# Identification and Characterization of Two New Derivatives of Chlorogenic Acids in Arnica (*Arnica montana* L.) Flowers by High-Performance Liquid Chromatography/Tandem Mass Spectrometry

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**Figure S1**. $MS^4$ spectra of 1,3,5-tricaffeoylquinic acid (**13**) (pseudomolecular ion at *m/z* 677 in negative ion mode) and targeted $MS^3$ spectra of *m/z* 677+353.

**Figure S2**. $MS^3$ spectra of 1-caffeoyl-5-feruloylquinic acid (**15**) (pseudomolecular ion at *m/z* 529 in negative ion mode).

**Figure S3**. $MS^4$ spectra of 1,5-dicaffeoyl-3-methoxyoxaloylquinic acid (**16**) (pseudomolecular ion at *m/z* 601 in negative ion mode).

**Figure S4**. $MS^4$ spectra of 4,5-dicaffeoyl-1-methoxyoxaloylquinic acid (**19**) (pseudomolecular ion at *m/z* 601 in negative ion mode).

**Figure S5**. $MS^4$ spectra of 1,3-dicaffeoyl-4-methoxyoxaloylquinic acid (**17**) (pseudomolecular ion at *m/z* 601 in negative ion mode).

**Figure S6**. $MS^4$ spectra of 3,5-dicaffeoyl-4-methoxyoxaloylquinic acid (**18**) (pseudomolecular ion at *m/z* 601 in negative ion mode).

**Figure S7**. $MS^4$ spectra of 3-caffeoyl-4-feruloyl-5-methoxyoxaloylquinic acid (**20**) (pseudomolecular ion at *m/z* 615 in negative ion mode).

**Figure S8**. $MS^4$ spectra of 3-feruloyl-4-methoxyoxaloyl-5-caffeoylquinic acid (**21**) (pseudomolecular ion at *m/z* 615 in negative ion mode).

**Figure S9**. $MS^4$ spectra of 1,5-dicaffeoyl-4-fumaroylquinic acid (**22**) (pseudomolecular ion at *m/z* 613 in negative ion mode).

**Figure S10**. $MS^4$ spectra of 1,5-dicaffeoyl-3-fumaroylquinic acid (**23**) (pseudomolecular ion at *m/z* 613 in negative ion mode).

**Figure S11**. $MS^4$ spectra of 3,5-dicaffeoyl-1,4-dimethoxyoxaloylquinic acid (**24**) (pseudomolecular ion at *m/z* 687 in negative ion mode).

**Figure S12**. $MS^5$ spectra of 1-methoxyoxaloyl-3,4,5-tricaffeoylquinic acid (**25**) (pseudomolecular ion at *m/z* 763 in negative ion mode).

**Figure S13**. $MS^5$ spectra of 1,3,4-tricaffeoyl-5-methoxyoxaloylquinic acid (**26**) (pseudomolecular ion at *m/z* 763 in negative ion mode).

