2), 179.0704 (35), 181.0860 (18), 193.0859 (100), 197.0805 (2) |
| C179 | Loganin aglycone (III)            | 229.1073 [M-H]: 155.0702 (2), 169.0857 (12), 179.0706 (1), 197.0804 (1), 211.0965 (100)    |
|     |                                   | 211.0966 [M-H+H₂O]: 127.0387 (19), 141.0544 (20), 153.0544 (11), 171.0650 (100)           |
| C180 | Loganin aglycone (IV)             | 227.093 [M-H]: 111.0091 (15), 181.0505 (100)                                             |
|     |                                   | 229.1073 [M-H]: 165.0545 (34), 183.0649 (32), 211.0963 (100)                               |
| C181 | Hydrated product of loganin      | 407.1566 [M-H]: 313.1295 (38), 357.1195 (52), 375.1302 (56), 377.1455 (19), 389.1455 (100) |
|     |                                   | 409.1707 [M-H]: 169.0859 (31), 211.0966 (22), 229.1071 (100)                             |
|     |                                   | 229.1073 [M+H-hexose+H₂O]: 155.0701 (35), 169.0858 (92), 197.0807 (13), 211.0964 (100) |
| C183 | Hydroxytyrosol derivative 02     | 447.1512 [M-H]: 135.0453 (33), 315.1084 (100)                                            |
| C184 | Hydroxytyrosol derivative 03 (I)  | 323.1503 [M-H]: 187.0975 (100)                                                           |
| C185 | Hydroxytyrosol derivative 03 (II) | 323.1505 [M-H]: 139.0765 (13), 187.0976 (100)                                           |
|     |                                   | 325.1646 [M+H]: 137.0595 (100)                                                          |
| C | Compound                          | MS² and pseudo-MS⁵ spectra                                      |
|---|-----------------------------------|---------------------------------------------------------------|
| C186 | Hydroxytyrosol derivative 04    | 463.125 [M-H]: 291.0507 (100), 327.0719 (30)                 |
| C187 | Hydroxytyrosol derivative 05    | 279.1241 [M-H]: 143.0715 (100)                               |
| C188 | Hydroxytyrosol derivative 06    | 453.1558 [M-H]: 151.0402 (17), 203.0713 (11), 255.1027 (100), 273.1134 (65), 275.0924 (13), 299.0922 (23), 317.1032 (67), 383.1138 (67), 435.1454 (29) |
| C189 | Hydroxytyrosol derivative 07    | 393.1923 [M-H]: 257.1394 (100)                               |
| C190 | DEDA derivative 01              | 483.1879 [M-H]: 165.0558 (99), 183.0664 (100)                |
| C191 | DEDA derivative 02              | 357.1197 [M-H]: 165.0559 (100), 183.0664 (43), 339.1083 (11)  |
| C192 | DEDA derivative 03 (I)          | 518.2235 [M+NH₄⁺]: 167.0700 (9), 185.0806 (7), 303.1227 (14), 321.1329 (100), 329.1232 (11), 339.1433 (25) |
| C193 | DEDA derivative 03 (II)         | 367.1402 [M-H]: 139.0767 (14), 183.0663 (100)                |
| C194 | DEDA derivative 04 (I)          | 351.1455 [M-H]: 139.0766 (4), 165.0556 (1), 183.0663 (41), 215.0924 (83), 319.1186 (100) |
| C195 | DEDA derivative 04 (II)         | 499.1822 [M-H]: 199.0611 (100)                               |
| C196 | DEDA derivative 05              | 487.1976 [M-H]: 165.0558 (0), 183.0668 (0), 351.1451 (100)    |
| C197 | DEDA derivative 05 linked to hydroxytyrosol | 453.1558 [M-H]: 151.0402 (17), 203.0713 (11), 255.1027 (100), 273.1134 (65), 275.0924 (13), 299.0922 (23), 317.1032 (67), 383.1138 (67), 435.1454 (29) |
| C198 | Elenolic acid derivative 01     | 159.0667 [M-H+HCOOH⁺]: 95.0505 (10), 113.0610 (26), 121.0298 (100), 123.0454 (59), 141.0559 (38) 132.1018 [M+NH₄⁺]: 86.0962 (100) |
| C199 | Elenolic acid derivative 02 (I) | 274.0926 [M+NH₄⁺]: 167.0700 (9), 185.0806 (7), 303.1227 (14), 321.1329 (100), 329.1232 (11), 339.1433 (25) |
| C200 | Elenolic acid derivative 02 (II) | 255.0512 [M-H]: 165.0558 (100), 193.0506 (25), 209.0460 (1) |
