**Supporting Information**

# Identification of Phytochemical Compounds in Coffea arabica Whole Coffee Cherries and Their Extracts by LC-MS/MS

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**Supplementary Table and Figure captions**

**Supplementary Table 1**: Coffee Arabica LC-MS/MS compound identifications.

**Supplementary Figure 1**: LC-MS total ion chromatogram of WCC, WCCE-1 and WCCE-2 in positive ion mode.

**Supplementary Figure 2**: LC-MS/MS identification of caffeoylvaleroylquinic acid isoforms I - V. (A) Representative extracted ion chromatogram showing peak profile of the five isoforms of caffeoylvaleroylquinic acid. (B) Representative fragmentation spectrum of caffeoylvaleroyl quinic acid. (QA-quinic acid, CA-caffeic acid, VA - valeric acid, VQA- valeroylquinic acid).

**Supplementary Figure 3**: Peak intensity ratio of chlorogenic acid derivatives detected in WCCE-1 and WCCE-2 to WCC.

**Supplementary Figure 4**: LC-MS/MS analyses of carboxyatractyligenin derivatives. A) Overlayed extracted ion chromatograms (m/z 525.23) showing peak profiles of 2-O-glucopyranosyl-carboxyatractyligenin. (B) Fragment mass spectra of 2-O-glucopyranosyl-carboxyatractyligenin.

**Supplementary Figure 5**: Direct infusion ESI-MS analysis of WCC and its extracts. Total ion chromatograms showing the most abundant ions detected in WCC (top panel), WCCE-1 (middle panel), and WCCE-2 (lower panel).

Supplementary Table 1

Identified compounds in eachs sample are marked by "√"
RT - Retention time in minutes
I, II, III... IX - isoform number
m/z MS - precursor mass-to-charge ratio
m/z MS/MS -fragment mass-to-charge ratio
ND - not detected

| Id# | Compound | m/z MS | Adduct | RT | WCC | WCCE-1 | WCCE-2 | m/z MS/MS |
|---|---|---|---|---|---|---|---|---|
| **Organic acid & derivatives** | | | | | | | | |
| 1 | Malic acid | 133.0130 | M-H | 2.2 | √ | √ | √ | 71, 89, 115 |
| 2 | Citric acid | 191.0186 | M-H | 2.8 | √ | √ | √ | 102, 111, 129, 173 |
| 3 | Gluconic acid | 195.0504 | M-H | 1.6 | √ | √ | √ | 75, 99, 129, 159, 177 |
| 4 | 2-Hydroxyglutaric acid | 147.0279 | M-H | 3.5 | √ | √ | √ | 71, 103, 115, 129 |
| 5 | Glucaric acid | 209.0297 | M-H | 1.6 | √ | √ | √ | 85, 103, 133, 147, 191 |
| 6 | Quinic acid-I | 191.0551 | M-H | 1.7 | √ | √ | √ | 147, 173 |
| 7 | Quinic acid-II | 191.0551 | M-H | 20.0 | √ | √ | √ | 147, 173 |
| 8 | Quinic acid glucoside | 353.1088 | M-H | 1.8 | √ | √ | ND | 173, 191 |
| 9 | Valeroylquinic acid-I | 275.1135 | M-H | 14.7 | √ | √ | √ | 101 |
| 10 | Valeroylquinic acid-II | 275.1135 | M-H | 15.6 | √ | √ | √ | 101 |
| 11 | Valeroylquinic acid-III | 275.1135 | M-H | 20.9 | √ | √ | √ | 101, 173 |
| 12 | Valeroylquinic acid-IV | 275.1135 | M-H | 21.3 | √ | √ | √ | 101, 173 |
| 13 | Valeroylquinic acid-V | 275.1135 | M-H | 23.0 | √ | √ | √ | 93, 173, 191 |
| 14 | Valeroylquinic acid-VI | 275.1135 | M-H | 23.3 | √ | √ | √ | 93, 173, 191 |
| 15 | Valeroylquinic acid-VII | 275.1135 | M-H | 30.2 | √ | √ | √ | 101, 173 |
| 16 | Valeroylquinic acid-VIII | 275.1135 | M-H | 30.4 | √ | √ | √ | 101, 191 |
| 17 | Valeroylquinic acid-IX | 275.1135 | M-H | 31.4 | √ | √ | √ | 93, 101, 173 |
| **Phenolic acids & derivatives** | | | | | | | | |
| 18 | Protocatechuic acid | 153.0183 | M-H | 10.3 | √ | √ | √ | 65, 87, 109, 123 |
| 19 | Protocatechualdehyde | 137.0231 | M-H | 15.2 | √ | √ | √ | 93, 109, 119 |
| 20 | Coumaric acid | 163.0389 | M-H | 19.1 | √ | √ | √ | 119 |
| 21 | Vanillic acid | 167.0340 | M-H | 8.6 | √ | √ | √ | 123 |
| 22 | Gallic acid | 169.0133 | M-H | 5.3 | ND | √ | ND | 70, 123, 125, 151 |
| 23 | Caffeic acid | 179.0342 | M-H | 21.2 | √ | √ | √ | 135 |
| 24 | Ferulic acid | 193.0492 | M-H | 20.7 | √ | √ | √ | 111, 134, 149, 178 |
| 25 | Dimethylcaffeic acid | 207.0653 | M-H | 32.8 | √ | √ | √ | 135, 161, 179 |
| 26 | Caffeoyltryptophan | 365.1139 | M-H | 31.3 | √ | √ | √ | 135, 161, 186, 203, 229 |
| 27 | Dicaffeoyltryptophan I | 501.1655 | M-H | 33.3 | ND | √ | √ | 135, 161, 186, 203, 339, 365 |
| 28 | Dicaffeoyltryptophan II | 501.1655 | M-H | 33.4 | ND | √ | √ | |
| 29 | Dicaffeoyltryptophan III | 501.1655 | M-H | 35.1 | ND | √ | √ | |
| 30 | Dicaffeoyltryptophan derv I | 485.1709 | M-H | 34.8 | ND | √ | √ | 100, 135, 161, 349 |
| 31 | Dicaffeoyltryptophan derv II | 485.1709 | M-H | 36.6 | ND | √ | √ | |
| 32 | Caffeoyltryptophan dimer | 731.2357 | M-H | 31.3 | √ | √ | √ | 135, 161, 186, 229, 365 |
| 33 | Coumaroyltryptophan | 349.1193 | M-H | 33.1 | √ | √ | √ | 119, 145, 186, 305, 349 |
| 34 | Coumaroyltryptophan-derv | 417.1071 | M-H | 33.1 | √ | √ | √ | 119, 145, 186, 305, 349 |
| 35 | Coumaroyl-tryptophan dimer | 699.2464 | M-H | 33.1 | ND | √ | √ | 119, 145, 186, 305, 349 |