**Table S1**. High Resolution Mass (MS-TOF) Data of Chlorogenic Acids and their Pseudomolecular Ions (M-H).

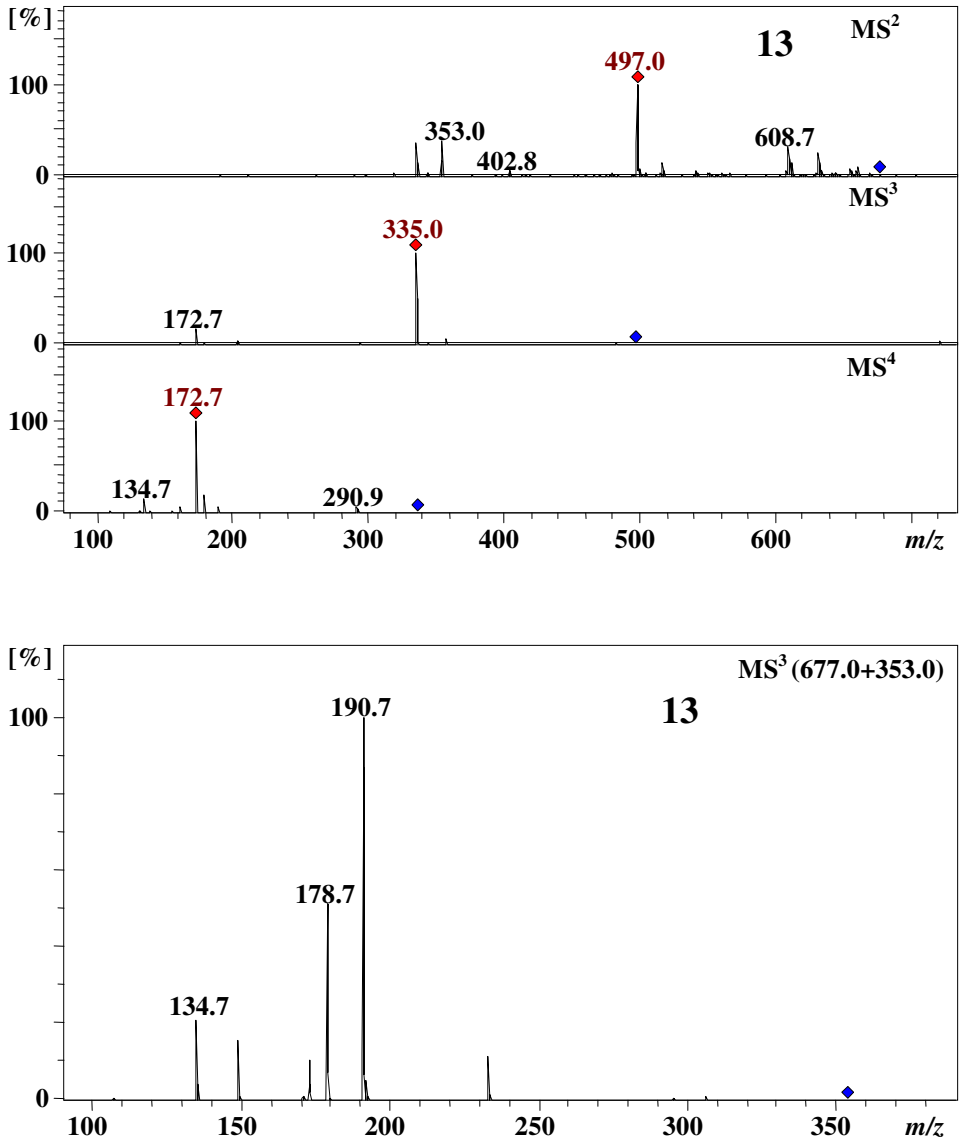


**Figure S1**. $MS^4$ spectra of 1,3,5-tricaffeoylquinic acid (**13**) (pseudomolecular ion at *m/z* 677 in negative ion mode) and targeted $MS^3$ spectra of *m/z* 677+353.

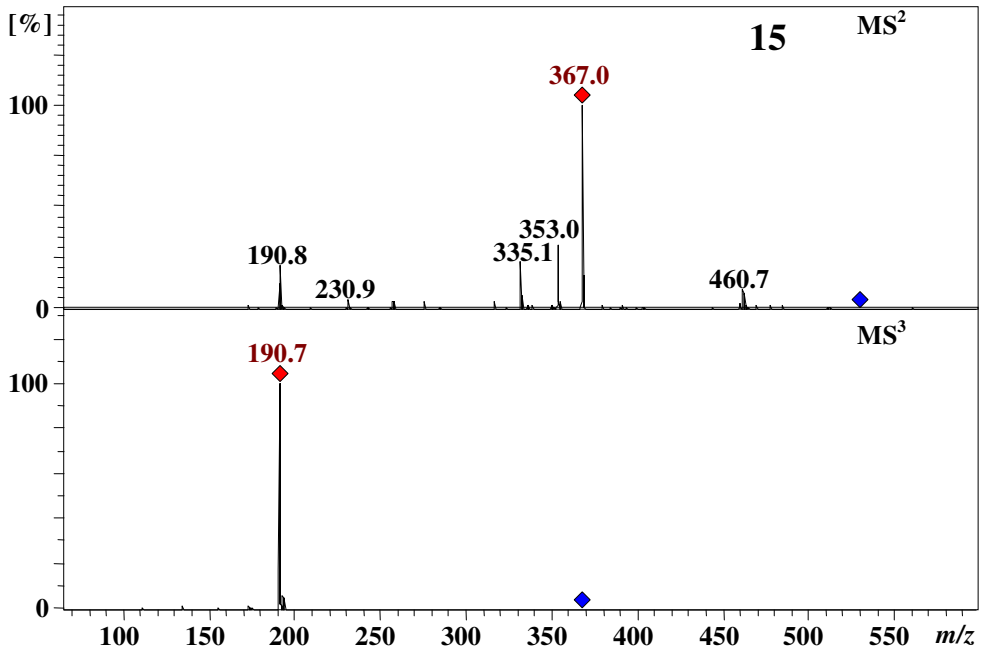


**Figure S2**. $MS^3$ spectra of 1-caffeoyl-5-feruloylquinic acid (**15**) (pseudomolecular ion at *m/z* 529 in negative ion mode).

