Supplementary Material

Chromatography Conditions Development by Design of Experiments for the Chemotype Differentiation of Four Bauhinia Species

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1 Supplementary Figures

**Figure S1.** Explained variance chart (%) for choosing the number of main components used in the PCA data processing.
## Supplementary Tables

**Table 1S. Results obtained from DoE – Step 1 showing number of chromatographic bands for tested column**

| Column                  | Normalized Levels (columns) | pH  | Normalized Levels (pH) | Organic Modifier | Levels | Responses (n° of chromatographic bands) |
|-------------------------|-----------------------------|-----|------------------------|------------------|--------|----------------------------------------|
| Raptor® Biphenyl        | -0.3791                     | 5.3 | -0.1351                | MeCN             | -1     | 72                                     |
| Raptor® Biphenyl        | -0.3791                     | 4.2 | -0.7298                | MeCN             | -1     | 84                                     |
| Raptor® Biphenyl        | -0.3791                     | 4.2 | -0.7298                | MeCN             | -1     | 80                                     |
| Raptor® Biphenyl        | -0.3791                     | 3.7 | -1                     | MeCN             | -1     | 65                                     |
| Raptor® Biphenyl        | -0.3791                     | 3.7 | -1                     | MeCN             | -1     | 58                                     |
| Raptor® Biphenyl        | -0.3791                     | 5.3 | -0.1351                | MeOH             | 1      | 84                                     |
| Raptor® Biphenyl        | -0.3791                     | 4.2 | -0.7298                | MeOH             | 1      | 81                                     |
| Raptor® Biphenyl        | -0.3791                     | 4.2 | -0.7298                | MeOH             | 1      | 80                                     |
| Raptor® Biphenyl        | -0.3791                     | 4.2 | -0.7298                | MeOH             | 1      | 87                                     |
| Raptor® Biphenyl        | -0.3791                     | 4.2 | -0.7298                | MeOH             | 1      | 84                                     |
| Raptor® Biphenyl        | -0.3791                     | 7.4 | 1                      | MeOH             | 1      | 64                                     |
| Raptor® Biphenyl        | -0.3791                     | 7.4 | 1                      | MeOH             | 1      | 57                                     |
| Raptor® Biphenyl        | -0.3791                     | 3.7 | -1                     | MeOH             | 1      | 77                                     |
| Raptor® Biphenyl        | -0.3791                     | 3.7 | -1                     | MeOH             | 1      | 67                                     |
| Kinetex® Biphenyl       | -1                          | 5.3 | -0.1351                | MeCN             | -1     | 82                                     |
| Kinetex® Biphenyl       | -1                          | 4.2 | -0.7298                | MeCN             | -1     | 90                                     |
| Kinetex® Biphenyl       | -1                          | 7.4 | 1                      | MeCN             | -1     | 77                                     |
| Kinetex® Biphenyl       | -1                          | 3.7 | -1                     | MeCN             | -1     | 76                                     |
| Kinetex® Biphenyl       | -1                          | 5.3 | -0.1351                | MeOH             | 1      | 89                                     |
| Kinetex® Biphenyl       | -1                          | 4.2 | -0.7298                | MeOH             | 1      | 90                                     |
| Kinetex® Biphenyl       | -1                          | 4.2 | -0.7298                | MeOH             | 1      | 92                                     |
| Kinetex® Biphenyl       | -1                          | 4.2 | -0.7298                | MeOH             | 1      | 94                                     |
| Kinetex® Biphenyl       | -1                          | 7.4 | 1                      | MeOH             | 1      | 71                                     |
| Kinetex® Biphenyl       | -1                          | 7.4 | 1                      | MeOH             | 1      | 69                                     |
| Kinetex® Biphenyl       | -1                          | 3.7 | -1                     | MeOH             | 1      | 89                                     |
| Ascentis® Express F5    | 0.3791                      | 5.3 | -0.1351                | MeCN             | -1     | 51                                     |
| Ascentis® Express F5    | 0.3791                      | 3.7 | -1                     | MeCN             | -1     | 43                                     |
| Ascentis® Express F5    | 0.3791                      | 5.3 | -0.1351                | MeOH             | 1      | 47                                     |
| Ascentis® Express F5    | 0.3791                      | 4.2 | -0.7298                | MeOH             | 1      | 80                                     |
| Ascentis® Express F5    | 0.3791                      | 4.2 | -0.7298                | MeOH             | 1      | 77                                     |
| Ascentis® Express F5    | 0.3791                      | 4.2 | -0.7298                | MeOH             | 1      | 75                                     |
| Ascentis® Express F5    | 0.3791                      | 4.2 | -0.7298                | MeOH             | 1      | 78                                     |
| Ascentis® Express F5    | 0.3791                      | 4.2 | -0.7298                | MeOH             | 1      | 47                                     |
| Ascentis® Express F5    | 0.3791                      | 7.4 | 1                      | MeOH             | 1      | 49                                     |
| Ascentis® Express F5    | 0.3791                      | 3.7 | -1                     | MeOH             | 1      | 40                                     |
| Ascentis® Express C18   | 1                           | 5.3 | -0.1351                | MeCN             | -1     | 68                                     |
| Ascentis® Express C18   | 1                           | 4.2 | -0.7298                | MeCN             | -1     | 67                                     |
| Ascentis® Express C18   | 1                           | 7.4 | 1                      | MeCN             | -1     | 55                                     |
| Ascentis® Express C18   | 1                           | 3.7 | -1                     | MeCN             | -1     | 55                                     |
| Ascentis® Express C18   | 1                           | 5.3 | -0.1351                | MeOH             | 1      | 62                                     |
| Ascentis® Express C18   | 1                           | 4.2 | -0.7298                | MeOH             | 1      | 66                                     |
| Ascentis® Express C18   | 1                           | 4.2 | -0.7298                | MeOH             | 1      | 69                                     |
| Ascentis® Express C18   | 1                           | 4.2 | -0.7298                | MeOH             | 1      | 70                                     |
| Ascentis® Express C18   | 1                           | 4.2 | -0.7298                | MeOH             | 1      | 71                                     |
| Ascentis® Express C18   | 1                           | 7.4 | 1                      | MeOH             | 1      | 70                                     |
| Ascentis® Express C18   | 1                           | 7.4 | 1                      | MeOH             | 1      | 61                                     |
| Ascentis® Express C18   | 1                           | 3.7 | -1                     | MeOH             | 1      | 60                                     |
Table S2. Analysis of variance from the DoE - Step 1.

| Source of variation     | Quadratic Sum | Degree of freedom | Quadratic mean | Fcal (95%) | Ftab (95%) | R²  |
|-------------------------|---------------|-------------------|----------------|------------|------------|-----|
| Regression (R)          | 7045.81       | 9                 | 782.87         | 10.09      | 2.12       | 0.97|
| Residue (r)            | 3180.23       | 41                | 77.57          |            |            |     |
| Pure error (EP)        | 175.01        | 19                | 9.21           | 14.83      | 2.13       |     |
| Lack of adjustment (Faj)| 3005.22       | 22                | 136.60         |            |            |     |
| Total                   | 8062.94       | 50                | 204.52         |            |            |     |

Table S3. Analysis of variance from DoE - Step 2

| Source of variation     | Quadratic Sum | Degree of freedom | Quadratic mean | Fcal (95%) | Ftab (95%) | R²  |
|-------------------------|---------------|-------------------|----------------|------------|------------|-----|
| Regression (R)          | 7799.53       | 4                 | 1949.89        | 81.43      | 3.36       | 0.97|
| Residue (r)            | 263.41        | 11                | 23.95          | 0          |            |     |
| Pure Error (EP)        | 24            | 4                 | 6              | 5.70       | 6.09       |     |
| Lack of adjustment (Faj)| 239.41        | 7                 | 34.21          | 0          |            |     |
| Total                   | 8062.94       | 15                | 537.53         | 0          |            |     |
### Table S4. Parameters for calculations of molecular characteristics by principal component analysis (PCA)

| Treatment | Parameter | Limiar value |
|-----------|-----------|--------------|
| Signal to Noise Ratio (S/N) | 5<sup>a</sup> or 15<sup>b</sup> |
| Correlation Coefficient Threshold | 0.7 |
| Minimum mass spectrum signal width* | 15 |

By analysis (samples) and calculation of buckets

| Parameter       | Limiar value |
|-----------------|--------------|
| Advanced bucket | 0.4 min e 1mDa |
| Normalization   | Sum of bucket values in analyzes |
| Bucket filter   | >=6 buckets within the *Bauhinia* group |
| Smoothing width | 7 |

Adducts and clusters

- [M-H]; [M+HCOOH-H]; [M+CH₃COOH-H]; [2M-H]; [2M+HCOOH-H]; [2M+CH₃COOH-H]; [3M-H].