Supplementary Table 1 (continued)

| Chlorogenic acids & derivatives | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 36 | Caffeoylvaleroylquinic acid-I | 437.1451 | M-H | 29.4 | √ | √ | √ | 101, 135, 179, 275 |
| 37 | Caffeoylvaleroylquinic acid-II | 437.1451 | M-H | 29.5 | √ | √ | √ | 173, 179, 257, 275 |
| 38 | Caffeoylvaleroylquinic acid-III | 437.1451 | M-H | 30.4 | √ | √ | √ | 101, 173, 275 |
| 39 | Caffeoylvaleroylquinic acid-IV | 437.1451 | M-H | 30.2 | √ | √ | √ | 101, 173 |
| 40 | Caffeoylvaleroylquinic acid-V | 437.1451 | M-H | 31.4 | √ | √ | √ | 101, 155, 173 |
| 41 | 3-Protocatechuoylaldehyde-feruloyquinic aci | 487.1248 | M-H | 29.0 | ND | √ | √ | |
| 42 | 5-Protocatechuoylaldehyde-feruloyquinic aci | 487.1248 | M-H | 29.6 | √ | √ | √ | 137, 173 |
| 43 | 4-Protocatechuoylaldehyde-feruloyquinic aci | 487.1248 | M-H | 30.5 | √ | √ | √ | |
| 44 | 3-Caffeoylquinic acid | 353.0875 | M-H | 14.3 | √ | √ | √ | 135, 173, 179, 191 |
| 45 | 5-Caffeoylquinic acid | 353.0875 | M-H | 20.0 | √ | √ | √ | 191 |
| 46 | 4-Caffeoylquinic acid | 353.0875 | M-H | 21.0 | √ | √ | √ | 135, 179, 191 |
| 49 | 3-Caffeoylquinic acid lactone | 335.0770 | M-H | 24.2 | ND | √ | √ | 146, 161, 173, 179 |
| 47 | 5-Caffeoylquinic acid lactone | 335.0770 | M-H | 24.5 | √ | √ | √ | 146, 161, 173, 179 |
| 48 | 4-Caffeoylquinic acid lactone | 335.0770 | M-H | 24.9 | √ | √ | √ | 146, 161 |
| 50 | cis-5-Caffeoylquinate--Na | 375.0698 | M-H | 20.2 | √ | √ | √ | |
| 51 | trans-3-Caffeoylquinate--Na | 375.0698 | M-H | 14.2 | √ | √ | √ | |
| 52 | trans-4-Caffeoylquinate--Na | 375.0698 | M-H | 21.0 | √ | √ | √ | 135, 179, 201 |
| 53 | trans-5-Caffeoylquinate--Na | 375.0698 | M-H | 20.0 | √ | √ | √ | |
| 54 | cis-4-Caffeoylquinate-Na | 375.0698 | M-H | 21.1 | √ | √ | √ | |
| 55 | 3-Caffeoylquinic acid-COO-Na | 421.0757 | M-H | 20.2 | √ | √ | √ | 191, 201, 375 |
| 56 | 4-Caffeoylquinic acid-COO-Na | 421.0762 | M-H | 20.0 | √ | √ | √ | |
| 57 | 3-Caffeoylquinic acid dimer | 707.1830 | M-H | 14.3 | √ | √ | √ | 179, 191, 353 |
| 58 | 5-Caffeoylquinic acid dimer | 707.1833 | M-H | 20.1 | √ | √ | √ | 191 |
| 59 | 4-Caffeoylquinic acid dimer | 707.1834 | M-H | 21.0 | √ | √ | √ | 179, 191, 353 |
| 60 | Diferruloy-caffeoylquinic acid-I | 743.2007 | M-H | 23.5 | √ | √ | √ | 355, 375, 549 |
| 61 | Diferruloy-caffeoylquinic acid-II | 743.2007 | M-H | 23.7 | ND | √ | √ | 393, 531, 549 |
| 62 | Diferruloy-caffeoylquinic acid-III | 743.2007 | M-H | 20.7 | ND | √ | √ | 373, 549, 567 |
| 63 | 3,4,5-tricaffeoylquinic acid | 677.1518 | M-H | 31.7 | √ | √ | √ | 335, 353, 515 |
| 64 | 3-Feruloylquinic acid | 367.1035 | M-H | 20.7 | √ | √ | √ | 134, 193 |
| 65 | 5-Feruloylquinic acid | 367.1032 | M-H | 23.5 | √ | √ | √ | 134, 191, 193 |
| 66 | 4-Feruloylquinic acid | 367.1032 | M-H | 23.7 | √ | √ | √ | 134, 193 |
| 67 | 3-Feruloylquinic acid dimer | 735.2144 | M-H | 23.5 | √ | √ | √ | 193 |
| 68 | 5-Feruloylquinic acid dimer | 735.2144 | M-H | 23.7 | √ | √ | √ | 173, 191 |
| 69 | 4-Feruloylquinic acid dimer | 735.2144 | M-H | 20.7 | √ | √ | √ | 173, 193 |
| 70 | 3-Feruloylquinate-dimer-Na | 757.1961 | M-H | 23.5 | √ | √ | √ | 173, 193 |
| 71 | 5-Feruloylquinate-dimer-Na | 757.1961 | M-H | 23.6 | √ | √ | √ | 173, 191 |
| 72 | 4-Feruloylquinate-dimer-Na | 757.1961 | M-H | 20.7 | √ | √ | √ | 173, 193 |
| 73 | 3-Coumaroylquinic acid | 337.0932 | M-H | 19.0 | √ | √ | √ | 119, 163, 191 |
| 74 | 5-Coumaroylquinic acid | 337.0933 | M-H | 22.5 | √ | √ | √ | 191 |
| 75 | 4-Coumaroylquinic acid | 337.0933 | M-H | 22.9 | √ | √ | √ | 163, 173, 191 |
| 76 | 3-Caffeoylshikimic acid | 335.0770 | M-H | 22.6 | √ | √ | √ | 173, 179, 191 |
| 77 | 5-Caffeoylshikimic acid | 335.0770 | M-H | 22.7 | √ | √ | √ | 161, 173, 179, 191 |
| 78 | 4-Caffeoylshikimic acid | 335.0770 | M-H | 23.2 | √ | √ | √ | 135, 161, 173, 179 |
| 79 | 3,4-Dicaffeoylshikimic acid | 497.1091 | M-H | 29.5 | √ | √ | ND | 135, 161, 179 |
| 80 | 3,5-Dicaffeoylshikimic acid | 497.1091 | M-H | 30.6 | √ | √ | ND | 135, 161, 173, 179 |
| 81 | 4,5-Dicaffeoylshikimic acid | 497.1091 | M-H | 30.2 | √ | √ | ND | 135, 161, 173, 179 |
| 82 | 2-Hydroxy-3-Caffeoylquinic acid | 371.0984 | M-H | 5.2 | √ | √ | √ | 135, 173, 179, 191 |
| 83 | 5-Hydroxy-5-Caffeoylquinic acid | 371.0984 | M-H | 5.1 | √ | √ | √ | 135, 173, 179, 191 |
| 84 | 6-Hydroxy-4-Caffeoylquinic acid | 371.0984 | M-H | 8.6 | √ | √ | √ | 135, 173, 191 |
| 85 | 2-Hydroxy-5-Caffeoylquinic acid | 371.0984 | M-H | 6.7 | √ | √ | √ | 191 |
| 86 | 5-Hydroxy-3-Caffeoylquinic acid | 371.0984 | M-H | 7.0 | √ | √ | √ | 135, 173, 191 |
| 87 | 2-Hydroxy-3-Caffeoylquinate--Na | 393.0807 | M-H | 5.3 | √ | √ | √ | 135, 146, 179, 201 |
| 88 | 5-Hydroxy-5-Caffeoylquinate--Na | 393.0807 | M-H | 5.1 | √ | √ | √ | 146, 179, 190, 201 |
| 89 | 6-Hydroxy-4-Caffeoylquinate--Na | 393.0807 | M-H | 8.6 | √ | √ | √ | 89, 146, 179, 201 |
| 90 | 2-Hydroxy-5-Caffeoylquinate--Na | 393.0807 | M-H | 6.7 | √ | √ | √ | 146, 179, 190, 201 |