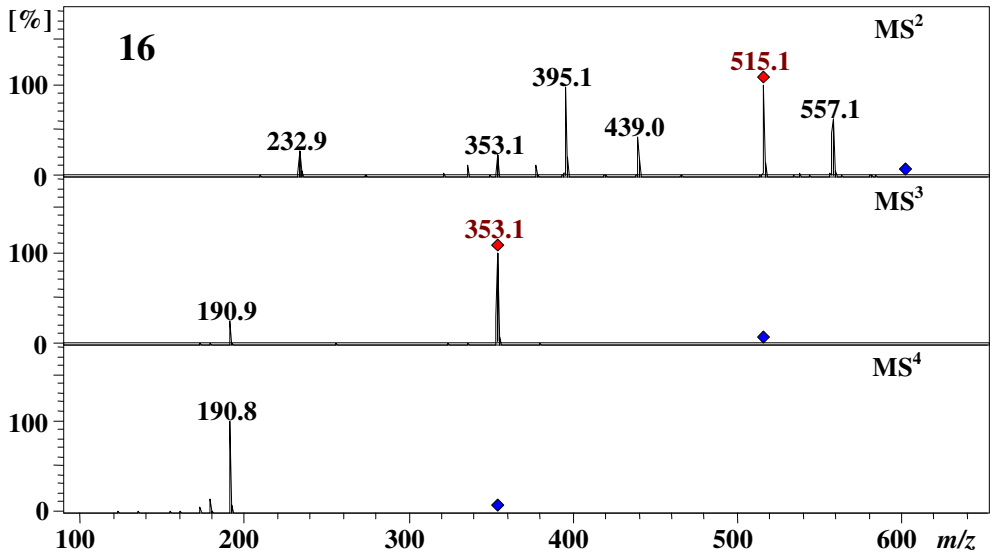


**Figure S3**. $MS^4$ spectra of 1,5-dicaffeoyl-3-methoxyoxaloylquinic acid (**16**) (pseudomolecular ion at *m/z* 601 in negative ion mode).

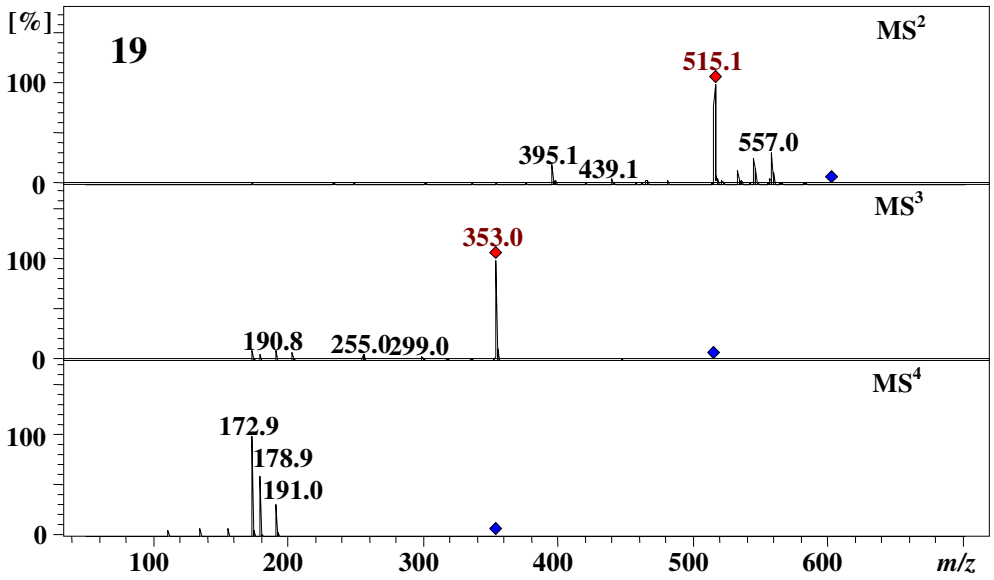


**Figure S4**. $MS^4$ spectra of 1-methoxyoxaloyl-4,5-dicaffeoylquinic acid (**19**) (pseudomolecular ion at *m/z* 601 in negative ion mode).