| Variables (buckets) | PCA e HCA | Variance |
|---------------------|-----------|----------|
| Calculation of principal component analysis | % Variance |
| Compound ID | Compound name                          | Rt (min) | m/z Experimental [M-H] | Error (ppm) | Molecular formula [M-H] | Collision Energy (eV) | Fragment ions (%) |
|-------------|----------------------------------------|----------|------------------------|-------------|-------------------------|-----------------------|-------------------|
| 1           | Hexose-hexose                          | 0.5      | 341.1093               | -1.1        | C_{12}H_{22}O_{11}      | 20                   | 179.0563(100); 161.0461(54.1) |
| 2           | Gallic acid                            | 0.6      | 169.0140               | 1.5         | C_{7}H_{10}O_{5}        | 20                   | 125.0245(100)    |
| 3           | Dihydroxybenzoic acid-pentoside        | 0.7      | 285.0619               | 1.1         | C_{12}H_{13}O_{8}      | 30                   | 108.0215(100); 152.0116(90) |
| 4           | Phenylalanine                          | 1.0      | 164.0719               | -1.2        | C_{8}H_{10}NO_{2}      | 25                   | 147.0442(100); 103.0550(33.7); 164.0719(12.6). |
| 5           | Pantotenic acid                        | 1.1      | 218.1034               | 2.7         | C_{16}H_{16}NO_{5}     | 10                   | 218.1028(100); 216.0875(64.6); 146.0824(22.4) |
| 6           | Tryptophan                             | 1.6      | 203.0827               | -0.5        | C_{11}H_{11}N_{2}O_{2} | 20                   | 116.0505(100); 142.0663(32.1) |
| 7           | Methoxycinnamic acid                   | 1.6      | 177.0557               | -0.5        | C_{10}H_{8}O_{3}       | 20                   | 133.0653(100)    |
| 8           | Chlorogenic acid                       | 1.9      | 353.0878               | -3.9        | C_{16}H_{17}O_{5}      | 50                   | 191.0565(100); 135.0450(9.2); 127.0405(8.6) |
| 9           | Caffeic acid                           | 1.7      | 179.0346               | 2.1         | C_{9}H_{14}O_{4}       | 20                   | 135.0451(100)    |
| 10          | (epi)Gallocatechin                     | 2.4      | 305.0665               | 0.6         | C_{15}H_{13}O_{7}      | 20                   | 125.0243(100); 167.0349(44.1); 305.0665(43.1); 219.0662(34.2); 221.0452(17.6); 261.0768(17.1); 237.0769(6.8) |
| 11          | Coumaric acid                          | 2.6      | 163.0401               | 0.2         | C_{8}H_{6}O_{3}        | 30                   | 119.0506(100)    |
| 12          | Coumaric acid-hexoxide                 | 3.0      | 325.0917               | 3.7         | C_{15}H_{17}O_{5}      | 10                   | 163.0394(100); 119.0495(3.6) |
| 13          | Quinic acid-coumaroyl                  | 3.2      | 337.0915               | 4.1         | C_{16}H_{17}O_{8}      | 20                   | 191.0566(100); 173.0458(29.4); 163.0404(13.0) |
| 14          | (epi)afzelechin-(epi)galocatechin      | 3.1      | 575.1182               | 2.3         | C_{30}H_{25}O_{12}     | 20                   | 303.0518(100); 285.0400(71.9); 439.0667(26.3); 125.0247(28.5); 245.0089(17.6) |
| 15          | (epi)afzelechin-(epi)catechin I        | 4.0      | 561.1421               | -3.3        | C_{30}H_{25}O_{11}     | 30                   | 289.0719(100); 290.0754(15.1); 245.0819(9.8); 125.0246(5.7); 137.0246(4.8) |
| 16          | Catechin                               | 4.3      | 289.0716               | 0.6         | C_{15}H_{13}O_{6}      | 20                   | 245.0818(94.3); 203.0709(53.3); 125.0242(39.5); 205.0504(38.6); 151.0398(29.2) |
| 17          | (epi)Catechin-(epi)Catechin            | 4.5      | 577.1357               | -1.0        | C_{30}H_{25}O_{12}     | 20                   | 305.0668(100); 425.0880(60.2); 289.0718(41.4); 407.0774(29.8); 451.1035(23.6); 125.0244(13.6) |
| 18          | (epi)afzelechin-(epi)catechin II       | 5.3      | 561.1420               | -3.1        | C_{30}H_{25}O_{11}     | 20                   | 125.0248(100); 273.0772(96.6); 287.0564(32.1); 289.0719(23.7); 409.0937(13.7); 435.1095(9.5) |
| 19          | Medioresinol                           | 6.0      | 387.1668               | 1.9         | C_{18}H_{22}O_{9}      | 20                   | 387.1668(100); 207.1030(68.8); 163.1132(21.7); 113.0246(15.9) |
| 20          | (epi)afzelechin-(epi)afzelechin        | 6.2      | 545.1449               | 0.8         | C_{30}H_{25}O_{10}     | 20                   | 273.0770(100); 271.0612(17.8); 312.0639(17.6); 274.0809(16); 164.0120(14.2) |
| 21          | Proantocidin C1                        | 6.3      | 865.1995               | -1.1        | C_{45}H_{37}O_{18}     | 45                   | 289.0718(100); 287.0558(91.5); 125.0248(84.1); 407.0774(58.4); 161.0245(31.4) |
**Table S5.** LC-HRMS data of the 55 inferred compounds identified based on the data of Brucker spectral libraries (continued)

| Compound ID | Compound name | Rt (min) | m/z | Error (ppm) | Molecular formula [M-H] | Collision Energy (eV) | Fragment ions (%) |
|-------------|---------------|----------|-----|-------------|-------------------------|----------------------|------------------|
| 22          | afzelechin(4→8aAfzelechin(II) | 6.6      | 545.1432 | 3.9 | C_{20}H_{25}O_{10} | 30 | 273.0771(100); 125.0243(17.4); 164.0115(16.6); 312.0643(14.0) |
| 23          | Orientin      | 6.7      | 447.0947 | -5.6 | C_{21}H_{19}O_{11} | 30 | 327.0516(100); 357.0618(48.9); 297.0401(10.9); 285.0408(5.3); 229.0562(4.9); 339.0518(3.9) |
| 24          | Kaempferol-hexose-deoxyhexose | 6.8      | 593.1502 | -0.3 | C_{22}H_{29}O_{15} | 20 | 285.0406(100); 447.0919(48.1) |
| 25          | Myricetin-pentose(II) | 6.9      | 449.0754 | -6.3 | C_{20}H_{17}O_{12} | 40 | 316.0223(100); 271.0243(27.2); 317.0272(22.7); 287.0193(15.4); 178.9982(5.0); 151.0034(4.2) |
| 26          | Catechin gallate | 7.0     | 441.0832 | -1.1 | C_{22}H_{17}O_{10} | 40 | 169.0140(100); 125.0241(79.8); 245.0814(15.4); 289.0709(13.6); 203.0715(11.1); 137.0242(9.3); 151.0396(9.3) |
| 27          | Myricitrin    | 7.3      | 463.0874 | -0.6 | C_{21}H_{19}O_{12} | 40 | 316.0221(100); 271.0243(25.1); 287.0194(9.8); 151.0033(3.1) |
| 28          | Myricitin-215 | 7.4      | 531.0753 | -5.9 | C_{31}H_{15}O_{9} | 20 | 316.0224(100); 271.0242(15.9); 287.0199(7.9); 178.9984(4.3); 151.0034(3.5); 137.0238(1.4) |
| 29          | Quercetin-441 | 7.5      | 741.1896 | 1.2  | C_{32}H_{37}O_{20} | 50 | 300.0277(100); 178.9983(2.8); 271.0248(2.2); 255.0295(1.1); 151.0034(1.0) |
| 30          | Isovitexin    | 7.6      | 431.0998 | -3.3 | C_{21}H_{19}O_{10} | 30 | 311.0574(100); 283.0618(14.1); 341.0683(9.6); 323.0563(2.4) |
| 31          | Pellettoside  | 7.7      | 595.1316 | -1.9 | C_{26}H_{27}O_{16} | 20 | 300.0276(100); 301.0322(22.0); 178.9987(1.6); 255.0296(1.1); 151.0035(0.7); 463.0890(0.5) |
| 32          | Kaempferol-deoxyhexose-deoxyhexose-hexose | 7.8      | 739.2126 | -4.7 | C_{33}H_{39}O_{19} | 50 | 284.0331(100); 255.0303(4.1); 178.9986(1.5); 227.0350(1.7); 151.0038(1.2) |
| 33          | Quercetin-309 | 7.8      | 609.1461 | -1.3 | C_{22}H_{29}O_{16} | 40 | 300.0276(100); 271.0248(2.3); 178.9985(1.6); 255.0296(0.9); 151.0031(0.8) |
| 34          | Quercetin-hexose | 7.8     | 463.0886 | -0.9 | C_{21}H_{19}O_{12} | 30 | 300.0277(100); 271.0249(2.9); 178.9985(1.6); 151.0038(1.4) |
| 35          | Isorhamnetin-471 | 7.9     | 785.2153 | -0.9 | C_{34}H_{31}O_{21} | 50 | 314.0430(100); 315.0496(54.3); 299.0198(9.3); 316.0535(8.6); 300.0247(4.8); 178.9979(2.9) |
| 36          | Kaempferol-308 | 8.1      | 593.1536 | -4.1 | C_{27}H_{29}O_{15} | 50 | 284.0331(100); 285.0388(31.8); 227.0351(10.2); 151.0040(1.4) |
| 37          | NCGC00384841  | 8.1      | 539.2110 | 4.5  | C_{26}H_{35}O_{12} | 30 | 491.1924(100); 165.0556(32.1); 195.0656(21); 343.1390(20.6); 329.1393(19.7) |
| 38          | Azelaic acid  | 8.2      | 187.0969 | 3.6  | C_{6}H_{15}O_{4}  | 20 | 125.0564(100); 169.0860(10.8) |
| 39          | Vitexin       | 8.3      | 431.0985 | -0.3 | C_{21}H_{19}O_{10} | 40 | 311.0563(100); 283.0612(99.9); 164.0112(31.7); 341.0668(31); 323.0561(20.8) |
| 40          | Methylquercetin-455 | 8.4     | 769.2211 | -1.9 | C_{34}H_{41}O_{20} | 50 | 314.0433(100); 299.0198(0.8); 178.9982(2.3); 151.0034(1.2) |
| 41          | Avicularin (quercetin-3-O-arabinofuranoside) | 8.5     | 433.0774 | 0.5  | C_{20}H_{17}O_{11} | 40 | 300.0246(100); 271.0220(45.2); 255.0270(19.3); 151.0017(7.1) |
| 42          | Kaempferol-308(II) | 8.5     | 593.1537 | -4.2 | C_{27}H_{29}O_{15} | 45 | 284.0330(100); 255.0300(10.3); 227.0353(3.5) |
| Compound ID | Compound name                                              | Rt (min) | m/z     | Error (ppm) | Molecular formula [M-H] | Collision Energy (eV) | Fragment ions (%) |
|-------------|-----------------------------------------------------------|----------|---------|-------------|-------------------------|----------------------|-------------------|
| 43          | Quercetin (Quercetin 3-O-rhamnoside)                      | 9.1      | 447.0907| 5.8         | C_{21}H_{19}O_{11}      | 40                   | 300.0250(100); 284.0302(21.6); 151.0026(2.6); 178.9971(2.7) |
| 44          | (epi)afzelechin-(epi)catechin(II)                         | 9.2      | 561.1430| -4.9        | C_{30}H_{25}O_{11}      | 30                   | 289.0720(100); 271.0615(11.9); 245.0823(10.1); 137.0246(7.2); 125.0243(6.3) |
| 45          | Isorhamnetin-hexose                                        | 9.9      | 477.1038| 1.2         | C_{22}H_{21}O_{12}      | 40                   | 314.0429(100); 243.0294(34.9); 271.0243(32.8); 285.0401(29.9); 257.0451(13.8) |
| 46          | Naringenin 7-O-glucoside                                  | 10.1     | 433.1160| -4.6        | C_{21}H_{21}O_{10}      | 35                   | 271.0622 (100); 268.0391(66.7); 151.0046(37.6); 119.0514(10.1) |
| 47          | Kaempferol-131                                            | 10.3     | 415.1946| 6.6         | C_{20}H_{31}O_{9}       | 30                   | 284.0321(100); 137.0243(29.8); 151.0410(22.9); 125.0246(17.4); 227.0346(15.3); 255.0297(14.4) |
| 48          | 3',4',7,8-Tetrahydroxyflavone                             | 10.4     | 287.0561| 0.0         | C_{15}H_{11}O_{6}       | 20                   | 151.0039(100); 135.0454(60.9); 283.2640(8.4) |
| 49          | Kaempferol-214                                            | 10.5     | 499.0860| 4.4         | C_{14}H_{9}O_{12}       | 40                   | 285.0398(100); 255.0295(4.2); 227.0350(1.6) |
| 50          | Kaempferide-116                                           | 10.7     | 417.2119| -1.7        | C_{20}H_{33}O_{9}       | 40                   | 284.0317(100); 301.0367(91.5); 255.0284(81.0); 227.0355(60.9); 151.0396(54.4) |
| 51          | Quercetin-313                                             | 10.8     | 475.0874| 1.7         | C_{22}H_{19}O_{12}      | 20                   | 300.0276(100); 285.0402(35.8); 271.0245 (3.0); 255.0295(1.8); 178.9986(1.1) |
| 52          | Trihydroxyflavone-dimethyl-161                            | 11.7     | 461.1450| 0.7         | C_{23}H_{25}O_{10}      | 20                   | 269.0455(100); 284.0685(75); 241.0506(64.9); 225.0552(25.7); 240.0419(22.3) |
| 53          | 7,4'- Dimethoxy-5-hydroxyflavone-203                     | 11.7     | 503.1558| 0.6         | C_{25}H_{27}O_{11}      | 40                   | 284.0690(100); 269.0459(34.2); 299.0925(27.2); 241.0506(19.6) |
| 54          | Naringenin Falcone                                         | 12.1     | 271.0614| -0.7        | C_{15}H_{11}O_{5}       | 30                   | 119.0502(100); 151.0035(60.5); 107.0132(16.0); 187.0396 |
| 55          | Bauhiniastatin 2                                           | 14.6     | 299.0917| -5.3        | C_{17}H_{15}O_{5}       | 30                   | 225.0556(100); 197.0605(83.1); 241.0505(75.3); 210.0320(36.1) |
Table S6. Presence of the compounds in the ethanolic extracts of leaves of *B. forficata*, *B. variegata*, *B. longifolia*, and *B. affinis*, at the experimental conditions evaluated for sample preparation and analysis.

