# Supplementary Material

**Table S1.** Recovery results of the developed liquid chromatography–mass spectrometry (LC–MS) method.

| Analytes | Number | Original Amount (mg) | Spiked Amount (mg) | Found Amount (mg) | Recovery (%) | Average Recovery (%) | RSD (%) |
|---|---|---|---|---|---|---|---|
| **Aesculin** | 1 | 0.101 | 0.0807 | 0.183 | 102 | 102 | 1.34 |
| | 2 | 0.0904 | 0.0807 | 0.171 | 99.9 | | |
| | 3 | 0.0886 | 0.0807 | 0.170 | 101 | | |
| | 4 | 0.0891 | 0.0807 | 0.173 | 104 | | |
| | 5 | 0.0912 | 0.0807 | 0.173 | 101 | | |
| | 6 | 0.0907 | 0.0807 | 0.173 | 102 | | |
| **Aesculetin** | 1 | 0.186 | 0.151 | 0.342 | 103 | 101 | 2.47 |
| | 2 | 0.166 | 0.151 | 0.318 | 101 | | |
| | 3 | 0.163 | 0.151 | 0.317 | 102 | | |
| | 4 | 0.163 | 0.151 | 0.316 | 101 | | |
| | 5 | 0.167 | 0.151 | 0.312 | 96.0 | | |
| | 6 | 0.166 | 0.151 | 0.319 | 101 | | |