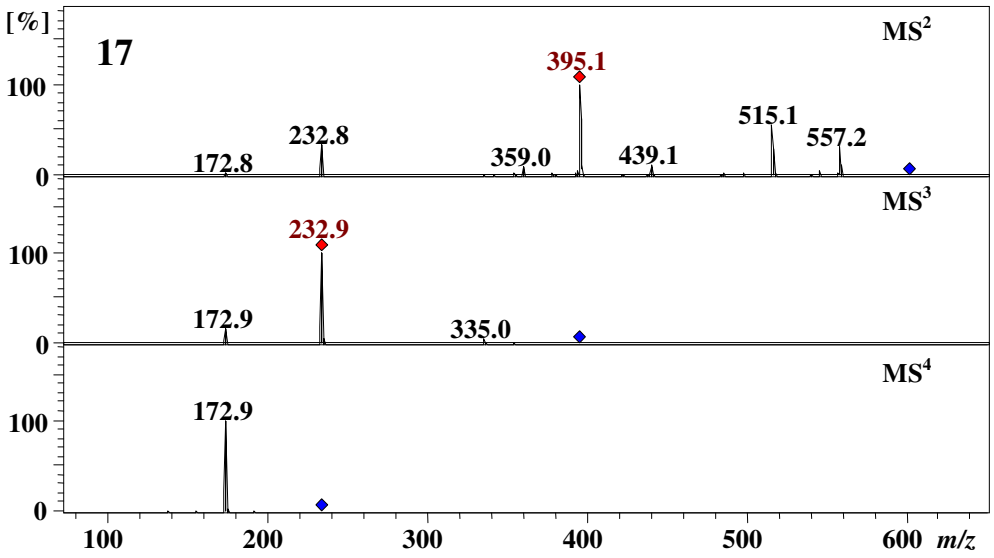


**Figure S5**. $MS^4$ spectra of 1,3-dicaffeoyl-4-methoxyoxaloylquinic acid (**17**) (pseudomolecular ion at *m/z* 601 in negative ion mode).

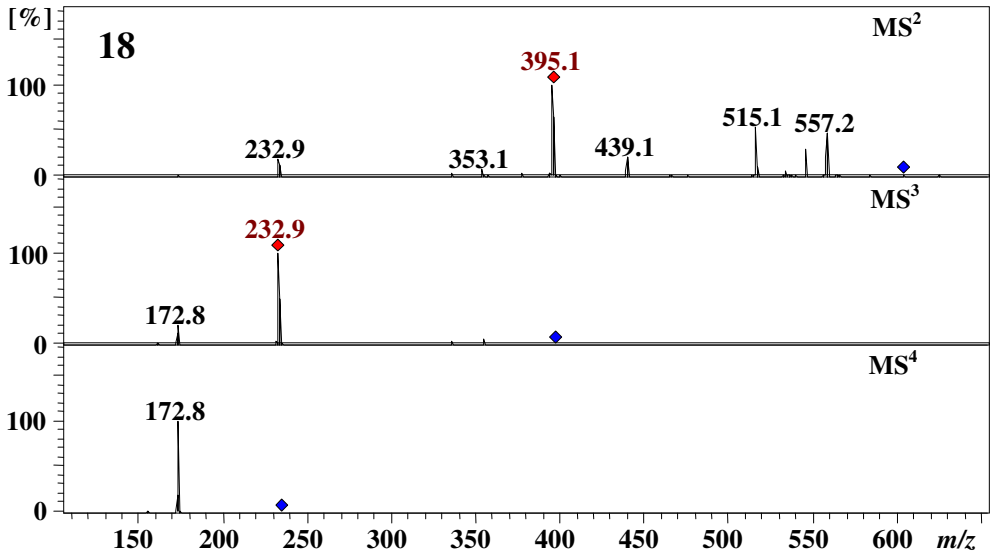


**Figure S6**. $MS^4$ spectra of 3,5-dicaffeoyl-4-methoxyoxaloylquinic acid (**18**) (pseudomolecular ion at *m/z* 601 in negative ion mode).

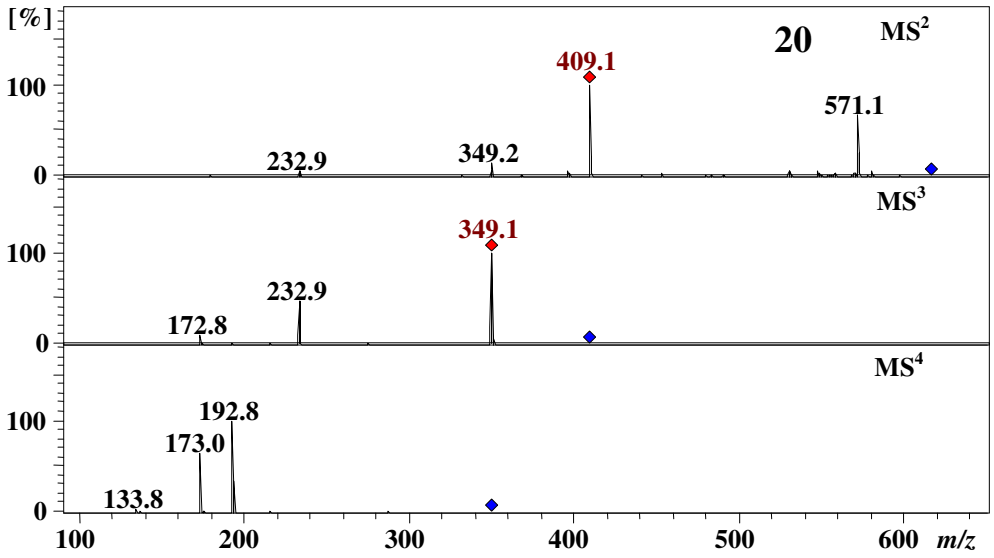


**Figure S7**. $MS^4$ spectra of 3-caffeoyl-4-feruloyl-5-methoxyoxaloylquinic acid (**20**) (pseudomolecular ion at *m/z* 615 in negative ion mode).