| C201 | Elenolic acid derivative 03     | 555.209 [M-H]: 165.0559 (9), 185.0559 (7), 226.0712 (36), 238.0711 (100), 256.0817 (89) |
| C202 | Elenolic acid derivative 04     | 493.1353 [M-H]: 135.0453 (11), 165.0558 (10), 209.0456 (12), 225.1132 (15), 327.1083 (14), 345.1192 (45), 511.2188 (100) |
| C203 | Unknown 001 (glucoside)         | 292.1404 [M-H]: 130.0877 (81), 191.1074 (28), 202.1085 (100), 244.1188 (55) 294.1549 [M-H]: 276.1442 (100) |
| C204 | Unknown 002 (glucoside)         | 323.1707 [M-H]: 143.1066 (76), 305.1600 (100)                |
| C205 | Unknown 003 (glucoside)         | 301.093 [M-H]: 101.0246 (21), 113.0246 (16), 124.0168 (23), 139.0402 (63), 159.0303 (10), 161.0457 (100) |
| C206 | Unknown 004 glucoside          | 333.1547 [M-H]: 111.0802 (15), 153.0909 (91), 171.1016 (100) |
| C208 | Unknown 005 (glucoside)         | 467.1775 [M-H+HCOOH⁺]: 371.1351 (100) 423.1867 [M-H]: 243.1231 (100) |
| C  | Compound                     | MS² and pseudo-MS² spectra                                                                 |
|----|------------------------------|-------------------------------------------------------------------------------------------|
| C209 | Unknown 006 (glucoside)     | 387.2015 [M+H⁺]: 189.1268 (17), 207.1380 (100), 369.1906 (21)                           |
| C210 | Unknown 007 (glucoside)     | 403.1978 [M-H⁻]: 161.0457 (13), 223.1340 (20), 241.1445 (100)                          |
| C211 | Unknown 008 (glucoside)     | 523.181 [M+H⁺]: 361.1283 (100), 491.1547 (40)                                          |
| C213 | Unknown 009 (glucoside)     | 553.157 [M-H⁻]: 167.0350 (84), 209.0456 (85), 289.0352 (13), 289.0714 (39), 321.0613 (90), 341.0671 (22), 359.0770 (76), 373.0932 (23), 391.1035 (100), 521.1313 (30) |
| C214 | Unknown 010 (glucoside)     | 691.2249 [M-H⁻]: 377.1238 (12), 403.1244 (14), 459.1296 (25), 497.1452 (16), 511.1603 (2), 529.1714 (18), 539.1766 (100) |
| C215 | Unknown 011 glucoside       | 583.2038 [M-H⁻]: 223.0614 (13), 403.1249 (79), 421.1505 (17), 537.1613 (100)          |
| C216 | Unknown 011                 | 421.1508 [M-H⁻]: 151.0400 (23), 223.0614 (12), 319.1185 (94), 351.1083 (100), 389.1243 (34) |
| C217 | Unknown 012 (glucoside)     | 729.2982 [M-H⁻]: 387.1810 (51), 549.2337 (100), 567.2433 (6)                         |
| C218 | Unknown 013 (I)             | 266.1037 [M-H⁻]: 222.1136 (100)                                                         |
| C219 | Unknown 013 (II)            |                                                                                          |
| C221 | Unknown 014 (II)            |                                                                                          |
| C222 | Unknown 014 (III)           | 189.1122 [M-H⁻]: 141.0909 (65), 159.1011 (85), 171.1014 (100)                         |
| C223 | Unknown 014 (IV)            | 187.0978 [M-H⁻]: 95.0869 (40), 169.0871 (100)                                          |
| C224 | Unknown 015 (I)             | 185.0820 [M-H⁻]: 111.0818 (100)                                                        |
| C225 | Unknown 015 (II)            | 185.0822 [M-H⁻]: 141.0923 (100)                                                        |
| C226 | Unknown 016 (I)             | 461.1672 [M-H⁺HCOOH⁺]: 179.0713 (35), 415.1612 (100)                                  |
| C227 | Unknown 016 (II)            |                                                                                          |
| C228 | Unknown 017 (I)             | 583.2034 [M-H⁺HCOOH⁺]: 375.1450 (11), 537.1974 (100)                                  |
| C230 | Unknown 018 (I)             | 507.2805 [M+H⁺]: 165.0551 (13), 225.0756 (100), 475.1602 (44)                         |
| C231 | Unknown 018 (II)            | 505.2648 [M-H⁺]: 373.2230 (100)                                                        |