Supplementary Table 1 (continued)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 91 | 5-Hydroxy-3-Caffeoylquinate--Na | 393.0807 | M-H | 7.0 | √ | √ | √ | 164, 179, 190, 201 |
| 92 | Dimethyl-caffeoylquinic acid-I | 381.1193 | M-H | 26.8 | √ | √ | √ | 161, 173 |
| 93 | Dimethyl-caffeoylquinic acid-II | 381.1193 | M-H | 26.2 | ND | √ | √ | 135, 161 |
| 94 | Dimethyl-caffeoylquinic acid-III | 381.1196 | M-H | 24.5 | √ | √ | √ | 207 |
| 95 | Dimethyl-caffeoylquinic acid-IV | 381.1196 | M-H | 24.7 | ND | √ | √ | 161 |
| 96 | 2-Acetaldehyde-3-Caffeoylquninic acid | 397.1142 | M-H | 20.5 | ND | √ | √ | 161, 173, 191, 205 |
| 97 | 5-Acetaldehyde-5-Caffeoylquninic acid | 397.1142 | M-H | 22.6 | ND | √ | √ | 135, 161, 179, 191 |
| 98 | 6-Acetaldehyde-4-Caffeoylquninic acid | 397.1142 | M-H | 22.5 | ND | √ | √ | 135, 161 |
| 99 | Dimethyl-caffeoylquinic acid dervative-I | 449.1070 | M-H | 27.1 | √ | √ | √ | 173 |
| 100 | Dimethyl-caffeoylquinic acid dervative-II | 449.1070 | M-H | 26.8 | √ | √ | √ | 173, 207 |
| 101 | Dimethyl-caffeoylquinic acid dervative-III | 449.1070 | M-H | 26.2 | ND | √ | √ | 135, 161, 167 |
| 102 | Dimethyl-caffeoylquinic acid dervative-IV | 449.1074 | M-H | 24.5 | ND | √ | √ | 173, 207 |
| 103 | Dimethyl-caffeoylquinic acid dervative-V | 449.1074 | M-H | 24.7 | ND | √ | √ | 161 |
| 104 | 3,4-Dicaffeoylquinic acid lactone | 497.1091 | M-H | 32.6 | ND | √ | √ | 135, 161, 179 |
| 105 | 3,5-Dicaffeoylquinic acid lactone | 497.1091 | M-H | 31.8 | √ | √ | √ | 135, 137, 161, 179 |
| 106 | 3-Coumaroyl-4-caffeoylquinic acid | 499.1252 | M-H | 28.4 | √ | √ | √ | 163, 173, 179, 353 |
| 107 | 3-Coumaroyl-5-caffeoylquinic acid | 499.1253 | M-H | 29.1 | √ | √ | √ | 163 |
| 108 | 4-Coumaroyl-5-caffeoylquinic acid | 499.1253 | M-H | 29.8 | √ | √ | √ | 163, 173, 191 |
| 109 | 3-Caffeoyl-5-coumaroylquinic acid | 499.1253 | M-H | 29.9 | √ | √ | √ | 173, 179, 191, 353 |
| 110 | 4-Caffeoyl-5-coumaroylquinic acid | 499.1253 | M-H | 28.7 | √ | √ | √ | , 155, 163, 173, |
| 111 | 3,4-Dicaffeoyl quinic acid | 515.1189 | M-H | 28.1 | √ | √ | √ | 173, 179, 191, 353 |
| 112 | 3,5-Dicaffeoyl quinic acid | 515.1190 | M-H | 26.9 | √ | √ | √ | 179, 191, 335, 353 |
| 113 | 4,5-Dicaffeoyl quinic acid | 515.1195 | M-H | 27.4 | √ | √ | √ | 135, 179, 191, 353 |
| 114 | 3-Caffeoyl-4-feruloylquinic acid | 529.1355 | M-H | 28.9 | √ | √ | √ | 173, 193 |
| 115 | 3-Caffeoyl-5-feruloylquinic acid | 529.1356 | M-H | 28.6 | √ | √ | √ | 161, 173, 179, 193 |
| 116 | 4-Caffeoyl-5-feruloylquinic acid | 529.1356 | M-H | 30.1 | √ | √ | √ | 173, 179, 191, 353 |
| 117 | 3-feruloyl-4-caffeoylquinic acid | 529.1356 | M-H | 29.7 | √ | √ | √ | 135, 173, 179, 191 |
| 118 | 3-feruloyl-5-caffeoylquinic acid | 529.1357 | M-H | 29.5 | √ | √ | √ | 173, 191, 193 |
| 119 | 4-feruloyl-5-caffeoylquinic acid | 529.1357 | M-H | 30.0 | √ | √ | √ | 173, 193 |
| 120 | 3-caffeoyl-5-hydroxycaffeoylquinic acid | 533.1303 | M-H | 24.0 | √ | √ | √ | 135,135, 179, 191 |
| 121 | 3-caffeoyl-4-hydroxycaffeoyquinic acid | 533.1303 | M-H | 22.9 | √ | √ | √ | 135,135, 179, 192 |
| 122 | 3-caffeoyl-4-hydroxycaffeoyquinic acid | 533.1303 | M-H | 23.2 | √ | √ | √ | 135,135, 179, 193 |
| 123 | 3-hydroxycaffeoyl-4-caffeoylquinic acid | 533.1303 | M-H | 23.9 | √ | √ | √ | 135,135, 179, 194 |
| 124 | 4-caffeoyl-5-hydroxycaffeoylquinic acid | 533.1303 | M-H | 24.9 | √ | √ | √ | 135,135, 179, 195 |
| 125 | 3-hydroxycaffeoyl-5-caffeoylquinic acid | 533.1303 | M-H | 24.3 | √ | √ | √ | 135,135, 179, 196 |
| 126 | 4-hydroxycaffeoyl-5-caffeoylquinic acid | 533.1303 | M-H | 25.1 | √ | √ | √ | 135,135, 179, 197 |
| 127 | 3-caffeoyl-5-hydroxycaffeoylquinic acid | 533.1303 | M-H | 24.1 | √ | √ | √ | 135,135, 179, 198 |
| 128 | 3-hydroxycaffeoyl-4-caffeoylquinic acid | 533.1303 | M-H | 23.7 | √ | √ | √ | 135,135, 179, 199 |
| 129 | 4-caffeoyl-5-hydroxycaffeoylquinic acid | 533.1303 | M-H | 24.7 | √ | √ | √ | 135,135, 179, 200 |
| 130 | 3-hydroxycaffeoyl-5-caffeoylquinic acid | 533.1303 | M-H | 24.5 | √ | √ | √ | 135,135, 179, 201 |
| 131 | cis-3,4-Dicaffeoyl quinate--Na | 537.1014 | M-H | 28.1 | √ | √ | √ | 179, 201, 335, 375 |
| 132 | cis-3,5-Dicaffeoyl quinate--Na | 537.1010 | M-H | 27.4 | √ | √ | √ | 201, 335, 357, 375 |
| 133 | cis-4,5-Dicaffeoyl quinate--Na | 537.1010 | M-H | 26.9 | √ | √ | √ | 161, 179, 375 |
| 134 | Caffeoylquinic acid-glucoside dervitative -I | 541.2652 | M-H | 27.6 | √ | √ | √ | 179, 191, 333, 377 |
| 135 | Caffeoylquinic acid-glucoside dervitative -II | 541.2652 | M-H | 27.8 | √ | √ | √ | 333 |
| 136 | Caffeoylquinic acid-glucoside dervitative -III | 541.2652 | M-H | 28.2 | √ | √ | √ | 161, 173, 179, 333 |
| 137 | Methylated-caffeoylferruloylquinic acid-I | 543.1503 | M-H | 30.8 | √ | √ | √ | 173, 179, 207, 335 |
| 138 | Methylated-caffeoylferruloylquinic acid-II | 543.1503 | M-H | 32.1 | √ | √ | √ | 193, 207, 381, 497 |
| 139 | Dimethyl-3,5-dicaffeoylquinic acid | 543.1503 | M-H | 32.3 | √ | √ | √ | 179, 193, 207, 381 |
| 140 | 3,4-Diferruloylquinic acid | 543.1503 | M-H | 30.7 | √ | √ | √ | 305, 335, 349, 383 |
| 141 | 3,5-Diferruloylquinic acid | 543.1503 | M-H | 31.7 | √ | √ | √ | 134, 173, 193, 349 |
| 142 | Dimethyl-3,4-dicaffeoylquinic acid | 543.1503 | M-H | 31.3 | ND | √ | √ | 135, 161, 381 |
| 143 | Dimethyl-4,5-dicaffeoylquinic acid | 543.1503 | M-H | 33.0 | ND | √ | √ | 135, 161, 179, 381 |
| 144 | 3-Ferruloyl-4-Caffeoylquinate-Na | 551.1172 | M-H | 28.9 | √ | √ | √ | 201, 335, 357, 375 |
| 145 | 3-Caffeoyl-4-ferruloylquinate-Na | 551.1172 | M-H | 29.5 | √ | √ | √ | 173, 201, 335, 389 |
| 146 | 3-Ferruloyl-5-Caffeoylquinate-Na | 551.1172 | M-H | 30.1 | √ | √ | √ | 179, 201, 335, 375 |
| 147 | 3-Caffeoyl-5-ferruloylquinate-Na | 551.1172 | M-H | 28.6 | √ | √ | √ | 201, 335, 357, 375 |
| 148 | 4-Ferruloyl-5-Caffeoylquinate-Na | 551.1172 | M-H | 29.7 | √ | √ | √ | 179, 193, 201, 375 |
| 149 | Caffeoylquinic acid-glucoside dervative-I | 553.2296 | M-H | 25.7 | √ | √ | √ | 101, 119, 173, 191 |
| 150 | Caffeoylquinic acid-glucoside dervative-II | 553.2296 | M-H | 26.3 | √ | √ | ND | 119, 179, 191, 345 |
| 151 | Caffeoylquinate-Na-glucoside dervative-I | 558.2552 | M-H | 28.2 | √ | √ | √ | 179, 201, 353, 375 |
| 152 | Caffeoylquinate-Na-glucoside dervative-II | 558.2552 | M-H | 27.6 | ND | √ | ND | 61, 161, 179, 201 |
| 153 | Caffeoylquinate-Na-glucoside dervative-III | 558.2552 | M-H | 27.8 | ND | √ | ND | 61, 161, 179, 202 |