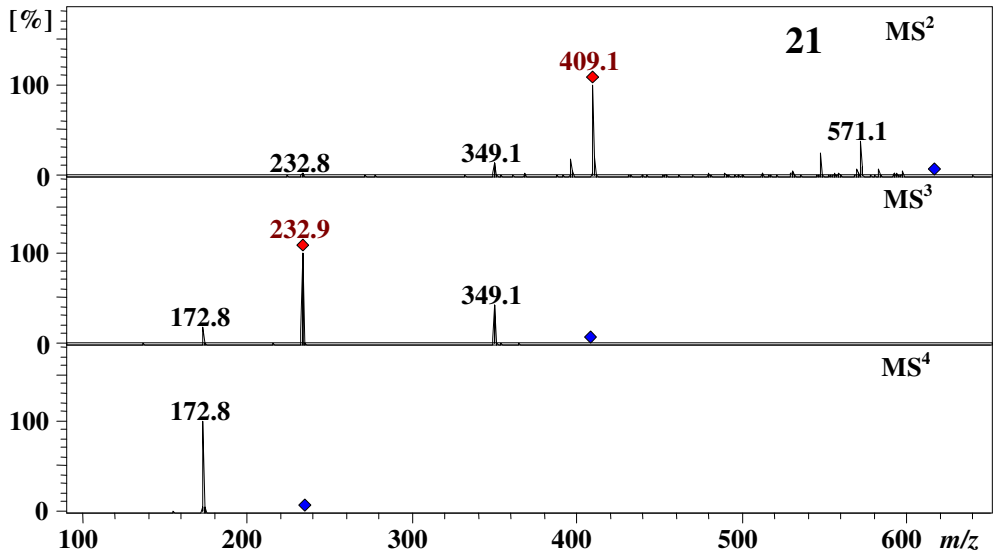


**Figure S8**. $MS^4$ spectra of 3-feruloyl-4-methoxyoxaloyl-5-caffeoylquinic acid (**21**) (pseudomolecular ion at *m/z* 615 in negative ion mode).

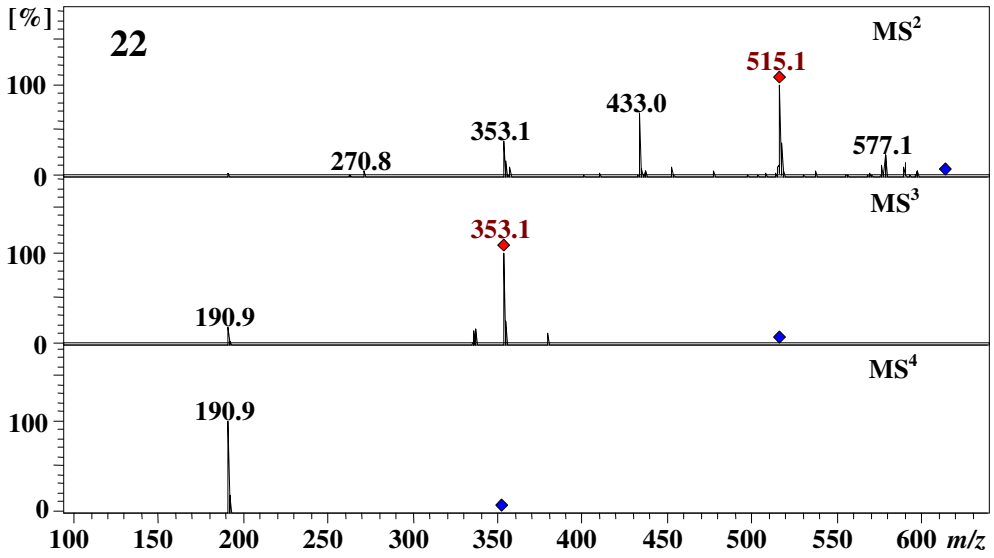


**Figure S9**. $MS^4$ spectra of 1,5-dicaffeoyl-4-fumaroylquinic acid (**22**) (pseudomolecular ion at *m/z* 613 in negative ion mode).