| C232 | Unknown 019 (I)             | 365.1599 [M-H⁺]: 191.0971 (14), 191.1177 (18), 191.1352 (11), 201.1653 (25), 231.1755 (50), 245.1542 (16), 275.1651 (100), 319.1546 (27), 365.1599 [M+H⁺]: 221.0807 (14), 283.1330 (14), 301.1434 (70), 305.1385 (65), 319.1543 (86), 329.1385 (68), 347.1488 (100) |
| C234 | Unknown 020 (I)             | 197.1174 [M-H⁺]: 135.1167 (68), 161.0960 (16), 179.1067 (100)                         |
| C   | Compound        | MS² and pseudo-MSⁿ spectra                                                                 |
|-----|-----------------|------------------------------------------------------------------------------------------|
| C235 Unknown 020 (II) | 197.1176 [M+H]⁺: 151.0753 (100)                                                              |
| C236 Unknown 021 (I)  | 579.2092 [M-H]: 241.0724 (12), 293.1028 (41), 337.1290 (100)                               |
| C238 Unknown 022 (I)  | 307.1544 [M+H]⁺: 137.0595 (100), 171.1015 (66)                                              |
| C239 Unknown 022 (II) | 305.1394 [M-H]: 89.0056 (12), 89.0089 (11), 89.0537 (11), 123.0819 (93), 137.0610 (100), 167.0718 (24), 185.0822 (77), 191.1026 (17), 191.1262 (15) 307.1542 [M+H]⁺: 85.0641 (11), 121.0646 (100), 271.0413 (12) |
| C241 Unknown 023 (II) | 349.1644 [M+H]⁺: 137.0594 (100), 167.0702 (15), 195.1012 (12), 213.1121 (32), 277.1067 (17), 303.1227 (73), 331.1546 (42), 340.1951 (16) |
| C242 Unknown 024 (I)  | 485.1827 [M-H]: 227.1079 (23), 243.1392 (100), 271.0977 (13), 287.1288 (67), 407.1502 (23), 423.1811 (13), 467.1717 (12) |
| C243 Unknown 024 (II) | 485.1827 [M-H]: 227.1077 (26), 243.1392 (100), 271.0978 (13), 287.1288 (68), 407.1502 (17) |
| C244 Unknown 025 (I)  | 227.1290 [M-H]: 165.1287 (100), 183.1391 (82)                                               |
| C245 Unknown 025 (II) | 227.1293 [M-H]: 183.1391 (100), 209.1185 (23), 229.1439 [M+H]⁺: 193.1223 (37), 211.1330 (100) |
| C246 Unknown 026 (I)  | 577.2690 [M-H]: 184.0926 (10), 184.1798 (11), 225.0075 (100), 243.0180 (12), 299.0438 (47), 342.1432 (22) |
| C247 Unknown 026 (II) | 577.2690 [M-H]: 225.0074 (100), 299.0439 (77)                                              |
| C248 Unknown 027      | 272.9593 [M-H]: 158.9787 (100), 228.9691 (17)                                               |
| C249 Unknown 028      | 102.0338 [M+H]⁺: 61.0070 (100), 70.0123 (33), 81.5203 (77), 90.5257 (24)                   |
| C253 Unknown 032      | 290.0765 [M-H]: 200.0440 (100)                                                             |
| C255 Unknown 034      | 116.0705 [M-H]: 56.0082 (10), 56.0138 (16), 56.0257 (15), 70.0648 (100), 85.1075 (13)    |
| C256 Unknown 035      | 191.0737 [M-H]: 85.0298 (19), 93.0349 (11), 117.0367 (100), 127.0403 (16)                 |
| C258 Unknown 037      | 317.0549 [M-H]: 125.0245 (12), 225.0075 (100)                                             |
| C263 Unknown 042      | 305.1349 [M+Na]: 227.1027 (50), 233.0921 (18), 251.1027 (24), 269.1133 (40), 287.1240 (100) |
| C264 Unknown 043      | 512.1985 [M+NH₄⁺]: 171.0651 (100), 297.0974 (12), 333.1180 (28)                          |
| C266 Unknown 045      | 333.1196 [M-H]: 151.0402 (29), 181.0719 (100)                                             |
| C267 Unknown 046      | 147.0303 [M-H]: 57.0349 (24), 85.0298 (100), 87.0090 (64), 129.0196 (59)                  |
| C271 Unknown 050      | 217.0720 [M-H]: 129.0560 (11), 173.0457 (100), 199.0613 (22)                              |
| C273 Unknown 052      | 418.1512 [M-H]: 374.1610 (100)                                                            |
| C276 Unknown 055      | 252.1234 [M+NH₄⁺]: 166.0862 (100)                                                         |