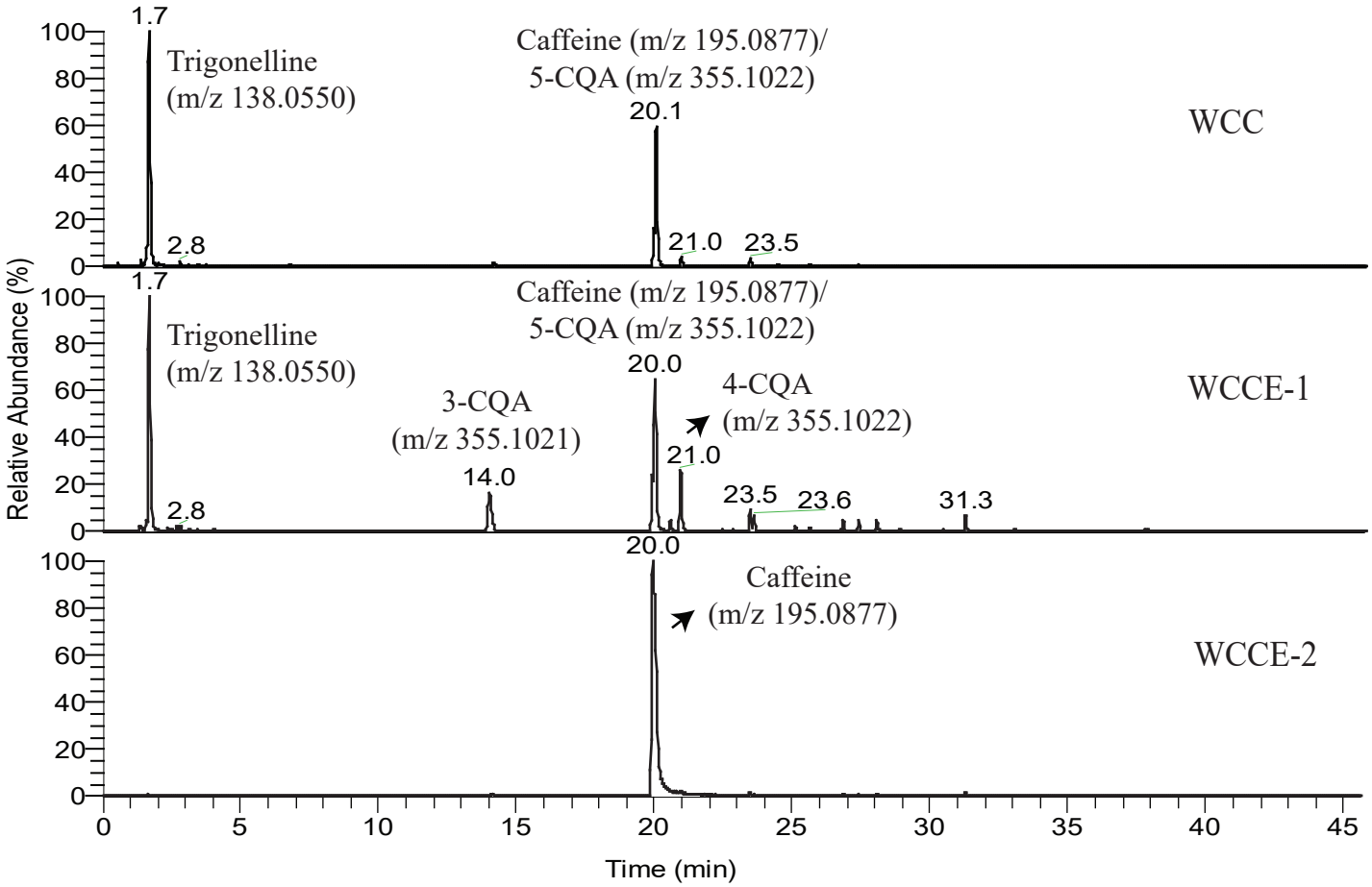
Supplementary Table 1 (continued)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Diterpenoid derivatives** | | | | | | | | |
| 154 | Atractyligenin | 319.1899 | M-H | 27.7 | √ | √ | √ | 275 |
| 155 | Iso-atractyligenin | 319.1899 | M-H | 28.4 | √ | √ | √ | 275 |
| 156 | 2-O-glucopyranosyl-atractyligenin I | 481.2442 | M-H | 24.5 | √ | √ | √ | 89, 119, 301 |
| 157 | 2-O-glucopyranosyl-atractyligenin II | 481.2442 | M-H | 25.1 | √ | √ | √ | 89, 119, 301 |
| 158 | 2-O-glucopyranosyl-carboxyatractyligenin | 525.2344 | M-H | 24.5 | √ | √ | √ | 119, 301, 481 |
| 159 | 2-O-glucopyranosyl-carboxyatractyligenin (Na adduct) | 549.2317 | M-H | 24.5 | √ | √ | ND | 401, 481, 503 |
| 160 | 2-O-glucopyranosyl-iso-carboxyatractyligenin (Na adduct) | 549.2317 | M-H | 25.1 | √ | √ | √ | 401, 481, 503 |
| 161 | 2-O-glucopyranosyl-dicarboxyatractyligenin (Na adduct) | 593.2203 | M-H | 24.5 | √ | √ | ND | 393, 481, 503 |
| 162 | 2-O-glucopyranosyl-atractyligenin dimer | 963.4965 | M-H | 25.1 | √ | √ | ND | 119, 301, 481 |
| 163 | 2-O-glucopyranosyl-deoxyhexopyranose-atractyligenin | 627.2991 | M-H | 24.9 | √ | √ | ND | 205, 301, 481 |
| 164 | 2-O-glucopyranosyl-deoxyhexopyranose-iso-atractyligenin | 627.2991 | M-H | 25.3 | √ | √ | √ | 205, 301, 481 |
| 165 | 2-O-glucopyranosyl-deoxyhexopyranose-carboxyatractyligenin | 671.2889 | M-H | 24.9 | √ | √ | ND | 301, 481, 627 |
| 166 | 2-O-glucopyranosyl-deoxyhexopyranose-dicarboxyatractyligenin | 739.2768 | M-H | 24.9 | √ | ND | ND | 503, 627, 649 |
| 167 | 2-O-glucoside-2-O-isovaleroyl-atractyligenin-I | 565.2995 | M-H | 30.1 | √ | √ | ND | 226, 301, 463 |
| 168 | 2-O-glucoside-2-O-isovaleroyl-atractyligenin-II | 565.2995 | M-H | 30.3 | √ | √ | ND | 226, 301, 463 |
| 169 | 2-O-glucoside-2-O-isovaleroyl-atractyligenin-III | 565.3023 | M-H | 32.1 | √ | √ | ND | 226, 301, 463 |
| 170 | 2-O-glucoside-2-O-isovaleroyl-atractyligenin-IV | 565.3023 | M-H | 32.3 | √ | √ | ND | 226, 301, 463 |
| 171 | 2-O-glucoside-2-O-isovaleroyl-atractyligenin-V | 565.3023 | M-H | 32.5 | √ | √ | ND | 226, 301, 463 |
| 172 | 2-O-glucoside-2-O-isovaleroyl-atractyligenin-VI | 565.3023 | M-H | 32.7 | √ | √ | ND | 226, 301, 463 |
| 173 | 2-O-glucoside-2-O-isovaleroyl-atractyligenin-VII | 565.3023 | M-H | 33.0 | √ | √ | √ | 226, 301, 463 |
| 174 | 2-O-glucoside-2-O-isovaleroyl-atractyligenin-VII | 565.3023 | M-H | 33.3 | √ | √ | ND | 226, 301, 463 |
| 175 | 2-O-glucoside-2-O-isovaleroyl-atractyligenin-VII | 565.3023 | M-H | 33.8 | √ | √ | ND | 226, 301, 464 |
| 176 | 2-O-glucoside-2-O-isovaleroyl-atractyligenin-VII | 565.3023 | M-H | 33.9 | √ | √ | √ | 226, 301, 465 |
| 177 | 2-O-glucoside-2-O-isovaleroyl-carboxyatractyligenin (Na-adduct) | 633.2899 | M-H | 33.0 | √ | √ | ND | 301, 463, 565 |
| 178 | 2-O-glucoside-2-O-isovaleroyl-iso-carboxyatractyligenin (Na-adduct) | 633.2899 | M-H | 33.9 | √ | √ | ND | 301, 463, 565 |
| 179 | 2-O-glucoside-(3-O-glucoside-2-O-isovaleryl)-atractyligenin I | 727.3545 | M-H | 28.1 | √ | √ | ND | 463, 625, 643 |