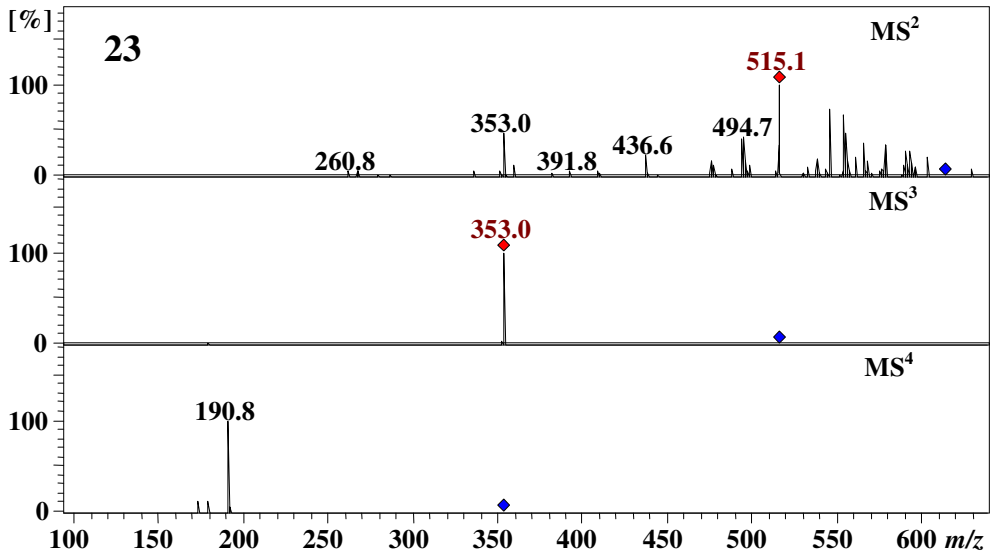


**Figure S10**. $MS^4$ spectra of 1,5-dicaffeoyl-3-fumaroylquinic acid (**23**) (pseudomolecular ion at *m/z* 613 in negative ion mode).

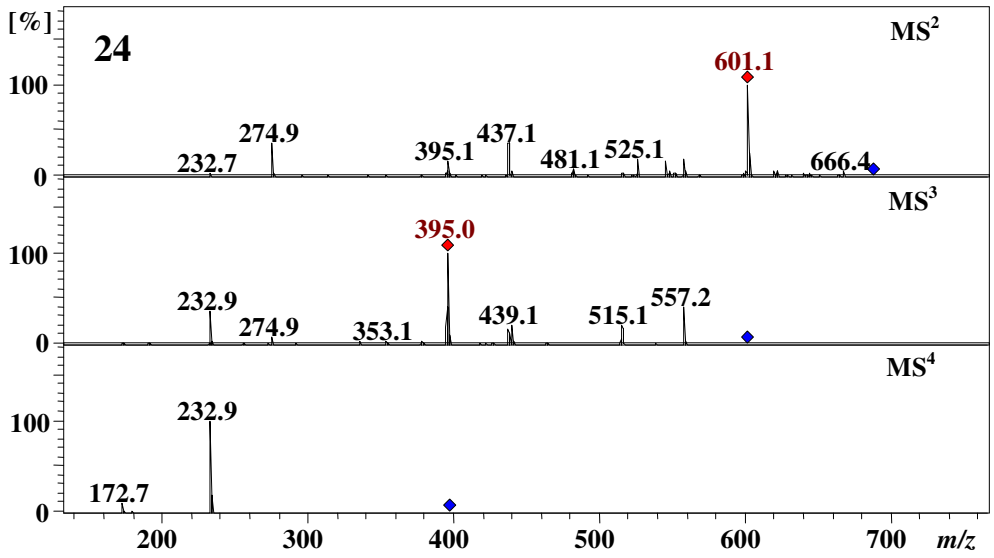


**Figure S11**. $MS^4$ spectra of 3,5-dicaffeoyl-1,4-dimethoxyoxaloylquinic acid (**24**) (pseudomolecular ion at *m/z* 687 in negative ion mode).