| C  | Compound          | MS² and pseudo-MSⁿ spectra                                                                 |
|----|-------------------|------------------------------------------------------------------------------------------|
| C280 Unknown 059 | 310.0936 [M-H]: 115.0040 (95), 150.0563 (14), 194.0823 (84), 222.1140 (26), 266.1035 (100) |
|     | 312.1089 [M+H]: 250.1077 (19), 266.1025 (26), 268.1182 (18), 280.0817 (11), 294.0976 (100) |
| C281 Unknown 060 | 275.0773 [M-H]: 155.0351 (41), 199.0611 (100), 229.0719 (23), 243.0509 (14)                |
| C282 Unknown 061 | 161.0458 [M-H]: 71.0142 (49), 115.0039 (15), 143.0350 (100)                                |
| C283 Unknown 062 | 147.0665 [M-H]: 57.0349 (53), 69.1375 (12), 69.1655 (12), 69.1874 (10), 92.0751 (10), 99.0090 (38), 101.0247 (100), 101.0609 (15), 129.0561 (14) |
| C284 Unknown 063 | 280.1190 [M-H]: 150.0562 (27), 194.0823 (100)                                             |
|     | 282.1338 [M+H]: 178.0862 (29), 196.0968 (100)                                             |
| C285 Unknown 064 | 381.1406 [M-H]: 155.0715 (41), 181.0717 (39), 199.0612 (100), 363.1297 (19)               |
| C286 Unknown 065 | 326.1242 [M+H]: 251.0754 (100)                                                           |
| C288 Unknown 067 | 375.1298 [M-H]: 331.1398 (100)                                                           |
| C289 Unknown 068 | 755.2993 [M-H]: 347.1345 (100), 389.1461 (12), 407.1558 (82)                              |
| C291 Unknown 070 | 181.0509 [M-H]: 135.0453 (12), 163.0402 (100)                                            |
|     | 183.0577 [M+H]: 85.0745 (20), 123.0438 (100), 135.0660 (12), 155.0462 (11), 165.0545 (62), 199.1991 (13) |
| C294 Unknown 073 | 196.0972 [M+NH₄]: 178.0864 (100)                                                         |
| C295 Unknown 074 | 252.1600 [M+NH₄]: 120.0806 (78), 166.1225 (100), 206.1176 (22)                           |
| C296 Unknown 075 | 175.0615 [M-H]: 85.0661 (88), 113.0611 (53), 115.0403 (100), 157.0508 (38)              |
| C298 Unknown 077 | 431.1567 [M-H]: 113.0246 (14), 131.0351 (27), 149.0456 (58), 191.0561 (26), 299.1134 (100) |
|     | 433.1607 [M+H]: 318.1345 (10), 389.1713 (100), 415.1504 (25), 416.1345 (42)             |
| C299 Unknown 078 | 348.1656 [M+NH₄]: 151.0753 (100), 169.0859 (16), 265.1072 (10), 277.1072 (36), 295.1176 (40), 331.1389 (34) |
| C300 Unknown 079 | 266.1390 [M+NH₄]: 180.1018 (100)                                                         |
| C302 Unknown 081 | 344.1343 [M+NH₄]: 147.0439 (97), 165.0545 (100), 180.0867 (12), 309.0970 (15)           |
| C303 Unknown 082 | 390.1761 [M+NH₄]: 161.0595 (27), 193.0857 (100)                                          |
| C304 Unknown 083 | 611.1835 [M-H]: 403.1245 (81), 565.1772 (100)                                            |
| C306 Unknown 085 | 318.1703 [M+NH₄]: 272.1281 (100)                                                         |
| C307 Unknown 086 | 401.1455 [M-H]: 161.0458 (20), 269.1030 (100)                                            |
|     | 420.1852 [M+NH₄]: 115.0388 (51), 133.0494 (62), 223.0965 (74), 241.0704 (13), 253.1076 (18), 259.0813 (70), 295.1024 (100) |
| C     | Compound     | MS² and pseudo-MSⁿ spectra                                                                 |
|-------|--------------|--------------------------------------------------------------------------------------------|
| C308  | Unknown 087  | 305.0702 [M-H]: 126.0624 (10), 126.1088 (11), 225.1130 (100)                                    |
|       |              | 307.0852 [M+H]: 85.1032 (19), 85.1163 (14), 131.1372 (12), 191.0825 (17), 192.1650 (18), 199.0713 (22), 199.0949 (14), 199.1530 (22), 227.1277 (100) |
| C309  | Unknown 088  | 519.1721 [M-H]: 193.0505 (100), 235.0612 (29), 265.0716 (16), 295.0821 (21), 325.1138 (32) |