| 180 | 2-O-glucoside-(3-O-glucoside-2-O-isovaleryl)-atractyligenin II | 727.3545 | M-H | 28.3 | √ | √ | ND | 463, 625, 643 |
| 181 | 2-O-glucoside-(3-O-glucoside-2-O-isovaleryl)-atractyligenin III | 727.3545 | M-H | 30.2 | √ | √ | √ | 463, 625, 644 |
| 182 | 2-O-glucoside-(3-O-glucoside-2-O-isovaleryl)-atractyligenin IV | 727.3545 | M-H | 30.5 | √ | √ | √ | 463, 625, 645 |
| 183 | 2-O-glucoside-(3-O-glucoside-2-O-isovaleryl)-carboxyatractyligenin | 771.3405 | M-H | 28.1 | √ | √ | ND | 625, 643, 627 |
| 184 | 2-O-glucoside-(3-O-glucoside-2-O-isovaleryl)-iso-carboxyatractyligenin | 771.3405 | M-H | 28.3 | √ | √ | ND | 625, 643, 628 |
| 185 | 2-O-glucoside-(3-O-glucoside-2-O-isovaleryl)-iso-carboxyatractyligenin I | 795.3426 | M-H | 28.1 | √ | ND | ND | 625, 647, 727 |
| 186 | 2-O-glucoside-(3-O-glucoside-2-O-isovaleryl)-iso-carboxyatractyligenin II | 795.3426 | M-H | 28.3 | √ | ND | ND | 625, 647, 728 |
| 187 | 2-O-glucoside-(3-O-glucoside-2-O-isovaleryl)-iso-carboxyatractyligenin III | 795.3426 | M-H | 30.2 | √ | √ | ND | 625, 647, 729 |
| 188 | 2-O-glucoside-(3-O-glucoside-2-O-isovaleryl)-iso-carboxyatractyligenin IV | 795.3426 | M-H | 30.5 | √ | √ | √ | 625, 647, 730 |
| 189 | 2-O-glucoside-(3-O-glucoside-2-O-isovaleryl)--dicarboxyatractyligenin I | 795.3426 | M-H | 28.3 | √ | ND | ND | 625, 647, 731 |
| 190 | 2-O-glucoside-(3-O-glucoside-2-O-isovaleryl)--dicarboxyatractyligenin II | 863.3304 | M-H | 30.2 | ND | √ | ND | 625, 643, 727 |
| 191 | 2-O-glucoside-(3-O-glucoside-2-O-isovaleryl)-dicarboxyatractyligenin III | 863.3304 | M-H | 30.5 | √ | √ | √ | 625, 643, 728 |
| **Amino acids** | | | | | | | | |
| 192 | Aspartic acid | 132.0290 | M-H | 1.6 | √ | √ | √ | , 88, 114, 115 |
| 193 | Asparagine | 131.0451 | M-H | 1.6 | √ | √ | √ | , 95, 114, 115 |
| 194 | Glutamic acid | 146.0438 | M-H | 1.6 | √ | √ | √ | 102, 109, 128 |
| 195 | Histidine | 154.0611 | M-H | 1.6 | √ | √ | ND | 93, 110, 137 |
| 196 | Phenylalanine | 166.0861 | M+H | 6.8 | √ | √ | √ | 120, 166 |
| 197 | Tryptophan | 205.0974 | M+H | 14.5 | √ | √ | √ | 146, 188 |
| **Flavonoids** | | | | | | | | |
| 198 | Rutin-I | 609.1437 | M-H | 25.2 | √ | ND | ND | 151, 300, 301 |
| 199 | Rutin-II | 609.1437 | M-H | 25.3 | √ | ND | ND | |
| 200 | Naringenin-I | 271.0604 | M-H | 34.4 | √ | ND | ND | 151, 227, 271 |
| 201 | Naringenin-II | 271.0604 | M-H | 34.9 | √ | ND | ND | 271, 300, 301 |
| 202 | Naringenin glucoside | 433.1121 | M-H | 25.6 | √ | ND | ND | 151, 271 |
| 203 | Quercetin glucoside-I | 463.0863 | M-H | 25.8 | √ | ND | ND | 151, 300, 301 |
| 204 | Quercetin glucoside-II | 463.0863 | M-H | 26.0 | √ | ND | ND | |
| 205 | Quercetin diglucoside-I | 625.1387 | M-H | 23.7 | √ | ND | ND | 178, 301, 463 |
| 206 | Quercetin diglucoside-II | 625.1387 | M-H | 23.8 | √ | ND | ND | |
| 207 | Kaempferol glucoside-I | 447.0915 | M-H | 26.8 | √ | ND | ND | 285 (284) |
| 208 | Kaempferol glucoside-II | 447.0915 | M-H | 27.3 | √ | ND | ND | |
| 209 | Kaempferol diglucoside-I | 609.1435 | M-H | 24.7 | √ | ND | ND | 85 (284), 447 |
| 210 | Kaempferol diglucoside-II | 609.1435 | M-H | 24.8 | √ | ND | ND | |