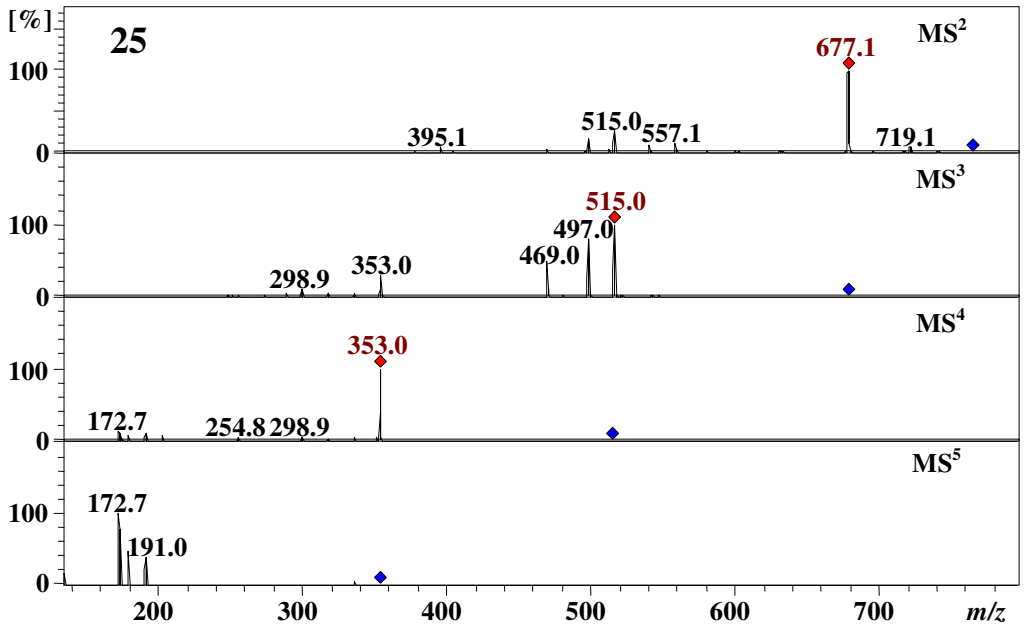


**Figure S12**. $MS^5$ spectra of 1-methoxyoxaloyl-3,4,5-tricaffeoylquinic acid (**25**) (pseudomolecular ion at *m/z* 763 in negative ion mode).

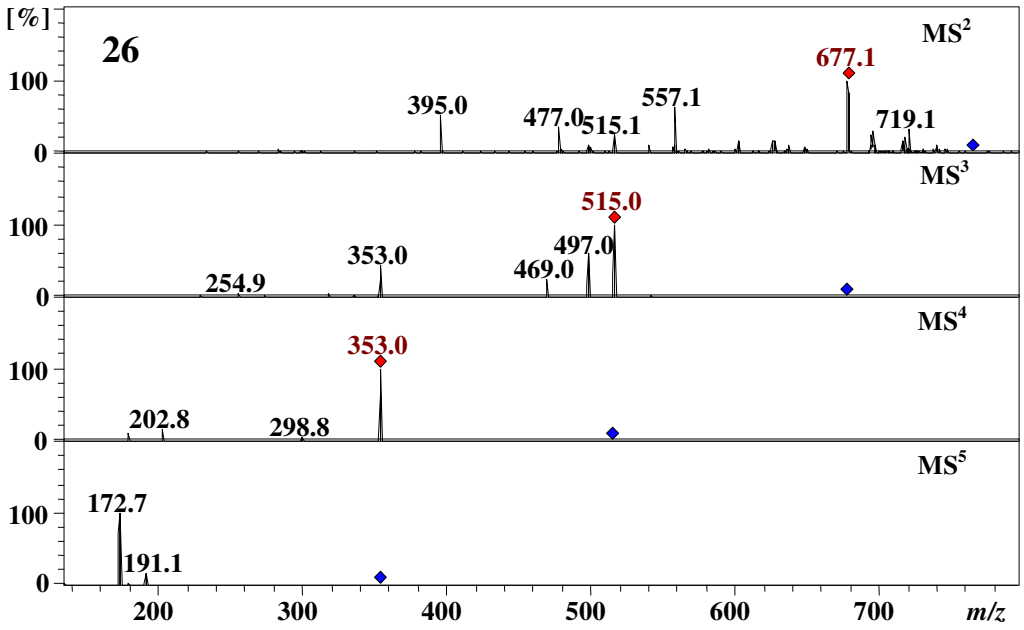


**Figure S13**. $MS^5$ spectra of 1,3,4-tricaffeoyl-5-methoxyoxaloylquinic acid (**26**) (pseudomolecular ion at *m/z* 763 in negative ion mode).