| C311  | Unknown 090  | 424.1827 [M+H⁺]: 131.1557 (12), 136.0987 (14), 136.1104 (11), 136.1274 (13), 192.1911 (11), 271.0181 (15), 340.1530 (43), 389.1442 (100) |
| C312  | Unknown 091  | 302.1601 [M+H⁺]: 145.0494 (12), 163.0598 (14), 285.1331 (100)                                |
| C313  | Unknown 092  | 420.2238 [M+H⁺]: 161.1322 (17), 205.1222 (85), 223.1328 (100), 241.1438 (24), 271.0229 (12) |
| C314  | Unknown 093  | 412.2183 [M+H⁺]: 115.0389 (34), 136.0987 (14), 136.1104 (11), 136.1274 (13), 192.1911 (11), 271.0181 (15), 340.1530 (43), 389.1442 (100) |
| C315  | Unknown 094  | 439.1827 [M-H]: 393.1768 (100)                                                               |
| C317  | Unknown 096  | 183.1017 [M+H⁺]: 123.0438 (10), 151.0752 (100)                                              |
| C318  | Unknown 097  | 551.1774 [M-H]: 337.0927 (100)                                                               |
| C319  | Unknown 098  | 446.1808 [M+H⁺]: 180.1018 (11), 206.0812 (30), 224.0917 (14), 292.1182 (100), 310.1288 (17), 360.1444 (25) |
| C320  | Unknown 099  | 511.2396 [M-H]: 325.1138 (100), 343.1241 (18)                                               |
| C322  | Unknown 101  | 253.0724 [M-H]: 117.0196 (100)                                                               |
| C324  | Unknown 103  | 441.1773 [M-H]: 153.0922 (41), 197.0819 (100), 243.0875 (19)                                |
| C325  | Unknown 104  | 775.2317 [M-H]: 345.1189 (46), 371.0979 (18), 389.1089 (12), 403.1241 (12), 499.1463 (13), 525.1245 (16), 537.1605 (13) |
| C328  | Unknown 107  | 543.2088 [M-H]: 389.1453 (10), 513.1982 (42), 525.1980 (100)                                |
| C330  | Unknown 109  | 319.1176 [M-H]: 179.0701 (53), 241.0857 (15), 259.0962 (100), 275.0912 (100), 283.0962 (15), 301.1071 (56) |
| C332  | Unknown 111  | 401.1597 [M+H⁺]: 167.0702 (22), 351.1529 (17), 369.1435 (17), 383.1489 (100)              |
| C333  | Unknown 112  | 291.1235 [M-H]: 137.0596 (100)                                                               |
| C334  | Unknown 113  | 461.1455 [M-H]: 145.0296 (57), 307.0820 (100), 315.1083 (24)                                |
| C335  | Unknown 114  | 623.1987 [M-H+HCOOH]: 191.0909 (15), 191.1109 (17), 191.1265 (14), 342.0139 (26), 577.1924 (100) |
|       |              | 596.2350 [M+H⁺]: 187.0760 (10), 192.1430 (11), 199.0822 (14), 199.0901 (14), 199.1710 (14), 203.0703 (16), 233.0806 (100), 339.1219 (15), 357.1341 (41) |
| C337  | Unknown 116  | 491.1558 [M-H]: 337.0927 (100)                                                               |
|       |              | 493.1707 [M-H]: 177.0545 (60), 195.0652 (10), 263.0915 (15), 299.1124 (14), 339.1074 (32), 439.1382 (10), 457.1489 (24), 475.1597 (100) |
| C338  | Unknown 117  | 789.2477 [M-H]: 342.0599 (30), 371.0975 (11), 403.1242 (100), 445.1353 (28), 557.1467 (12), 595.1657 (16) |
| C   | Compound  | MS² and pseudo-MSⁿ spectra                                                                 |
|-----|-----------|---------------------------------------------------------------------------------------------|
| C339| Unknown 118 | 623.2356 [M-H]: 191.1036 (12), 191.1175 (12), 191.1328 (10), 331.1212 (13), 349.1288 (19), 363.1436 (20), 381.1555 (100), 461.1654 (59) |
| C340| Unknown 119 | 484.2184 [M+NH₄⁺]: 167.0703 (37), 305.1381 (12), 311.1136 (11), 329.1230 (35), 449.1808 (77), 467.1913 (100) |
| C342| Unknown 121 | 539.1257 [M+H⁺]: 231.0288 (14), 269.0810 (11), 495.1255 (10), 521.1074 (100) |
| C343| Unknown 122 | 655.2402 [M-H]: 259.0976 (47), 291.0871 (100), 361.1294 (89), 517.1561 (35), 539.1765 (11) |
| C344| Unknown 123 | 717.1472 [M-H]: 321.0403 (15), 519.0930 (100)                                                 |