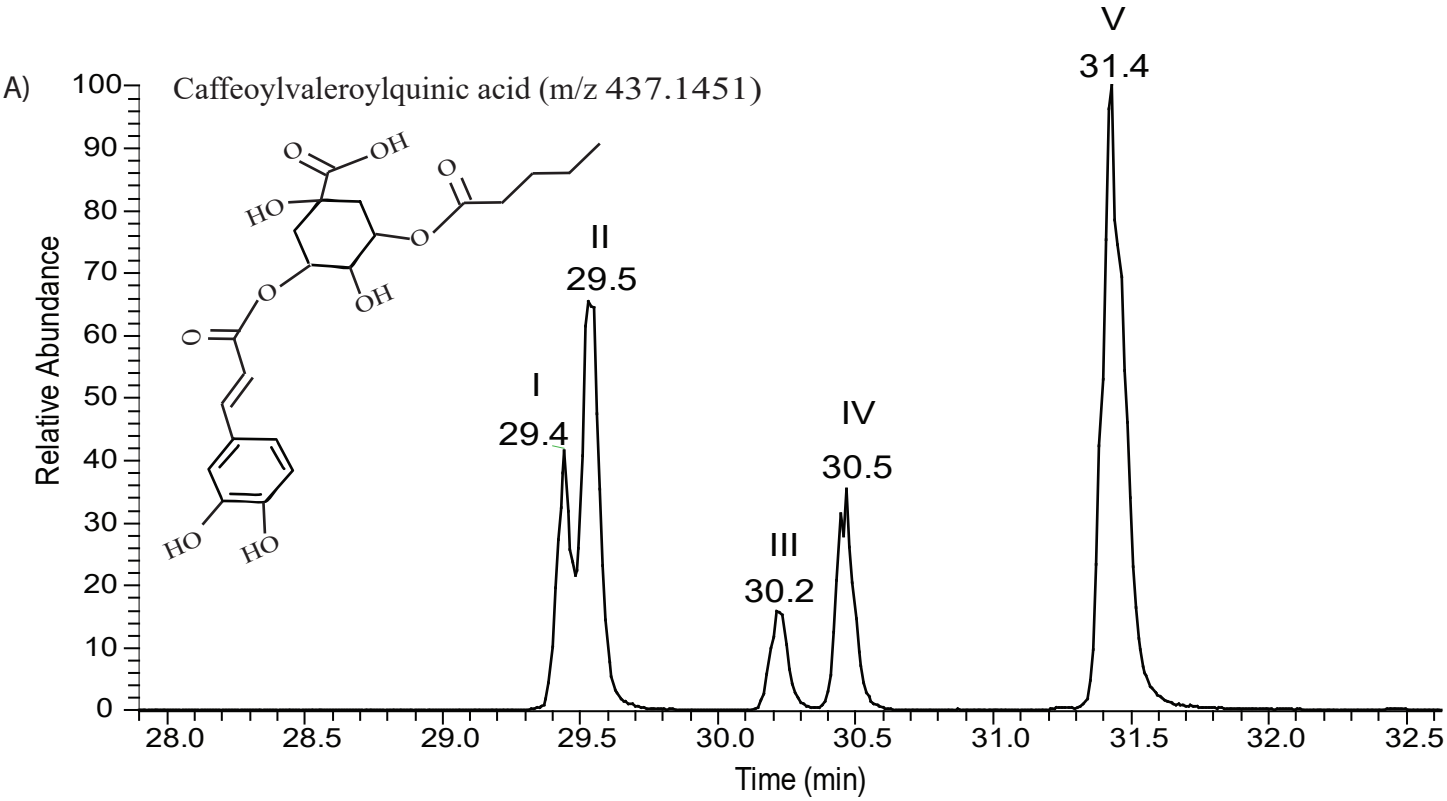
Supplementary Table 1 (continued)