**Table S1**. High Resolution Mass (MS-TOF) Data of Chlorogenic Acids and their Pseudomolecular Ions ($M-H^+$)

| No. | Name | Abbreviation | Mol. formula | Theor. *m/z* (M-H) | Exp. *m/z* ($M-H^+$) | Error (ppm) |
|---|---|---|---|---|---|---|
| **1** | 1-*O*-caffeoylquinic acid | 1-CQA | $C_{16}H_{18}O_9$ | 353.0878 | 353.0868 | 2.8 |
| **2** | 3-*O*-caffeoylquinic acid | 3-CQA | $C_{16}H_{18}O_9$ | 353.0878 | 353.0886 | -2.3 |
| **3** | 5-*O*-caffeoylquinic acid | 5-CQA | $C_{16}H_{18}O_9$ | 353.0878 | 353.0875 | 1.0 |
| **4** | 4-*O*-caffeoylquinic acid | 4-CQA | $C_{16}H_{18}O_9$ | 353.0878 | 353.0873 | 1.3 |
| **5** | *Cis*-5-*O*-feruloylquinic acid [a] | *Cis*-5-CQA | $C_{16}H_{18}O_9$ | 353.0878 | 353.0877 | 0.2 |
| **6** | 1,5-di-*O*-caffeoylquinic acid | 1,5-diCQA | $C_{25}H_{24}O_{12}$ | 515.1195 | 515.1183 | 2.4 |
| **7** | 3,5-di-*O*-caffeoylquinic acid | 3,5-diCQA | $C_{25}H_{24}O_{12}$ | 515.1195 | 515.1216 | -4.2 |
| **8** | A *cis*-3,5-di-*O*-caffeoylquinic acid [a] | A *cis*-3,5-diCQA | $C_{25}H_{24}O_{12}$ | 515.1195 | 515.1182 | 2.5 |
| **9** | A *cis*-3,5-di-*O*-caffeoylquinic acid [a] | A *cis*-3,5-diCQA | $C_{25}H_{24}O_{12}$ | 515.1195 | 515.1216 | -4.2 |
| **10** | 3,4-di-*O*-caffeoylquinic acid | 3,4-diCQA | $C_{25}H_{24}O_{12}$ | 515.1195 | 515.1204 | -1.8 |
| **11** | 4,5-di-*O*-caffeoylquinic acid | 4,5-diCQA | $C_{25}H_{24}O_{12}$ | 515.1195 | 515.1210 | -2.9 |
| **12** | 3,4,5-tri-*O*-caffeoylquinic acid | 3,4,5-triCQA | $C_{34}H_{30}O_{15}$ | 677.1512 | 677.1502 | 1.4 |
| **13** | 1,3,5-tri-*O*-caffeoylquinic acid [a] | 1,3,5-triCQA | $C_{34}H_{30}O_{15}$ | 677.1512 | 677.1506 | 0.9 |
| **14** | 5-*O*-feruloylquinic acid | 5-FQA | $C_{17}H_{20}O_9$ | 367.0929 | 367.1040 | -1.6 |
| **15** | 1-*O*-caffeoyl-5-*O*-feruloylquinic acid [a] | 1-C-5-FQA | $C_{26}H_{26}O_{12}$ | 529.1351 | 529.1356 | -0.9 |
| **16** | 1,5-di-*O*-caffeoyl-3-*O*-methoxyoxaloylquinic acid | 1,5-diC-3-MOQA | $C_{28}H_{26}O_{15}$ | 601.1199 | 601.1205 | -1.1 |
| **17** | 1,3-di-*O*-caffeoyl-4-*O*-methoxyoxaloylquinic acid [a, b] | 1,3-diC-4-MOQA | $C_{28}H_{26}O_{15}$ | 601.1199 | 601.1189 | 1.6 |
| **18** | 3,5-di-*O*-caffeoyl-4-*O*-methoxyoxaloylquinic acid [a, b] | 3,5-diC-4-MOQA | $C_{28}H_{26}O_{15}$ | 601.1199 | 601.1206 | -1.2 |
| **19** | 1-*O*-methoxyoxaloyl-4,5-di-*O*-caffeoylquinic acid | 1-MO-4,5-diCQA | $C_{28}H_{26}O_{15}$ | 601.1199 | 601.1206 | -1.2 |
| **20** | 3-*O*-caffeoyl-4-*O*-feruloyl-5-*O*-methoxyoxaloylquinic acid [a, b] | 3-C-4-F-5-MOQA | $C_{29}H_{28}O_{15}$ | 615.1355 | 615.1373 | -2.8 |
| **21** | 3-*O*-feruloyl-4-*O*-methoxyoxaloyl-5-*O*-caffeoylquinic acid [a, b] | 3-F-4-MO-5-CQA | $C_{29}H_{28}O_{15}$ | 615.1355 | 615.1363 | -1.2 |
| **22** | 1,5-di-*O*-caffeoyl-4-*O*-fumaroylquinic acid [a, b] | 1,5-diC-4-FuQA | $C_{29}H_{26}O_{15}$ | 613.1199 | 613.1198 | 0.2 |
| **23** | 1,5-di-*O*-caffeoyl-3-*O*-fumaroylquinic acid [a, b] | 1,5-diC-3-FuQA | $C_{29}H_{26}O_{15}$ | 613.1199 | 613.1169 | 4.8 |
| **24** | 3,5-di-*O*-caffeoyl-1-4-di-*O*-methoxyoxaloylquinic acid [a, b] | 3,5-diC-1,4-diMOQA | $C_{31}H_{28}O_{18}$ | 687.1203 | 687.1207 | -0.6 |
| **25** | 1-*O*-methoxyoxaloyl-3,4,5-tri-*O*-caffeoylquinic acid [a, b] | 1-MO-3,4,5-triCQA | $C_{37}H_{32}O_{18}$ | 763.1516 | 763.1544 | -3.7 |
| **26** | 1,3,4 -tri-*O*-caffeoyl-5-*O*-methoxyoxaloylquinic acid [a, b] | 1,3,5-triC-4-MOQA | $C_{37}H_{32}O_{18}$ | 763.1516 | 763.1521 | -0.6 |