| Compound ID | Compound                          | B. forficata | B. longifolia | B. variegata | B. affinis |
|-------------|-----------------------------------|--------------|--------------|-------------|------------|
| 1           | Hexose-hexose                     | X            | X            | X           | X          |
| 2           | Gallic acid                       | X            | X            | X           |            |
| 3           | Dihydroxybenzoic acid-pentoside   | X            | X            | X           | X          |
| 4           | Phenylalanine                     | X            | X            | X           | X          |
| 5           | Pantotenic acid                   | X            | X            | X           | X          |
| 6           | Tryptophan                        | X            | X            | X           | X          |
| 7           | Methoxycinnamic acid              | X            | X            | X           |            |
| 8           | Chlorogenic acid                  | X            | X            | X           |            |
| 9           | Caffeic acid                      | X            | X            | X           |            |
| 10          | (epi)Gallocatechin                | X            | X            | X           |            |
| 11          | Coumaric acid                     | X            | X            | X           | X          |
| 12          | Coumaric acid-hexoside            | X            | X            | X           | X          |
| 13          | Quinic acid-coumaroyl             | X            | X            | X           |            |
| 14          | (epi)afzelechin-(epi)galocatechin | X            | X            | X           |            |
| 15          | (epi)afzelechin-(epi)catechin I   | X            | X            |            |            |
| 16          | Catechin                          | X            | X            | X           |            |
| 17          | (epi)catechin-(epi)catechin       | X            | X            | X           |            |
| 18          | (epi)afzelechin-(epi)catechin II  | X            | X            | X           |            |
| 19          | Medioresinol                      | X            | X            | X           | X          |
| 20          | (epi)afzelechin-(epi)afzelechin   | X            | X            | X           |            |
| 21          | ProantociadinC1                   | X            |            | X           |            |
| 22          | afzelechin(4→8)afzelechin(II)     | X            | X            | X           |            |
| 23          | Orientin                          | X            | X            | X           |            |
Table S6. Presence of the compounds in the ethanolic extracts of leaves of *B. forficata*, *B. variegata*, *B. longifolia*, and *B. affinis*, at the experimental conditions evaluated for sample preparation and analysis (continued)

| Compound ID | Compound | *B. forficata* | *B. longifolia* | *B. variegata* | *B. affinis* |
|-------------|----------|----------------|----------------|----------------|-------------|
| 24          | Kaempferol-hexose-deoxyhexose | X               |               |                |             |
| 25          | Myricetin-pentose(II) | X               |               |                |             |
| 26          | Catechin gallate | X               |               |                |             |
| 27          | Myricitin | X               |               |                |             |
| 28          | Myricitrin-215 | X               |               |                |             |
| 29          | Quercetin-441 | X               |               |                |             |
| 30          | Isovitexin | X               | X             | X              |             |
| 31          | Peltatoside | X               |               | X              |             |
| 32          | Kaempferol-deoxyhexose-deoxyhexose-hexose | X               |               | X              |             |
| 33          | Quercetin-309 | X               | X             | X              | X           |
| 34          | Quercetin-hexose | X               | X             | X              | X           |
| 35          | Isorhamnetin-471 | X               |               |                | X           |
| 36          | Kaempferol-308 | X               |               |                |             |
| 37          | NCGC00384841 | X               |               |                | X           |
| 38          | Azelaic acid | X               | X             | X              | X           |
| 39          | Vitexin | X               |               |                |             |
| 40          | Methylquercetin-455 | X               | X             |                |             |
| 41          | Avicularin (quercetin-3-O-arabinofuranoside) | X               | X             | X              | X           |
| 42          | Kaempferol-308(II) | X               | X             | X              | X           |
| 43          | Quercetin (Quercetin 3-O-rhamnioside) | X               | X             | X              | X           |
| 44          | (epi)afzelechin-(epi)catechin(II) | X               | X             | X              |             |
| 45          | Isorhamnetin-hexose | X               |               |                | X           |
| 46          | Naringenin 7-O-glucoside | X               |               |                | X           |
| 47          | Kaempferol-131 | X               | X             | X              |             |
| 48          | 3',4',7,8-Tetrahydroxyflavanone | X               |               |                |             |
Table S6. Presence of the compounds in the ethanolic extracts of leaves of *B. forficata*, *B. variegata*, *B. longifolia*, and *B. affinis*, at the experimental conditions evaluated for sample preparation and analysis (continued)

| Compound ID | Compound                          | *B. forficata* | *B. longifolia* | *B. variegata* | *B. affinis* |
|-------------|-----------------------------------|----------------|-----------------|----------------|--------------|
| 49          | Kaempferol-214                     |                |                 |                | X            |
| 50          | Kaempferide-116                    | X              | X               | X              | X            |
| 51          | Quercetin-313                      |                |                 |                | X            |
| 52          | Trihydroxyflavone-dimethyl-161     | X              | X               | X              | X            |
| 53          | 7,4’-Dimethoxy-5-hydroxyflavone-203| X              |                 |                | X            |
| 54          | Naringenin Falcone                  |                |                 |                | X            |
| 55          | Bauhiniastatin 2                    | X              | X               | X              | X            |
SECTION 1. Secondary Metabolites Chemical Characterization by LC-HRMS

1.1. Hexose-Hexose

The hexose-hexose (1) disaccharide (other isomers) was identified according to fragmentation of the deprotonated molecular ion [M-H]\(^-\) at \(m/z\) 341.1077 (C\(_{12}\)H\(_{21}\)O\(_{11}\)), which produced fragment ions at \(m/z\) 179.0564 and \(m/z\) 161.0453, attributed to the monosaccharide. Also, the spectrum of this disaccharide was compared with literature data (Matsuda et al., 2010; Matsusa et al., 2016; Valgimigli et al., 2012).