|     |            | 736.1874 [M+NH₄⁺]: 521.1078 (100), 666.0363 (12), 719.1621 (29)                              |
| C347| Unknown 126 | 221.1901 [M+H⁺]: 95.0851 (12), 109.1011 (19), 119.0854 (16), 133.1011 (15), 135.1168 (19), 147.1168 (20), 161.1323 (16), 203.1795 (100), 212.1142 (12) |
| C348| Unknown 127 | 419.2639 [M+H⁺]: 124.1740 (13), 124.1925 (13), 131.1732 (18), 199.1484 (26), 260.0016 (25), 271.0545 (37), 340.1811 (100), 354.0295 (51) |
| C350| Unknown 129 | 601.2142 [M-H]: 197.0820 (100), 403.1249 (20)                                               |
| C353| Unknown 142 | 289.1439 [M+H⁺]: 121.0646 (100), 169.0859 (36)                                             |
| C354| Unknown 143 | 388.1404 [M-H]: 284.1292 (52), 344.1505 (100), 360.1454 (12)                               |
|     |            | 390.1549 [M+H⁺]: 178.0863 (15), 222.0760 (100)                                             |
| C357| Unknown 146 | 393.1196 [M-H]: 317.1030 (100), 349.1286 (19), 361.0931 (12)                                |
| C361| Unknown 150 | 471.1665 [M-H]: 165.0558 (17), 195.0663 (100), 319.1187 (27)                               |
|     |            | 490.2079 [M+NH₄⁺]: 137.0594 (38), 271.0309 (10), 303.1230 (100), 321.1333 (31), 455.1699 (11) |
| C362| Unknown 151 | 319.1192 [DOA-H⁺]: 165.0558 (22), 195.0663 (100)                                           |
| C363| Unknown 152 | 331.2494 [M-H]: 171.1028 (13)                                                              |
| C364| Unknown 153 | 609.2250 [M-H]: 473.1817 (100)                                                             |
| C367| Unknown 156 | 287.2229 [M-H]: 267.1966 (14)                                                              |
| C368| Unknown 157 | 271.1180 [M-H]: 137.0594 (10), 194.0592 (13), 225.0753 (12), 239.0911 (100)               |
| C369| Unknown 158 | 319.1542 [M-H]: 121.0646 (100)                                                             |
| C372| Unknown 161 | 345.1710 [M-H]: 301.1806 (100)                                                             |
| C373| Unknown 162 | 485.2187 [M-H]: 349.1657 (100)                                                             |
| C374| Unknown 163 | 721.3642 [M-H]: 270.1878 (32), 342.0111 (100), 342.0580 (16), 449.1723 (16), 475.0255 (35), 598.1650 (15), 669.0986 (58) |
| C378| Unknown 167 | 555.2849 [M-H]: 225.0075 (100), 299.0440 (62)                                              |
**Figure S1.** Scores plot of the samples in the space described by the first two principal components based on data obtained in untargeted analysis in positive (above) and negative (below) modes (samples indicated in red are the quality controls).

Letters refer to the different analyzed products (each one was prepared in triplicate), which characteristics are in Table 4. Red points refer to quality control samples.
Figure S2. Heat map of discriminant features according to the part of the plant used.
Abbreviations: B, buds-based products; F, fruit-based products; L, leave-based products.

Blue and orange cells correspond to low- and high-metabolite levels, respectively. Columns are samples (codified as indicated in Table 4), and rows are compounds colored by behavior distribution among products’ classes (B, F or L). The symbology (e.g., “F > (B & L)”) indicates the behavior of the compound distribution among the products’ categories according to the Kruskal-Wallis test.
Figure S3. Boxplots of selected compounds characteristic of products made from a particular part of the olive plant.
**Figure S4.** Pie charts of total amount of compounds by product.

**Figure S5.** Pie charts of proportion of phenolic and non-phenolic compounds present in each product.
Table S3. Estimated daily intake (mg/day) of the quantified compounds according to the recommended dose.