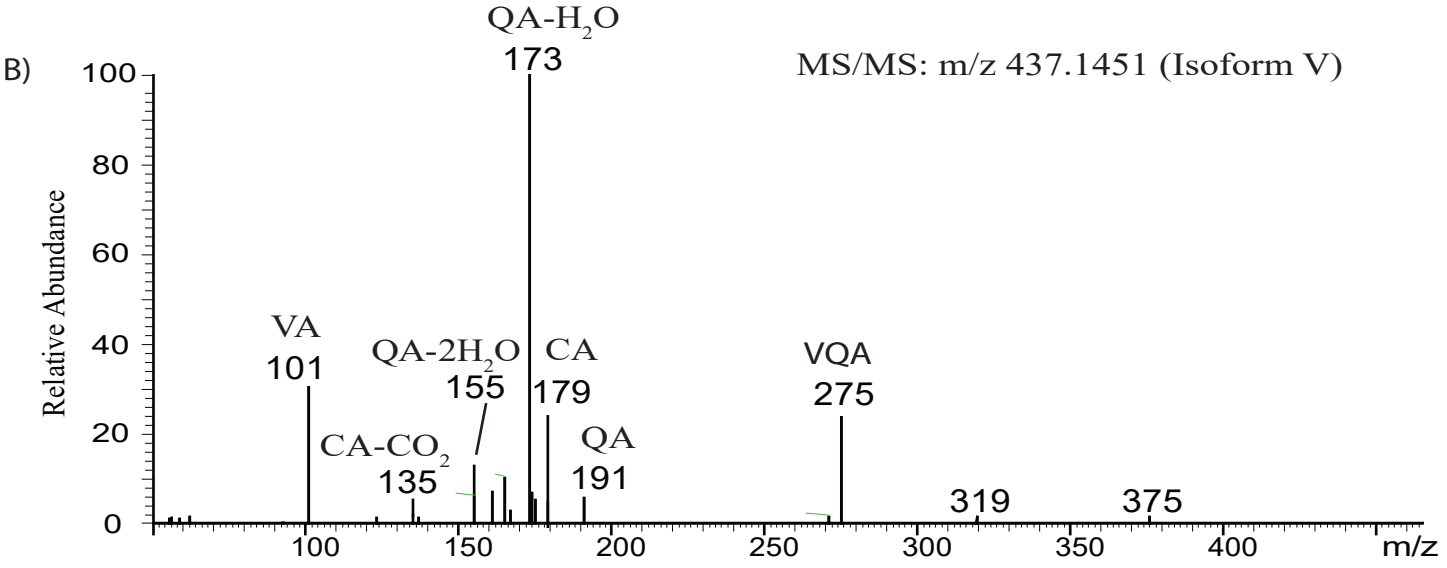
| **Other compounds** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 211 | Pantothenic acid | 218.1017 | M-H | 8.8 | √ | √ | √ | 71, 88, 146 |
| 212 | Trigonellin | 138.0548 | M+H | 1.7 | √ | √ | √ | 94, 138 |
| 213 | Caffeine | 195.0875 | M+H | 20.1 | √ | √ | √ | 138 |
| 214 | Choline | 104.1073 | M+H | 1.6 | √ | √ | √ | 60 |
| 215 | Glycerophosphocholine | 258.1098 | M+H | 1.6 | √ | √ | √ | 104 |
| 216 | Glycerophosphocholine-Na | 280.0915 | M+H | 1.6 | √ | √ | √ | 104, 221 |
| 217 | Glycerophosphocholine-derv | 296.0655 | M+H | 1.6 | √ | √ | √ | 86, 104, 236 |
| 218 | Xanthine | 151.0256 | M-H | 3.1 | √ | √ | ND | 108 |
| 219 | Sucrose | 341.1087 | M-H | 1.8 | √ | √ | ND | 119, 161, 179 |