1.2. Organic acids and aminoacids

Compound (3) was characterized as dihydroxybenzoic acid-pentoside with a deprotonated molecular ion at \(m/z\) 285.0619, yielding fragment ions at \(m/z\) 108.0214 (loss of HCO\(_2\)) and \(m/z\) 109.0281 [M-H-44]\(^-\) (loss of CO\(_2\)), depending on the collision energy dissociation applied, which is a characteristic of the dihydroxybenzoic acid and the isomers gentisic acid and protocatechuic acids, both previously reported for the genus Bauhinia (Compaoré et al., 2012; Nageshwar et al., 1986). Additionally, the compound (3) also produced fragment ions at \(m/z\) 153.0192, 152.0117 and loss of pentose [M-H-132]\(^-\), being another characteristic of dihydroxybenzoic acid-pentoside. Pantothenic acid (5) was inferred based on the exact mass at \(m/z\) 218.1026 and by comparison of the fragment ion at \(m/z\) 146.0816 (loss of C\(_3\)H\(_4\)O\(_2\)) with the MassBank database. (Kakazu & Horai, 2016)

Phenylalanine (4) was identified based on the exact mass at \(m/z\) 164.0709 and fragment ions at \(m/z\) 147, which is related to the loss of one amino group and one hydrogen atom from the benzylic ring. This phenomenon may occur due to the rearrangement of a proton from the benzylic position to a carboxyl group through a five-membered ring transition state, resulting in the formation of an intermediate having a carbanion at the benzyl position. By increasing the collision dissociation energy, the relative intensity of the fragment ion at \(m/z\) 103 increases, while the fragment ion at \(m/z\) 147 decreases. This result suggests that the fragment ion at \(m/z\) 147 has a high internal energy and can be further fragmented via the loss of CO\(_2\) (44 Da) to form the fragment ion at \(m/z\) 103. (Matsuda et al., n.d.; Sekimoto et al., 2014)

Tryptophan’s (6) identification was based on the fragment ions at \(m/z\) 116, which represents the indole ion of the molecule obtained by loss of the sidechain (Kakazu & Horal, 2016; Lambert et al.,...
The Methoxycinamic acid (7) were identified based on the loss of CO$_2$ (44 Da) from m/z 177.0558, yielding the fragment ion m/z 133. (Metlin 6453, n.d.)

Chlorogenic acid (8) and quinic acid-cumaroyl (13), with the molecular formulas C$_{16}$H$_{18}$O$_9$ [M-H]$^-$ m/z 353.0892 and C$_{16}$H$_{18}$O$_8$ [M-H]$^-$ m/z 337.0915, respectively, were identified due to fragmentation by charge retention fragmentation (CRF) via remote hydrogen rearrangements (RHR), which promoted the neutral loss of the corresponding part of the molecule to caffeic acid (9) and coumaric acid (11), respectively. Also, the chlorogenic acid showed the fragment ion at m/z 191.0568 that is relative to quinic acid and the quinic-coumaroil acid showed fragment ions at m/z 163.0403 and 119.0503 due to the fragmentation of the coumaric acid.

1.3. Flavonoid O-glycosides, C-glycosides, and other compounds (25, 27, 29-30, 32-36, 40-43, and 45-54)

The fragment ions at m/z 284/285, 300, 314, 316 were characterized as the radical aglycon [Y$_0$-H]$^-$ and/or the aglycon ions [Y$_0$]$^-$ in the negative ionization mode (Aquino et al., 2019), from the flavonoid aglycones kaempferol (compounds 24, 32, 36, 42, 47, and 49), quercetin (29, 33, 34, 43, and 51), methylquercetin (40), and myricetin (25, 27, and 28), respectively. The complete fragmentation studies and the flavonoid’s spectra have been previously published (Aquino et al., 2019; Aquino & http://lattes.cnpq.br/6601636992092317, 2018).

Additionally, kaempferitrin, an alleged chemical marker of Bauhinia forficata, which shows a deprotonated molecular ion at m/z 577.1552 and adduct ions ([M-AF]$^-$ and [M-H$_2$O-H], and clusters ([2M-H]$^-$, [3M-H]$^-$, [2M+AF-H]$^-$) was not found in any of these forms. These data corroborate those previously published by Ferreres et al. (Ferreres et al., 2012), who also studied B. forficata Link subspecies pruinosa (Vogel) Fortunato & Wunderlin and did not found this substance.

Bauhniiastatin 2 is present in all species studied in this work, as illustrated in Table (7). This compound has been reported in B. purpurea, and its medicinal properties are related to anticancer activity, which demonstrates the potential of these 4 species of Bauhinia for this purpose.

1.4. Proanthocyanidin (Type B and A) and Procyanidin C1(14-18, 20, 22, and 44)

The identification of the proanthocyanidin type B dimers was based on their fragmentation patterns (Li and Deinzer, 2007; Demarque et al., 2016). For example, (epi)catechin-(epi)catechin (17),
(proanthocyanidin type B) exhibited a deprotonated molecular ion at $m/z$ 577.1365 and a fragment ion at $m/z$ 425, from a retro-Diels-Alder (RDA) cleavage. The fragment ions $m/z$ 451.1035 and 289.0718 were obtained via $\epsilon$-elimination indicating carbon-carbon bonding unit and (epi) catechin, respectively. The peak (14) was attributed to (epi) afzelechin-(2→7,4→8) (epi) gallocatechin, protoantocyanidin type A, due to the presence of fragment ions at $m/z$ 303.0508 and 439.0663 and exact mass $m/z$ 575.1115 (Li and Deinzer, 2007).

The fragmentation of the trimer (proanthocyanidin C1, compound 21 in table 6) was to be like the dimers. The fragment ion ([M-H-152]$^-$) at $m/z$ 713.1 was derived from an RDA reaction of B-type procyanidin trimer, and the fragment ion ([M-H-288]$^-$) at $m/z$ 577.1 was originated from the cleavage of the B-type trimer, which could take place at either the upper interflavonoid bond or the lower bond (Karonen et al., 2004; Li et al., 2012). Besides, fragment ions were detected at $m/z$ 425.0, 407.1, and 288.9. The fragment ions ([M-H-440]$^-$) at $m/z$ 425.0 was originated from an RDA, while the [M-H-458]$^-$ with a fragment ion at $m/z$ 407.1, owing to a loss of water.

1.5. Others

The compound 38 (azelaic acid/nonanedioic acid – medium-chain fatty acid) showed the following deprotonated molecular ion [M-H]$^-$ at $m/z$ 187.098 and fragment ion at $m/z$ 125.0975 (Metlin). The fragment ions of NCGC00384841 (37) were $m/z$ 491.1924 and 343.1390. For Medioresinol (19), the fragment ions were at $m/z$ 163 and 207. (Mona; Bonzanini et al., 2009; Bendif et al., 2020)
Section 2. Metabolite Spectra: Complete mass spectra of each compound are herein organized by retention time (Rt min), measured m/z, ion formula, error (ppm), and collision dissociation energy.

**Compound 1 - Hexose-hexose**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]⁻ | Theoretical m/z | Error (ppm) | eV(MS⁻) |
|----------------|--------------|---------------------|-----------------|-------------|---------|
| 0.5            | 341.1093     | C₁₂H₂₁O₁₁           | 341.1089        | 1.2         | 20      |

-MS²(341.1093), 20.0 eV, 0.5 min #30

| m/z   | I %   |
|-------|-------|
| 179.0563 | 100.0 |
| 341.1093 | 87.3  |
| 165.0403 | 61.1  |
| 297.1194 | 60.2  |
| 159.0301 | 56.4  |
| 161.0461 | 54.1  |
| 191.0563 | 52.7  |
| 128.0357 | 48.3  |
| 160.0617 | 47.0  |
| 113.0249 | 45.4  |
| 158.0459 | 40.0  |
| 119.0350 | 38.1  |
| 143.0352 | 22.1  |
Compound 2 - Galic-Acid

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H] | Theoretical m/z | Error (ppm) | eV(US') |
|----------------|--------------|-------------------|-----------------|-------------|---------|
| 0.60           | 169.0140     | C$_7$H$_5$O$_5$   | 169.0142        | -1.2        | 20      |

| m/z            | I % |
|----------------|-----|
| 125.0245       | 100.0 |
| 169.0140       | 7.4 |
| 124.0168       | 6.2 |
| 126.0279       | 6.1 |
| 107.0133       | 2.1 |
| 151.0038       | 1.0 |
| 127.0301       | 0.8 |

Compound 3 - Dihydroxybenzoic acid-pentoside

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H] | Theoretical m/z | Error (ppm) | eV(US') |
|----------------|--------------|-------------------|-----------------|-------------|---------|
| 0.68           | 285.0619     | C$_{12}$H$_{13}$O$_8$ | 285.0616        | 1.0         | 20      |

| m/z            | I % |
|----------------|-----|
| 152.0117       | 100.0 |
| 285.0619       | 72.6 |
| 153.0192       | 51.2 |
| 108.0214       | 37.8 |
| 243.0624       | 21.7 |
| 125.0246       | 21.6 |
| 283.2643       | 18.5 |
| 150.0421       | 16.4 |
| 200.0565       | 16.0 |
| 109.0281       | 8.8  |
| 286.0652       | 8.6  |
| 111.0197       | 6.2  |