| Compound                              | K   | D    | F    | J    | M    | L    | C    | O    | E    | I    | N    | H    | A    | G    |
|---------------------------------------|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Quinic acid                           | 1.1 | 1.2  | 0.29 | 0.91 | 25.3 | 41.6 | 2.3  | 1.5  | 1.5  | 30.6 | <LOQ | <LOQ | <LOQ | <LOQ |
| Malic acid                            | <LOQ| LOQ-0.29| <LOQ | 13.4 | 16   | 1.6  | 0.96 | 1.1  | 5.7  | <LOQ | <LOQ | <LOQ | 1.1  | 0.74 |
| Citric acid                           | <LOQ| ND   | <LOQ | <LOQ | 62.1 | 64.4 | 0.53 | 0.54 | 0.68 | 2.2  | <LOQ | <LOQ | LOQ-0.001| <LOQ |
| Isocitric acid                        | ND  | ND   | <LOQ | <LOQ | ND   | 0.31 | 0.46 | 0.11 | 0.12 | 0.01 | 0.01 | 0.25 | <LOQ | <LOQ |
| Succinic acid                         | <LOQ| <LOQ | <LOQ | <LOQ | 0.15 | 0.17 | <LOQ | 0.42 | 0.57 | <LOQ | <LOQ | <LOQ | LOQ-0.22| <LOQ |
| Sorbitol                              | 0.27-0.74| 0.57-0.61| 0.27-0.59| 6.1-7.5| 0.22-0.26| 0.96-0.98| 1.7-1.9| 0.03-0.04| 0.07-0.08| 0.28-0.31| <LOQ | <LOQ | 0.03-0.04| 0.8-0.81|
| Trihydroxyoctadecenoic acid (I)      | ND  | ND   | <LOQ | ND   | ND   | ND   | ND   | ND   | ND   | <LOQ | ND   | ND   | ND   | ND-0.01|
| Trihydroxyoctadecenoic acid (II)     | ND  | ND   | <LOQ | ND   | ND   | <LOQ | <LOQ | ND   | ND   | <LOQ | ND   | ND   | ND   | 0.005-0.01|
| Trihydroxyoctadecenoic acid (III)    | ND  | ND   | <LOQ | ND   | <LOQ | <LOQ | <LOQ | ND   | ND   | 0.02-0.03| 0.06-0.06| ND   | 0.03-0.01| ND   | 0.01-0.02|
| Verbascone (I)                        | ND  | ND   | ND   | ND   | ND   | ND   | ND   | ND   | ND   | ND   | ND   | ND   | ND   | 1.2-1.3|
| Hydrxy-Verbascone (II)                | ND  | ND   | ND   | ND   | ND   | ND   | ND   | ND   | ND   | ND   | ND   | ND   | ND   | 3-3.3|
| 3,4-Dihydroxyphenylglycol             | <LOQ| <LOQ | <LOQ | 5.2-5.7| 0.02-0.05| 0.21-0.22| 0.01-0.03| <LOQ | ND   | <LOQ | 0.04-0.05| <LOQ | 0.003-0.004| 0.12-0.15| 0.04-0.04|
| Hydroxytyrosol                        | <LOQ| <LOQ | <LOQ | 10.5-11.4| 0.4-0.53| 0.1-0.12| 0.26-0.34| 0.03-0.05| LOQ-0.07| 6.9-8.6| 7.7-11.3| 1.9-2.2| 6.0-8.0| 3.7-4.1|
| Hydroxytyrosol glucoside              | ND  | <LOQ | <LOQ | <LOQ | LOQ-1.5| <LOQ | LOQ-1.3| <LOQ | 0.14-0.2| 0.23-0.26| LOQ-0.6| 0.04-0.01| 0.68-1.2| 0.22-0.3|
| Hydroxytyrosol glucoside II           | <LOQ| <LOQ | <LOQ | LOQ-1.4| 0.15-0.2| 0.39-0.42| 4.4-4.8| <LOQ | 0.22-0.31| 0.31-0.37| LOQ-0.22| 0.002-0.003| 0.55-0.82| 0.22-0.27|
| Tyrosol                               | 0.19-0.2| 0.09-0.1| 0.1-0.12| ND   | 0.07-0.11| ND   | 0.02-0.03| ND   | 0.09-0.1| ND   | 0.05-0.06| 1.2-1.3| 2.3  | 1.3-1.3|
| Tyrosol glucoside                     | ND  | ND   | <LOQ | ND   | ND   | ND   | 64.0-73| ND   | ND   | 68.0-92| ND   | ND   | ND   | 4.3-4.8| 1.9-2.6|
| Oleuropein                            | <LOQ| LOQ-0.02| <LOQ | 9.6-10.4| 0.83-1.2| 0.74-0.77| 33.8-34.8| <LOQ | 18.8-20.9| 28.7-31.6| <LOQ | LOQ-0.002| 1.6-1.9| 0.07-0.09|
| Oleuropein isomer (I)                 | <LOQ| ND   | <LOQ | ND   | <LOQ | ND   | 0.02-0.01| ND   | ND   | ND   | 0.08-0.11| ND   | ND   | LOQ-0.005-0.01| LOQ-0.003|
| Oleuropein isomer (II)                | <LOQ| <LOQ | <LOQ | LOQ-0.28| <LOQ | 1.4-1.6| ND   | <LOQ | 0.25-0.31| 1.2-1.5| ND   | <LOQ | ND   | ND   | 0.02-0.03|
| Elenolic acid                         | <LOQ| <LOQ | ND   | 0.49-0.61| <LOQ | 0.06-0.08| <LOQ | <LOQ | 0.04-0.05| ND   | <LOQ | ND   | 0.48-0.55| 0.17-0.18|
| DEDA                                  | <LOQ| <LOQ | LOQ-1.4| <LOQ | <LOQ | LOQ-0.004| <LOQ | <LOQ | 0.09-0.1| LOQ-0.22| 0.07-0.08| 0.29-0.33| 0.74-0.85| <LOQ |
| Hydroxy-DEDA                          | <LOQ| <LOQ | <LOQ | <LOQ | <LOQ | 0.38-0.42| <LOQ | <LOQ | <LOQ | <LOQ | 0.05-0.002| 0.06-0.06| 0.64-0.71| <LOQ |
| DEDA hydrated (I)                     | <LOQ| <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | 0.04-0.05| LOQ-0.15| 0.02-0.03| 0.03-0.04| 0.02-0.04| <LOQ |
| DEDA hydrated (II)                    | ND  | ND   | <LOQ | ND   | ND   | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | 0.003-0.003| <LOQ | <LOQ |