Supplementary Figure 1

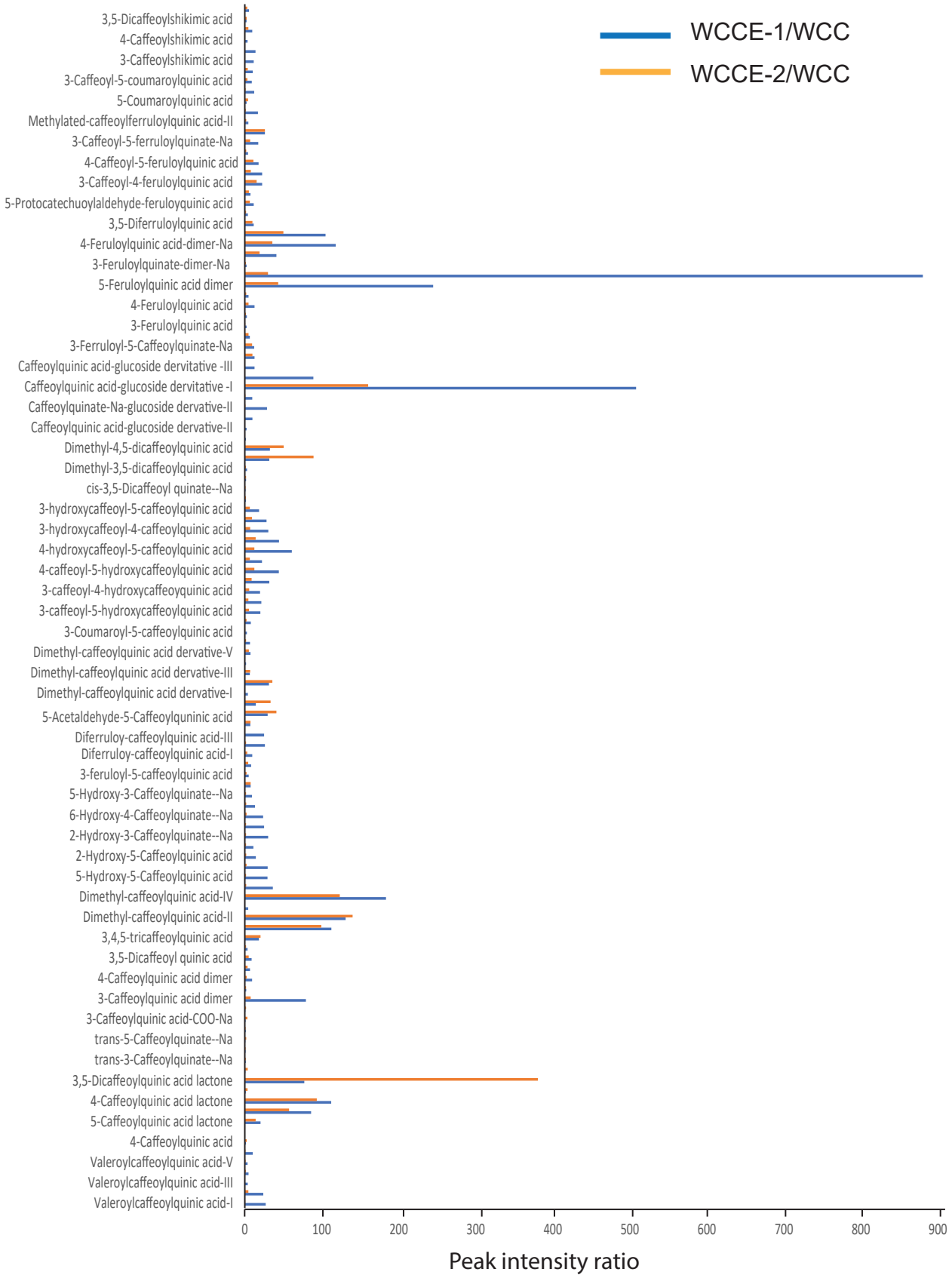


Supplementary Figure 2

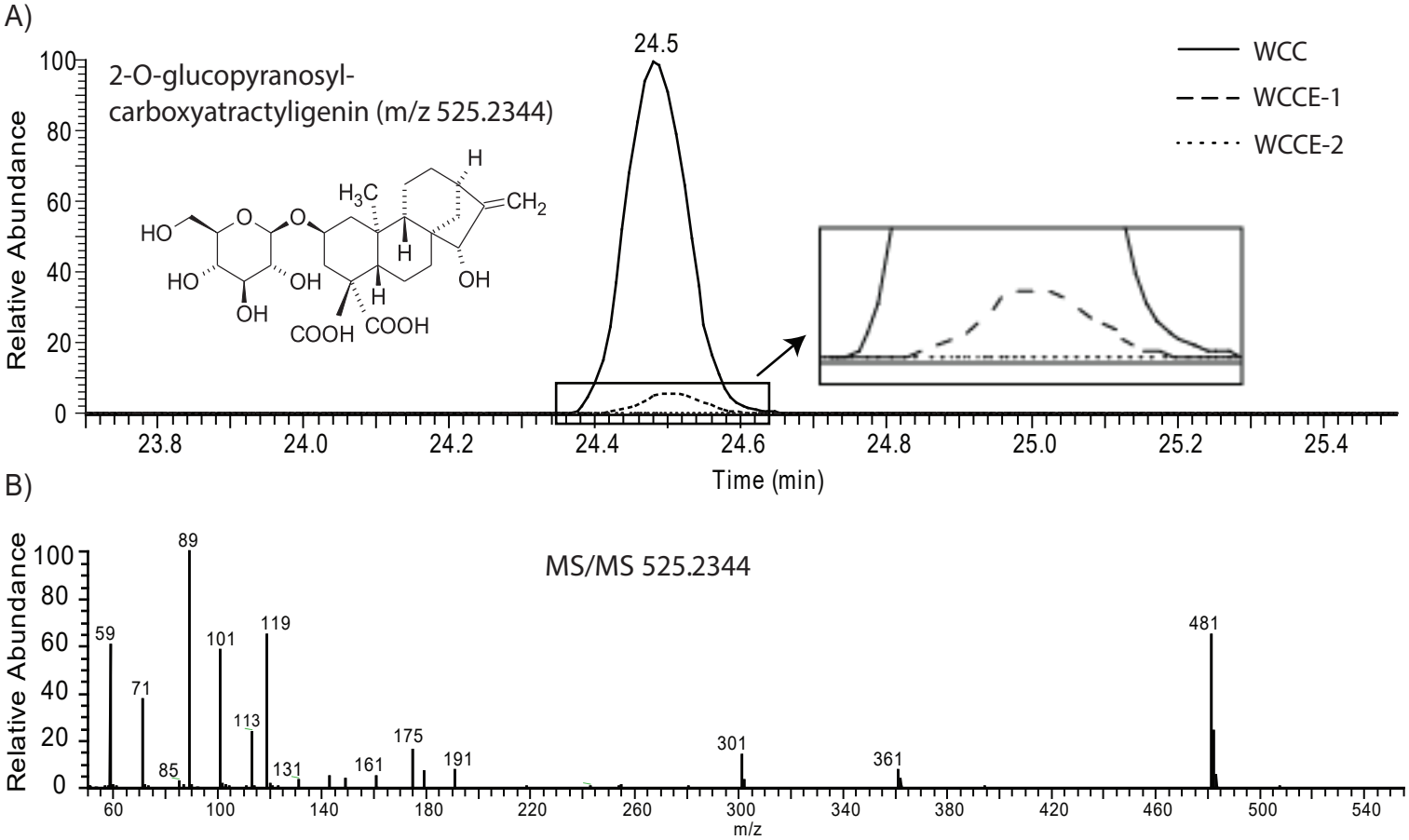
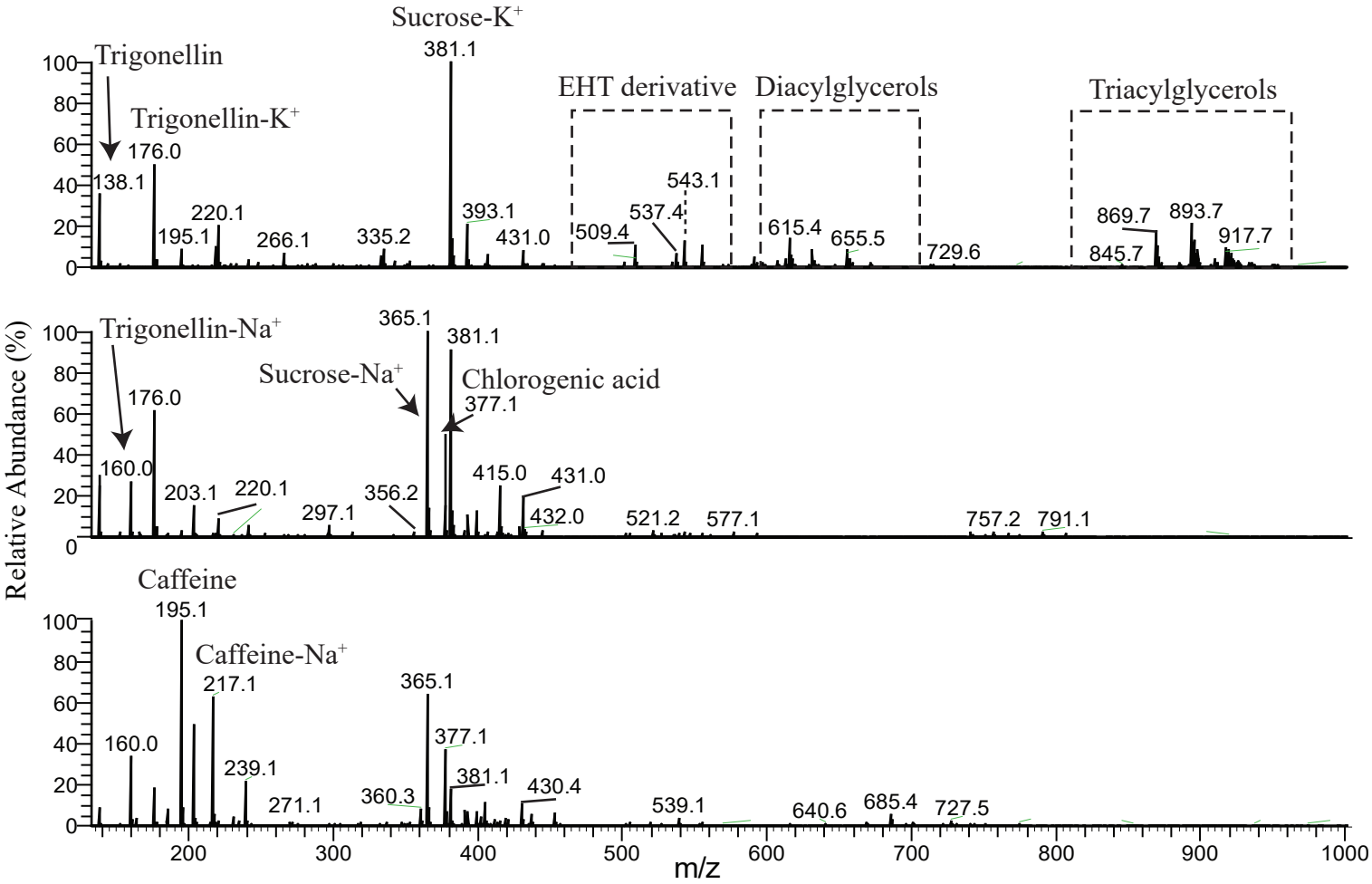


Supplementary Figure 3



Supplementary Figure 4



Supplementary Figure 5