15
### Compound 4 - Phenylalanine

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]  | m/z     | Error (ppm) | eV(MS⁻) |
|----------------|--------------|---------------------|---------|-------------|----------|
| 1.0            | 164.0712     | C₉H₁₀NO₂             | 164.0717| -3.0        | 25       |

**UHPLC (Rt min) Measured m/z Ion Formula [M-H] m/z Error (ppm) eV(MS⁻)**

### Compound 5 - Pantotenic acid

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]  | m/z     | Error (ppm) | eV(MS⁻) |
|----------------|--------------|---------------------|---------|-------------|----------|
| 1.1            | 218.1028     | C₁₀H₁₆NO₅            | 218.1034| -2.8        | 10       |

**UHPLC (Rt min) Measured m/z Ion Formula [M-H] m/z Error (ppm) eV(MS⁻)**
### Compound 6 - Tryptophan

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]^+ | m/z | Error (ppm) | eV(MS^-) |
|---------------|--------------|----------------------|-----|-------------|-----------|
| 1.6           | 203.0827     | C_{11}H_{11}N_{2}O_{2} | 203.0826 | -0.5        | 20        |

### Compound 7 - Methoxycinnamic acid

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]^+ | m/z | Error (ppm) | eV(MS^-) |
|---------------|--------------|----------------------|-----|-------------|-----------|
| 1.6           | 177.0558     | C_{10}H_{9}O_{3}     | 177.0557 | -0.6        | 20        |

### Mass Spectral Data

- Compound 6: m/z 203.0827, H 100.0, C 32.1, N 23.3, O 9.3
- Compound 7: m/z 177.0558, H 100.0, C 30.6, O 20.7, N 15.8
### Compound 8 - Chlorogenic acid

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H] | m/z     | Error (ppm) | eV(MS⁻) |
|----------------|--------------|--------------------|---------|-------------|---------|
| 1.9            | 353.0892     | C₁₆H₁₇O₉           | 353.0878| 4.0         | 50      |

**MS²(353.0892), 50.0eV, 1.9min #123**

| m/z     | I %     |
|---------|---------|
| 191.0565| 100.0   |
| 135.0450| 9.2     |
| 127.0405| 8.6     |
| 192.0605| 6.8     |
| 133.0296| 5.1     |
| 173.0461| 4.2     |
| 109.0296| 3.9     |
| 161.0251| 3.8     |

### Compound 9 - Caffeic acid

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H] | m/z     | Error (ppm) | eV(MS⁻) |
|----------------|--------------|--------------------|---------|-------------|---------|
| 1.7            | 179.0346     | C₉H₇O₄             | 179.0350| -2.2        | 20      |

**MS²(179.0346), 20.0eV, 1.7min #111**

| m/z     | I %     |
|---------|---------|
| 135.0451| 100.0   |
| 134.0371| 13.2    |
| 133.0295| 7.7     |
| 136.0484| 7.6     |
| 179.0346| 3.1     |
**Compound 10 - (epi)Gallocatechin**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H] | m/z  | Error (ppm) | eV(MS⁻) |
|----------------|--------------|--------------------|------|-------------|----------|
| 2.40           | 305.0665     | C₁₅H₁₃O₇           | 305.0667 | -0.7        | 20       |

**Compound 11 - Coumaric acid**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H] | m/z  | Error (ppm) | eV(MS⁻) |
|----------------|--------------|--------------------|------|-------------|----------|
| 2.6            | 163.0401     | C₉H₇O₃             | 163.0401 | 0.0        | 30       |

---

**Intens.**

![Graph](image)

| m/z  | I %   |
|------|-------|
| 125.0243 | 100.0 |
| 167.0349 | 44.1  |
| 305.0665 | 43.1  |
| 165.0190 | 40.2  |
| 179.0348 | 35.9  |
| 219.0662 | 34.2  |
| 137.0243 | 31.4  |
| 139.0398 | 29.8  |
| 221.0452 | 17.6  |
| 261.0768 | 17.1  |
| 111.0449 | 7.2   |
| 204.0422 | 7.0   |
| 237.0769 | 6.8   |

---

**Intens.**

![Graph](image)

| m/z  | I %   |
|------|-------|
| 119.0506 | 100.0 |
| 117.0348 | 15.3  |
| 120.0526 | 10.3  |
| 101.0380 | 6.7   |
| 147.8932 | 5.0   |
**Compound 12 - Coumaric acid-hexoside**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z   | Error (ppm) | eV(MS-) |
|----------------|--------------|---------------------|-------|-------------|---------|
| 3.0            | 325.0917     | C_{15}H_{17}O_{8}   | 325.0928 | -3.4        | 10      |

```

| m/z   | I % |
|-------|-----|
| 163.0394 | 100.0 |
| 325.0917 | 19.6  |
| 164.0428 | 7.9   |
| 119.0495 | 3.6   |
| 326.0954 | 2.4   |
```

**Compound 13 - Quinic acid-coumaroyl**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z   | Error (ppm) | eV(MS-) |
|----------------|--------------|---------------------|-------|-------------|---------|
| 3.00           | 337.0915     | C_{16}H_{17}O_{8}   | 337.0929 | -4.2        | 20      |

```

| m/z   | I % |
|-------|-----|
| 191.0566 | 100.0 |
| 173.0458 | 29.4  |
| 163.0404 | 13.0  |
| 192.0594 | 6.7   |
| 289.0716 | 4.0   |
| 119.0497 | 2.3   |
| 111.0446 | 2.2   |
| 179.0351 | 2.0   |
| 155.0343 | 1.8   |
| 145.0297 | 1.7   |
| 337.0915 | 1.5   |
| 174.0499 | 1.5   |
```
Compound 14 - (epi)afzelechin-(epi)galocatechin

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z   | Error (ppm) | eV(MS-) |
|----------------|--------------|---------------------|-------|-------------|----------|
| 3.11           | 575.1182     | C\textsubscript{30}H\textsubscript{23}O\textsubscript{12}   | 575.1195 | -2.3        | 20       |

m/z       I %
303.0518  100.0  
285.0400  71.9 
243.0301  36.6  
125.0247  28.5  
177.0197  27.1  
439.0667  26.3  
313.0357  26.2  
259.0610  22.7  
245.0089  17.6  
261.0398  17.6  
304.0545  14.9  
286.0448  14.1  
275.0553  14.0  

Compound 15 - (epi) afzelechin-(epi)catechin I

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z   | Error (ppm) | eV(MS-) |
|----------------|--------------|---------------------|-------|-------------|----------|
| 4.00           | 561.1421     | C\textsubscript{30}H\textsubscript{25}O\textsubscript{11}   | 561.1402 | 3.4        | 30       |

m/z       I %
289.0719  100.0  
290.0754  15.1 
245.0819  9.8 
271.0618  9.3 
407.0776  7.2 
125.0246  5.7 
273.0766  4.9 
137.0246  4.8 
435.1081  3.7 
164.0118  3.6 
165.0183  2.6 

UHPLC (Rt min) Measured m/z Ion Formula [M-H]- m/z Error (ppm) eV(MS-)  
3.11 575.1182 C\textsubscript{30}H\textsubscript{23}O\textsubscript{12} 575.1195 -2.3 20 
m/z I %  
303.0518 100.0  
285.0400 71.9  
243.0301 36.6  
125.0247 28.5  
177.0197 27.1  
439.0667 26.3  
313.0357 26.2  
259.0610 22.7  
245.0089 17.6  
261.0398 17.6  
304.0545 14.9  
286.0448 14.1  
275.0553 14.0  

UHPLC (Rt min) Measured m/z Ion Formula [M-H]- m/z Error (ppm) eV(MS-)  
4.00 561.1421 C\textsubscript{30}H\textsubscript{25}O\textsubscript{11} 561.1402 3.4 30 
m/z I %  
289.0719 100.0  
290.0754 15.1  
245.0819 9.8  
271.0618 9.3  
407.0776 7.2  
125.0246 5.7  
273.0766 4.9  
137.0246 4.8  
435.1081 3.7  
164.0118 3.6  
165.0183 2.6  

Intens. [counts] m/z  
125.0246 289.0719 
407.0776 575.0965 

Intens. \(x10^4\) m/z  
125.0246 289.0719
### Supplementary Material

#### Compound 16 - Catechin

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]^- | m/z | Error (ppm) | eV(MS^-) |
|---------------|--------------|---------------------|-----|-------------|----------|
| 4.27          | 289.0716     | C_{15}H_{13}O_{6}   | 289.0718 | -0.7        | 20       |

#### Compound 17 - (epi)Catechin-(epi)Catechin

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]^- | m/z | Error (ppm) | eV(MS^-) |
|---------------|--------------|---------------------|-----|-------------|----------|
| 4.50          | 577.1357     | C_{30}H_{25}O_{12}  | 577.1351 | 1.0         | 20       |

---

![Graph of Compound 16 - Catechin](image1)

![Graph of Compound 17 - (epi)Catechin-(epi)Catechin](image2)
Compound 18 - (epi) afzelechin-(epi)catechin II

| UHPLC (Rt min) | Measured m/z  | Ion Formula [M-H]       | m/z     | Error (ppm) | eV(MS⁻) |
|----------------|---------------|-------------------------|---------|-------------|---------|
| 5.26           | 561.1420      | C₃₀H₂₅O₁₁               | 561.1402| 3.2         | 20      |