Table S4. Parameters used for data processing with XCMS

| Step                        | Parameter                              | Value                        |
|-----------------------------|----------------------------------------|------------------------------|
| Peak detection              | Method                                 | centWave                    |
|                             | Relative deviation in the m/z dimension (ppm) | 20                           |
|                             | Peak width (range in seconds)          | 2, 40                        |
|                             | Prefilter (scans, intensity)           | 5, 1,000,000                 |
|                             | Signal-to-noise threshold              | 100                          |
|                             | Noise                                  | 3000                         |
|                             | Binning width in the profile matrix    | 0.001                        |
|                             | Integration method                     | 2                            |
| Peak filtering              | Number of data points                  | 5                            |
|                             | Minimal intensity                      | 1,000,000                    |
| Peak post-processing        | expandRt (seconds)                     | 2                            |
|                             | expandMz (Da)                          | 0.001                        |
|                             | ppm                                     | 10                           |
|                             | Intensity proportion                   | 0.66                         |
| Alignement                  | Method                                 | Loess                        |
|                             | Subset adjustment: method, samples     | Average, QC                  |
|                             | Degree of smoothing for local polynomial regression fitting | 0.3                         |
|                             | Fraction of samples a peak should be found in | 1                           |
| Peak grouping               | Sample group definition                | Commercial product           |
|                             | Fraction of samples a peak should be found in m/z width | 1                           |
|                             | Bandwidth of peaks                     | 3/2                          |
| Peak filling                | Method                                 | ChromPeakAreaParam           |
Table S5. Analytical standards used for the targeted analyses.

| Compound                          | Molecular Formula | PubChem CID | Chemical structure                  |
|-----------------------------------|-------------------|-------------|-------------------------------------|
| Quinic acid                       | C7H12O6           | 6508        | ![Chemical structure](image1.png)   |
| Malic acid                        | C4H6O5            | 525         | ![Chemical structure](image2.png)   |
| Isocitric acid                    | C6H8O7            | 1198        | ![Chemical structure](image3.png)   |
| Citric acid                       | C6H8O7            | 311         | ![Chemical structure](image4.png)   |
| Succinic acid                     | C4H6O4            | 1110        | ![Chemical structure](image5.png)   |
| Sorbitol                          | C6H14O6           | 5780        | ![Chemical structure](image6.png)   |
| 3,4-Dihydroxyphenylglycol         | C8H10O4           | 91528       | ![Chemical structure](image7.png)   |
| Hydroxytyrosol                    | C8H10O3           | 82755       | ![Chemical structure](image8.png)   |
| Oleuropein                        | C25H32O13         | 5281544     | ![Chemical structure](image9.png)   |
| Tyrosol                           | C8H10O2           | 10393       | ![Chemical structure](image10.png)  |
| Tyrosol glucoside (salidroside)   | C14H20O7          | 159278      | ![Chemical structure](image11.png)  |
| Verbascoside                      | C29H36O15         | 5281800     | ![Chemical structure](image12.png)  |