-MS²(561.1420), 30.0eV, 5.2min #346

Intens., x10⁴

| m/z       | I %       |
|-----------|-----------|
| 125.0248  | 100.0     |
| 273.0772  | 96.6      |
| 161.0248  | 35.2      |
| 287.0564  | 32.1      |
| 289.0719  | 23.7      |
| 274.0808  | 16.2      |
| 137.0249  | 13.7      |
| 409.0937  | 13.6      |
| 299.0563  | 12.2      |
| 435.1095  | 9.5       |
| 245.0456  | 8.1       |
| 177.0199  | 7.6       |
| 126.0282  | 6.5       |

Compound 19 - Medioresinol

| UHPLC (Rt min) | Measured m/z  | Ion Formula [M-H]       | m/z     | Error (ppm) | eV(MS⁻) |
|----------------|---------------|-------------------------|---------|-------------|---------|
| 6.02           | 387.1668      | C₁₉H₂₇O₉                | 387.1661| 1.8         | 20      |

-MS²(387.1668), 30.0eV, 6.0min #394

Intens., x10⁴

| m/z       | I %       |
|-----------|-----------|
| 387.1668  | 100.0     |
| 207.1030  | 68.8      |
| 163.1132  | 21.7      |
| 388.1702  | 16.9      |
| 113.0246  | 15.9      |
| 119.0352  | 8.6       |
| 208.1064  | 8.3       |
| 101.0245  | 5.2       |
| 389.1727  | 3.5       |
| 225.1141  | 3.5       |
Supplementary Material

Compound 20 - (epi)afzelechin-(epi)afzelechin

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z     | Error (ppm) | eV(MS^-) |
|----------------|--------------|---------------------|---------|-------------|-----------|
| 6.21           | 545.1449     | C_{30}H_{25}O_{10}  | 545.1453| -0.7        | 20        |

\[\text{-MS2(545.1449), 30.0eV, 6.2min #407}\]

| m/z   | I %  |
|-------|------|
| 273.0770 | 100.0|
| 271.0612 | 17.8 |
| 312.0639 | 17.6 |
| 274.0809 | 16.0 |
| 164.0120 | 14.2 |
| 125.0243 | 13.6 |
| 419.1145 | 9.1  |
| 313.0703 | 9.0  |
| 137.0247 | 6.0  |

Compound 21 - Proantociadina C1

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z     | Error (ppm) | eV(MS^-) |
|----------------|--------------|---------------------|---------|-------------|-----------|
| 6.25           | 865.1995     | C_{45}H_{37}O_{18}  | 865.1985| 1.2         | 45        |

\[\text{-MS2(865.1995), 45.0eV, 6.2min #408}\]

| m/z   | I %  |
|-------|------|
| 289.0718 | 100.0|
| 287.0558 | 91.5 |
| 125.0248 | 84.1 |
| 407.0774 | 58.4 |
| 161.0245 | 31.4 |
| 425.0891 | 30.0 |
| 243.0297 | 24.4 |
| 261.0406 | 22.4 |
| 451.1038 | 22.4 |
| 245.0463 | 20.6 |

24
### Compound 22 - afzelechin(4→8)afzelechin(II)

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z       | Error (ppm) | eV(MS') | I % |
|----------------|--------------|---------------------|-----------|-------------|---------|-----|
| 6.83           | 545.1432     | C_{30}H_{25}O_{10}  | 545.1453  | -3.9        | 30      |

- MS2(545.1432), 30.0eV, 6.6min #435

| m/z     | I % |
|---------|-----|
| 273.0771| 100.0 |
| 271.0614| 25.7  |
| 125.0247| 17.4  |
| 164.0115| 16.6  |
| 274.0805| 15.5  |
| 312.0643| 14.0  |
| 419.1136| 13.1  |
| 313.0701| 9.1   |
| 409.0940| 7.4   |
| 165.0178| 5.4   |
| 157.0872| 5.3   |

### Compound 23 - Orientin

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z       | Error (ppm) | eV(MS') | I % |
|----------------|--------------|---------------------|-----------|-------------|---------|-----|
| 6.80           | 447.0947     | C_{21}H_{19}O_{11}  | 447.0933  | 3.1         | 30      |

- MS2(447.0947), 30.0eV, 6.7min #446

| m/z     | I % |
|---------|-----|
| 327.0516| 100.0 |
| 357.0618| 48.9  |
| 328.0543| 16.8  |
| 297.0401| 10.9  |
| 358.0655| 9.2   |
| 174.9562| 6.1   |
| 285.0408| 5.3   |
| 299.0562| 4.9   |
| 339.0518| 3.9   |
| 289.0727| 3.9   |
| 369.0613| 3.8   |
Supplementary Material

Compound 24 - Kaempferol-hexose-deoxyhexose

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z     | Error (ppm) | eV(MS-) |
|----------------|--------------|---------------------|---------|-------------|---------|
| 6.80           | 593.1514     | C_{27}H_{29}O_{15}  | 593.1512| -0.3        | 20      |

-MS2(593.1514), 30.0eV, 6.7min #443

| m/z     | I %  |
|---------|------|
| 285.0406| 100.0|
| 447.0919| 48.1 |
| 446.0854| 41.3 |
| 593.1514| 29.4 |
| 431.0997| 13.5 |
| 286.0443| 12.9 |
| 327.0529| 10.3 |
| 448.0972| 9.7  |
| 594.1548| 8.8  |
| 125.0244| 6.2  |
| 289.0725| 5.9  |

Compound 25 - Myricetin-pentose(II)

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z     | Error (ppm) | eV(MS-) |
|----------------|--------------|---------------------|---------|-------------|---------|
| 6.90           | 449.0754     | C_{20}H_{17}O_{12}  | 449.0725| 6.5         | 20      |

-MS2(449.0754), 40.0eV, 6.9min #458

| m/z     | I %  |
|---------|------|
| 316.0223| 100.0|
| 271.0243| 27.2 |
| 317.0272| 22.7 |
| 287.0193| 15.4 |
| 270.0166| 8.3  |
| 178.9982| 5.0  |
| 288.0251| 4.5  |
| 151.0034| 4.2  |
| 272.0280| 4.1  |
| 318.0296| 3.7  |
| 259.0242| 3.3  |
| 242.0217| 3.1  |
| 214.0267| 1.8  |
| 243.0285| 1.5  |
| 137.0243| 1.3  |
### Compound 26 - Catechin gallate

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]⁻ | m/z | Error (ppm) | eV(MS⁻) |
|----------------|--------------|---------------------|-----|-------------|----------|
| 7.00           | 441.0832     | C₂₂H₁₇O₁₀           | 441.0827 | 1.1          | 40       |

#### Mass Spectrum

![Mass Spectrum](Image)

**-MS2(441.0832), 40.0 eV, 7.0 min #459**

### Compound 27 – Myricitrin-215

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]⁻ | m/z | Error (ppm) | eV(MS⁻) |
|----------------|--------------|---------------------|-----|-------------|----------|
| 7.4            | 531.0753     | C₃₁H₁₅O₉           | 531.0722 | 5.8          | 20       |

#### Mass Spectrum

![Mass Spectrum](Image)

**-MS2(531.0753), 50.0 eV, 7.4 min #486**

**m/z | I %**
---|---
169.0140 | 100.0
125.0241 | 79.8
245.0814 | 15.4
289.0709 | 13.6
124.0163 | 12.8
203.0715 | 11.1
137.0242 | 9.3
151.0396 | 9.3
109.0288 | 8.1
170.0167 | 7.6
205.0504 | 7.2
123.0452 | 6.0
179.0348 | 5.7

**m/z | I %**
---|---
316.0224 | 100.0
317.0278 | 27.9
271.0242 | 15.9
287.0199 | 7.9
270.0170 | 4.8
318.0306 | 4.6
178.9984 | 4.3
151.0034 | 3.5
288.0260 | 3.1
272.0278 | 2.4
137.0238 | 1.4
**Supplementary Material**

**Compound 28 - Myricitrin**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]^- | m/z | Error (ppm) | eV(MS^-) |
|----------------|--------------|----------------------|-----|-------------|-----------|
| 7.3            | 463.0874     | C_{21}H_{19}O_{12}   | 463.0882 | -1.7        | 40        |

![Graph showing the compound's spectrum](image)

**Compound 29 - Quercetin-441**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]^- | m/z | Error (ppm) | eV(MS^-) |
|----------------|--------------|----------------------|-----|-------------|-----------|
| 7.5            | 741.1896     | C_{32}H_{37}O_{20}   | 741.1883 | 1.75        | 50        |

![Graph showing the compound's spectrum](image)

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**m/z** | **%**
---|---
316.0221 | 100.0
317.0275 | 25.1
271.0243 | 18.2
287.0194 | 9.8
270.0166 | 5.8
178.9983 | 4.1
318.0297 | 3.9
288.0253 | 3.5
151.0033 | 3.1
272.0277 | 2.8

**m/z** | **%**
---|---
300.0277 | 100.0
301.0327 | 24.9
741.1898 | 3.6
302.0352 | 3.6
178.9983 | 2.8
271.0248 | 2.2
299.0194 | 2.0
742.1918 | 1.4
255.0295 | 1.1
151.0034 | 1.0
272.0313 | 0.7
289.0722 | 0.5
303.0392 | 0.5
## Compound 30 - Isovitexin

| UHPLC (Rt min) | Measured m/z     | Ion Formula [M-H]^− | m/z     | Error (ppm) | eV(MS') |
|----------------|------------------|---------------------|---------|-------------|---------|
| 7.6            | 431.0998         | C_{21}H_{19}O_{10}  | 431.0984| 3.2         | 30      |

### Mass Spectrum

| m/z   | %      |
|-------|--------|
| 311.0574 | 100.0  |
| 312.0606 | 19.5   |
| 313.0688 | 5.4    |
| 272.0664 | 2.4    |
| 284.0663 | 2.4    |
| 285.1246 | 2.3    |
| 151.0037 | 2.2    |
Compound 31 - Peltatoside

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z       | Error (ppm) | eV(MS) |
|----------------|--------------|---------------------|-----------|-------------|--------|
| 7.7            | 595.1316     | C_{26}H_{27}O_{16}  | 595.1305  | 1.84        | 20     |

| m/z           | I %          |
|---------------|--------------|
| 300.0276      | 100.0        |
| 301.0322      | 22.0         |
| 595.1316      | 6.1          |
| 302.0351      | 3.1          |
| 299.0199      | 2.7          |
| 271.0244      | 2.5          |
| 596.1345      | 1.6          |
| 178.9987      | 1.6          |
| 255.0296      | 1.1          |
| 270.0169      | 0.9          |
| 298.0120      | 0.8          |
| 272.0309      | 0.7          |
| 151.0035      | 0.7          |
| 463.0890      | 0.5          |
### Compound 32 - Kaempferol-deoxyhexose-deoxyhexose-hexose

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z   | Error (ppm) | eV(MS^-) |
|----------------|--------------|---------------------|-------|-------------|-----------|
| 7.8            | 739.2126     | C_{33}H_{39}O_{19}  | 739.2091 | 4.7         | 50        |

**Figure:**
- M^2(739.2126), 50.0eV, 7.8min #515

| m/z  | I %   |
|------|-------|
| 284.0331 | 100.0 |
| 285.0390 | 37.0  |
| 286.0424 | 5.5   |
| 255.0303 | 4.0   |
| 739.2126 | 3.1   |
| 227.0350 | 1.7   |
| 256.0369 | 1.7   |
| 283.0252 | 1.6   |
| 178.9986 | 1.5   |
| 740.2152 | 1.3   |
| 151.0038 | 1.2   |
| 257.0447 | 1.1   |

### Compound 33 - Quercetin-309

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z   | Error (ppm) | eV(MS^-) |
|----------------|--------------|---------------------|-------|-------------|-----------|
| 8.0            | 609.1468     | C_{27}H_{29}O_{16}  | 609.1450 | 3.0         | 35        |

**Figure:**
- M^2(609.1468), 35.0eV, 8.0min #527

| m/z  | I %   |
|------|-------|
| 300.0277 | 100.0 |
| 301.0348 | 75.7  |
| 609.1468 | 61.4  |
| 610.1501 | 17.9  |
| 302.0379 | 11.6  |
| 611.1527 | 4.5   |
| 178.9987 | 3.3   |
| 151.0038 | 2.3   |
| 343.0459 | 2.0   |
| 303.0405 | 1.3   |
**Supplementary Material**

**Compound 34 - Quercetin-hexose**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]^− | m/z  | Error (ppm) | eV(MS^−) |
|----------------|--------------|----------------------|------|-------------|-----------|
| 7.80           | 463.0886     | C_{21}H_{19}O_{12}   | 463.0882 | 0.8         | 30        |

![Graph showing mass spectra for Compound 34](image)

**Compound 35 - Isorhamnetin-471**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]^− | m/z  | Error (ppm) | eV(MS^−) |
|----------------|--------------|----------------------|------|-------------|-----------|
| 7.95           | 785.2153     | C_{34}H_{31}O_{21}   | 785.2146 | 0.9         | 50        |

![Graph showing mass spectra for Compound 35](image)

**Table: Mass Spectral Data**

| m/z       | I %       |
|-----------|-----------|
| 300.0277  | 100.0     |
| 301.0342  | 44.7      |
| 463.0886  | 13.7      |
| 302.0368  | 6.1       |
| 299.0194  | 3.0       |
| 271.0249  | 2.9       |
| 464.0917  | 2.6       |
| 298.0122  | 2.0       |
| 270.0175  | 1.8       |
| 178.9985  | 1.6       |
| 151.0038  | 1.4       |
Compound 36 - Kaempferol-308

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]⁻ | m/z      | Error (ppm) | eV(MS⁻) |
|---------------|--------------|---------------------|----------|-------------|---------|
| 8.1           | 593.1536     | C₂₇H₂₉O₁₅           | 593.1512 | 4.0         | 50      |

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Compound 37 - NCGC00384841

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]⁻ | m/z      | Error (ppm) | eV(MS⁻) |
|---------------|--------------|---------------------|----------|-------------|---------|
| 8.1           | 539.2110     | C₂₆H₅₅O₁₂           | 539.2134 | -4.5        | 30      |

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| m/z     | % |  
|---------|---|---|
| 284.0331 | 100.0 |  
| 285.0388 | 31.8 |  
| 255.0303 | 21.4 |  
| 227.0351 | 10.2 |  
| 256.0361 | 6.8 |  
| 341.0669 | 6.0 |  
| 286.0418 | 4.3 |  
| 257.0440 | 2.5 |  
| 229.0499 | 1.6 |  
| 228.0385 | 1.4 |  
| 151.0040 | 1.4 |  

---

| m/z     | % |  
|---------|---|---|
| 491.1924 | 100.0 |  
| 165.0556 | 32.1 |  
| 492.1962 | 24.9 |  
| 195.0656 | 21.0 |  
| 343.1390 | 20.6 |  
| 329.1393 | 19.7 |  
| 537.1955 | 6.2 |  
| 493.1980 | 6.0 |  
| 150.0326 | 6.0 |  
| 377.1621 | 5.9 |  
| 539.2110 | 5.8 |  

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33
## Compound 38 - Azelaic Acid

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]⁻ | m/z     | Error (ppm) | eV(MS⁻) |
|----------------|--------------|---------------------|---------|-------------|----------|
| 8.2            | 187.0969     | C₉H₁₅O₄             | 187.0976| -3.7        | 20       |

![Mass spectrum of Compound 38 - Azelaic Acid](image)

| m/z       | I %   |
|-----------|-------|
| 125.0964  | 100.0 |
| 187.0969  | 15.0  |
| 169.0860  | 10.8  |
| 126.1001  | 9.8   |
| 123.0810  | 9.1   |
| 143.1079  | 3.0   |
| 185.1179  | 2.5   |

## Compound 39 - Vitexin

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]⁻ | m/z     | Error (ppm) | eV(MS⁻) |
|----------------|--------------|---------------------|---------|-------------|----------|
| 8.3            | 431.0985     | C₂₁H₁₉O₁₀           | 431.0984| 0.2         | 40       |

![Mass spectrum of Compound 39 - Vitexin](image)

| m/z       | I %   |
|-----------|-------|
| 311.0563  | 100.0 |
| 283.0612  | 99.9  |
| 164.0112  | 31.7  |
| 341.0668  | 31.0  |
| 312.0601  | 21.4  |
| 323.0561  | 20.8  |
| 282.0527  | 18.8  |
| 284.0640  | 17.2  |
| 281.0459  | 16.5  |
| 165.0184  | 15.1  |
| 269.0454  | 15.0  |
**Compound 40 - Metilquercetin-455**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]⁻ | m/z | Error (ppm) | eV(MS⁻) |
|---------------|--------------|---------------------|-----|-------------|----------|
| 8.50          | 769.2211     | C₃₄H₄₁O₂₀         | 769.2197 | 1.8         | 50       |

**Compound 41 - Avicularin**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]⁻ | m/z | Error (ppm) | eV(MS⁻) |
|---------------|--------------|---------------------|-----|-------------|----------|
| 8.50          | 433.0774     | C₂₀H₁₇O₁₁          | 433.0776 | -0.5       | 40       |

---

**UHPLC**

- MS²(769.2211), 50.0 eV, 8.4 min #556
  - m/z 769.2211 I % 100.0
  - m/z 314.0433 I % 100.0
  - m/z 315.0488 I % 33.3
  - m/z 299.0198 I % 10.8
  - m/z 316.0522 I % 4.7
  - m/z 769.2211 I % 4.0
  - m/z 300.0254 I % 3.5
  - m/z 178.9982 I % 2.3
  - m/z 313.0352 I % 2.1
  - m/z 770.2237 I % 1.8
  - m/z 271.0247 I % 1.6
  - m/z 151.0034 I % 1.2

- MS²(433.0774), 40.0 eV, 8.5 min #566
  - m/z 300.0246 I % 100.0
  - m/z 271.0220 I % 45.2
  - m/z 301.0305 I % 36.0
  - m/z 255.0270 I % 19.3
  - m/z 272.0265 I % 7.7
  - m/z 151.0017 I % 7.1

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### Compound 42 - Kaempferol-308 II

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z   | Error (ppm) | eV (MS') |
|----------------|--------------|---------------------|-------|-------------|----------|
| 8.50           | 593.1537     | C<sub>27</sub>H<sub>20</sub>O<sub>15</sub> | 593.1512 | 4.2         | 45       |

### Compound 43 - Quercitrin

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z   | Error (ppm) | eV (MS') |
|----------------|--------------|---------------------|-------|-------------|----------|
| 9.10           | 447.0907     | C<sub>21</sub>H<sub>19</sub>O<sub>11</sub> | 447.0933 | -5.8       | 40       |

### Mass Spectrometry Data

#### Compound 42 - Kaempferol-308 II

- MS<sub>2</sub>(593.1537), 45.0 eV, 8.2 min #539

#### Compound 43 - Quercitrin

- MS<sub>2</sub>(447.0907), 25.0 eV, 9.1 min #610
Compound 44 - (epi)afzelechin-(epi)catechin(ii)

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]^- | m/z      | Error (ppm) | eV(MS^-) |
|----------------|--------------|----------------------|----------|-------------|----------|
| 9.20           | 561.1430     | C_{30}H_{25}O_{11}   | 561.1402 | 4.9         | 30       |

**UHPLC (Rt min)**

-MS2(561.1430), 30.0eV, 9.2min #606

| m/z         | I %   |
|-------------|-------|
| 289.0720    | 100.0 |
| 290.0755    | 16.8  |
| 271.0615    | 11.9  |
| 245.0823    | 10.1  |
| 137.0246    | 7.2   |
| 125.0243    | 6.3   |
| 164.0114    | 4.1   |
| 407.0769    | 4.0   |
| 273.0768    | 3.7   |
| 165.0184    | 2.5   |
| 291.0772    | 2.3   |
| 409.0923    | 2.2   |
| 179.0351    | 2.1   |

Compound 45 - Isorhamnetin-hexose

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]^- | m/z      | Error (ppm) | eV(MS^-) |
|----------------|--------------|----------------------|----------|-------------|----------|
| 9.9            | 477.1033     | C_{22}H_{21}O_{12}   | 477.1038 | -1.1        | 40       |

**UHPLC (Rt min)**

-MS2(477.1033), 40.0eV, 9.9min #651

| m/z         | I %   |
|-------------|-------|
| 314.0429    | 100.0 |
| 243.0294    | 34.9  |
| 271.0243    | 32.8  |
| 285.0401    | 29.9  |
| 315.0479    | 22.8  |
| 286.0473    | 20.0  |
| 257.0451    | 13.8  |
| 299.0190    | 13.1  |
| 271.0609    | 12.7  |
| 300.0260    | 5.6   |
| 272.0276    | 5.3   |
| 244.0324    | 4.6   |
**Compound 46 - Naringenin 7-O-glucoside**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]⁻ | m/z  | Error (ppm) | eV(MS⁻) |
|----------------|--------------|---------------------|------|-------------|---------|
| 10.05          | 433.1160     | C_{21}H_{21}O_{10}  | 433.1140 | 4.6         | 35      |

| m/z            | I %          |
|----------------|--------------|
| 271.0622       | 100.0        |
| 268.0391       | 66.7         |
| 151.0046       | 37.6         |
| 300.0283       | 25.8         |
| 269.0435       | 23.4         |
| 165.0203       | 18.8         |
| 431.1002       | 13.0         |
| 272.0661       | 11.5         |
| 119.0514       | 10.1         |
| 301.0331       | 9.6          |

**Compound 47 - Kaempferol-131**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]⁻ | m/z  | Error (ppm) | eV(MS⁻) |
|----------------|--------------|---------------------|------|-------------|---------|
| 10.3           | 415.1946     | C_{20}H_{31}O_{9}   | 415.1974 | -6.7       | 30      |

| m/z            | I %          |
|----------------|--------------|
| 284.0321       | 100.0        |
| 285.0399       | 41.7         |
| 137.0243       | 29.8         |
| 151.0410       | 22.9         |
| 125.0246       | 17.4         |
| 227.0346       | 15.3         |
| 255.0297       | 14.4         |
| 417.0823       | 13.4         |
| 113.0242       | 13.4         |
| 137.0965       | 11.7         |
| 119.0356       | 10.0         |
| 164.0108       | 9.6          |
Compound 48 - 3’, 4’, 7, 8-Tetrahydroxyflavone

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]^- | m/z | Error (ppm) | eV(MS^-) |
|----------------|--------------|----------------------|-----|-------------|-----------|
| 10.37          | 287.0561     | C_{13}H_{11}O_{6}    | 287.0561 | 0.0          | 20        |

![Mass spectrum of Compound 48](image)

| m/z     | I %   |
|---------|-------|
| 151.0039| 100.0 |
| 135.0454| 60.9  |
| 283.2640| 8.4   |
| 243.1018| 5.4   |
| 152.0075| 5.3   |
| 136.0492| 4.8   |
| 285.1328| 4.4   |
| 287.0561| 4.0   |

Compound 49 - Kaempferol-214

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]^- | m/z | Error (ppm) | eV(MS^-) |
|----------------|--------------|----------------------|-----|-------------|-----------|
| 10.5           | 499.0860     | C_{24}H_{19}O_{12}   | 499.0882 | -4.4        | 40        |

![Mass spectrum of Compound 49](image)

| m/z     | I %   |
|---------|-------|
| 285.0398| 100.0 |
| 284.0323| 71.7  |
| 286.0431| 15.1  |
| 255.0295| 4.2   |
| 257.0447| 2.5   |
| 431.0984| 2.4   |
| 287.0448| 2.1   |
| 229.0502| 2.1   |
| 256.0355| 2.0   |
| 227.0350| 1.6   |
| 307.0220| 1.5   |
**Compound 50 - Kaempferide-116**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]⁻ | m/z   | Error (ppm) | eV(MS⁻) |
|----------------|--------------|---------------------|-------|-------------|---------|
| 10.7           | 417.2126     | C₂₀H₃₃O₉            | 417.2119 | 1.7         | 40      |

**MS/MS**

| m/z     | I % (40eV) |
|---------|------------|
| 284.0317| 100.0      |
| 301.0367| 91.5       |
| 255.0284| 81.0       |
| 227.0355| 60.9       |
| 151.0396| 54.4       |
| 165.0541| 49.5       |
| 151.0038| 48.5       |
| 285.0393| 46.2       |
| 146.9612| 43.1       |
| 149.0238| 39.5       |
Compound 51 - Quercetin-313

| UHPLC (Rt min) | Measured $m/z$ | Ion Formula [M-H]$^{-}$ | $m/z$ | Error (ppm) | eV(MS$^{+}$) |
|----------------|----------------|--------------------------|-------|-------------|--------------|
| 10.80          | 475.0874       | C$_{22}$H$_{19}$O$_{12}$ | 475.0882 | -1.7        | 20           |

| $m/z$   | I % |
|---------|-----|
| 300.0276 | 100.0 |
| 285.0402 | 35.8  |
| 301.0327 | 24.8  |
| 431.0987 | 13.5  |
| 284.0323 | 12.0  |
| 475.0874 | 4.7   |
| 286.0434 | 4.6   |
| 302.0348 | 3.6   |
| 271.0295 | 3.0   |
| 432.1028 | 2.5   |
| 255.0295 | 1.8   |
| 178.9986 | 1.1   |
### Compound 52 - Trihydroxyflavone-dimethyl-161

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]^- | m/z     | Error (ppm) | eV(MS^-) |
|----------------|--------------|----------------------|---------|-------------|-----------|
| 11.7           | 461.1450     | C_{23}H_{25}O_{10}   | 461.1453| -0.7        | 20        |

**MS2**

- **MS2(461.1450), 20.0 eV, 11.8 min #778**
  - m/z: 299.0922
  - Intens. x10^4: 2.0
  - m/z: 461.1450
  - Intens. x10^4: 1.5

- **MS2(461.1450), 40.0 eV, 11.8 min #779**
  - m/z: 269.0455
  - Intens. x10^4: 0.8

| m/z     | I % (40 eV) |
|---------|-------------|
| 269.0455| 100.0       |
| 284.0685| 75.0        |
| 241.0506| 64.9        |
| 283.0610| 49.5        |
| 225.0552| 25.7        |
| 240.0419| 22.3        |
| 268.0373| 18.1        |
| 300.0272| 17.8        |
| 270.0491| 16.7        |
| 197.0603| 15.9        |
| 242.0534| 13.4        |
| 191.0349| 9.7         |
**Compound 53 - 7,4'-Dimethoxy-5-hydroxyflavone-203**

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z | Error (ppm) | eV(MS') |
|----------------|--------------|---------------------|-----|-------------|----------|
| 11.7           | 503.1557     | C_{25}H_{27}O_{11}  | 503.1547 | 1.9         | 35       |

| m/z | I %      |
|-----|----------|
| 284.0690 | 100.0    |
| 283.0617 | 34.5     |
| 269.0459 | 34.2     |
| 299.0925 | 27.2     |
| 241.0506 | 19.6     |
| 285.0724 | 16.2     |
| 225.0559 | 14.9     |
| 240.0792 | 6.4      |
| 285.0408 | 4.7      |
| 270.0492 | 4.7      |
| 240.0431 | 4.3      |
**Supplementary Material**

### Compound 54 - Naringenin Falcone

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z | Error (ppm) | eV(MS-^-) |
|----------------|--------------|---------------------|-----|-------------|------------|
| 12.1           | 271.0614     | C_{13}H_{11}O_{5}   | 271.0612 | 0.7         | 30         |

### Compound 55 - Bauhiniastatin2

| UHPLC (Rt min) | Measured m/z | Ion Formula [M-H]- | m/z | Error (ppm) | eV(MS^-^-) |
|----------------|--------------|---------------------|-----|-------------|------------|
| 14.60          | 299.1417     | C_{17}H_{15}O_{5}   | 299.1401 | 5.3         | 30         |

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**m/z** | I %
---|---
119.0502 | 100.0
151.0035 | 60.5
107.0132 | 16.0
187.0396 | 8.7
120.0538 | 7.9
177.0189 | 6.7
185.0604 | 5.5
152.0068 | 3.9
161.0602 | 3.8
165.0194 | 3.2
271.0614 | 3.1
145.0297 | 2.6

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**m/z** | I %
---|---
225.0556 | 100.0
197.0605 | 83.1
241.0505 | 75.3
210.0320 | 36.1
196.0525 | 27.2
269.0453 | 25.6
209.0605 | 19.7
226.0587 | 15.0
181.0657 | 12.0
195.0446 | 11.7
242.0536 | 11.0
198.0640 | 10.5
167.0499 | 9.2
224.0476 | 8.5