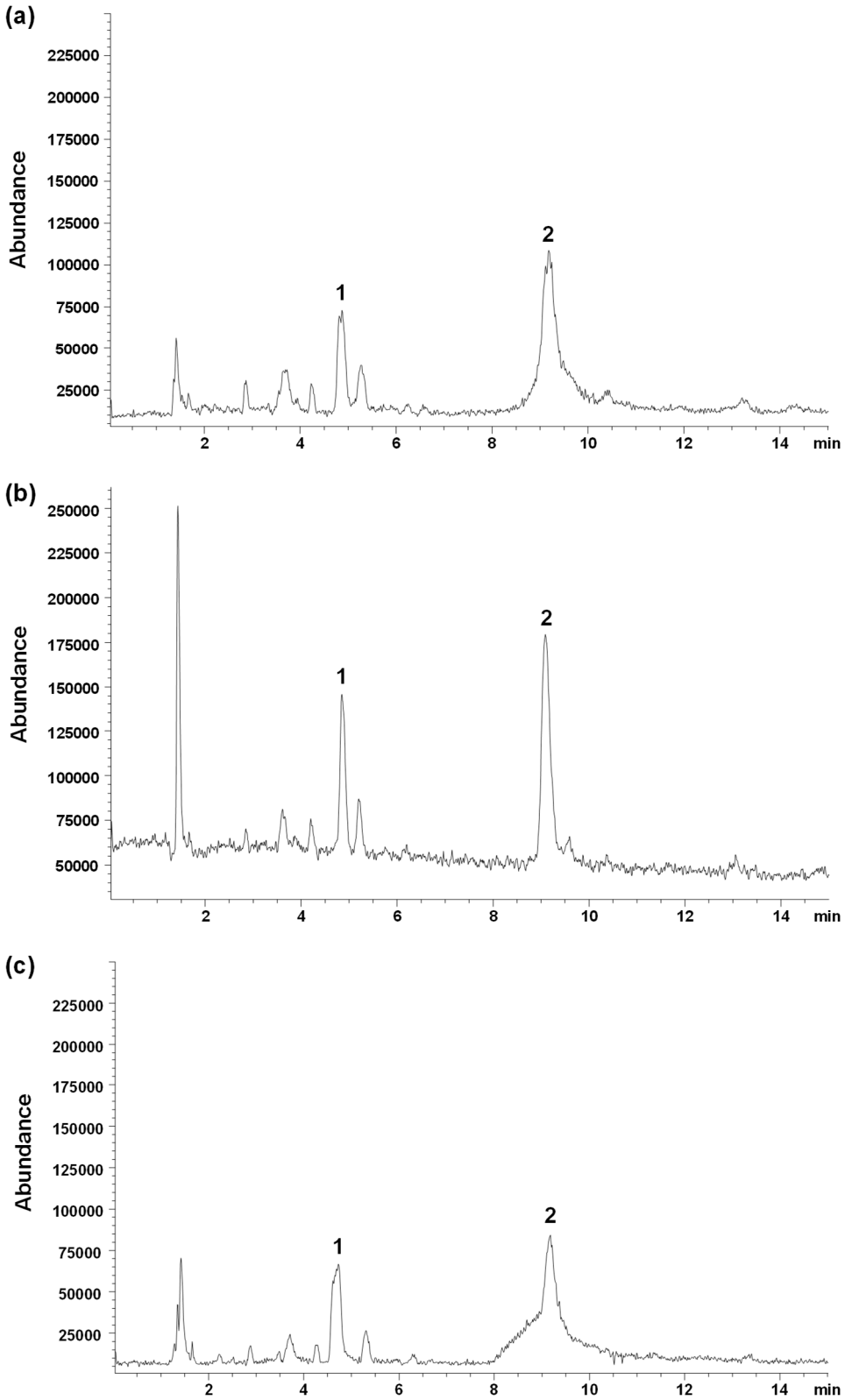


**Figure S1.** MS chromatograms of the mobile phase in water–acetonitrile (94:6, *v*/*v*) (**a**), 0.1% formic acid aqueous solution–acetonitrile (94:6, *v*/*v*) (**b**), and 1 mmol/L ammonium acetate–acetonitrile (94:6, *v*/*v*) (**c**) with identified peaks of aesculin (1) and aesculetin (2). LC separation conditions: Agilent InfinityLab Poroshell 120 EC-$C_{18}$ column (4.6 mm × 50 mm, 2.7 μm); column temperature, 40 °C; injection volume, 5 μL. MS detection mode: scan; scan range: 100–1000 *m*/*z*.

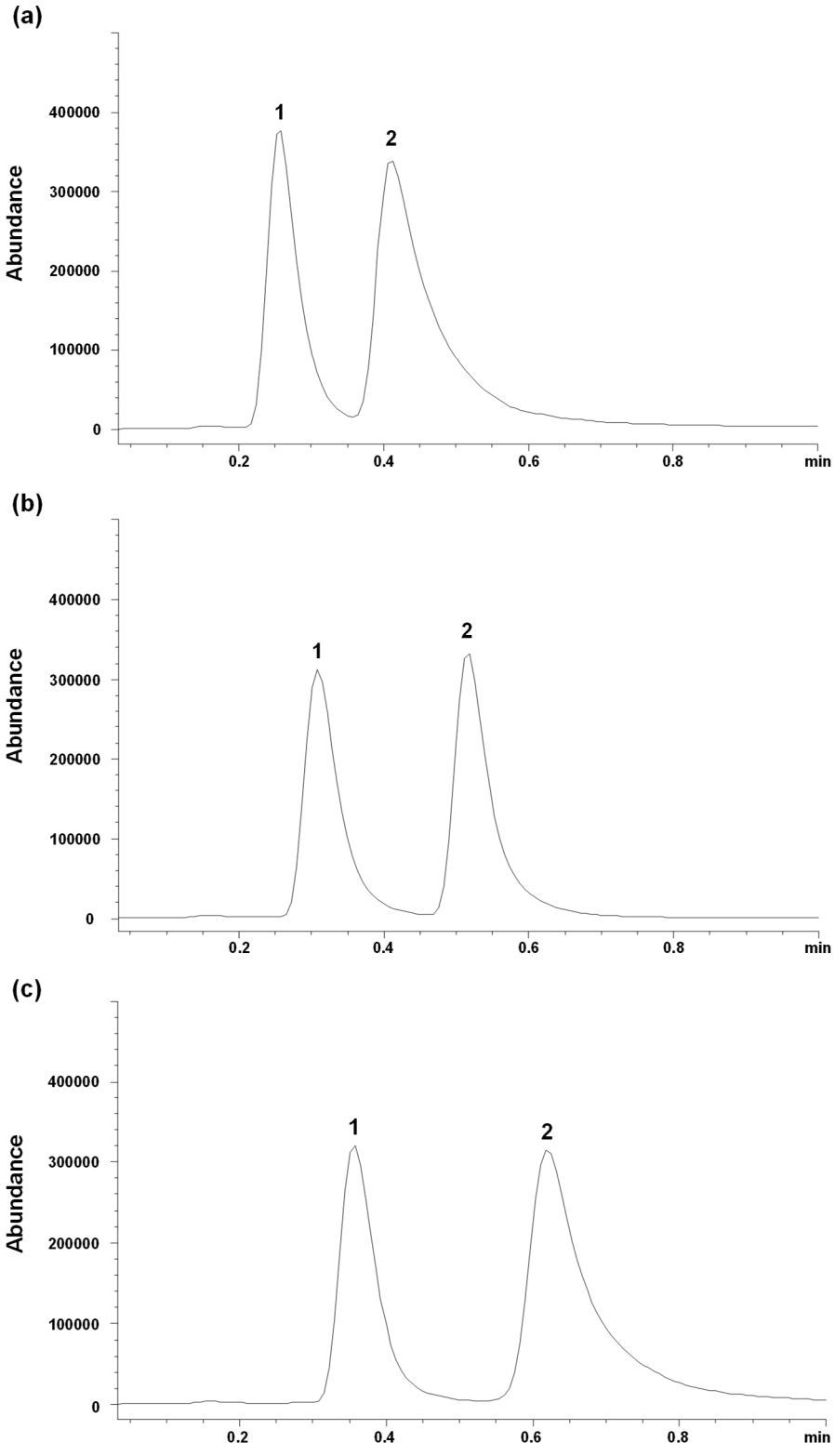


**Figure S2.** MS chromatograms of the mobile phase in 0.1% formic acid aqueous solution–acetonitrile (88:12, *v*/*v*) (**a**); 0.1% formic acid aqueous solution–acetonitrile (89:11, *v*/*v*) (**b**); 0.1% formic acid aqueous solution–acetonitrile (90:10, *v*/*v*) (**c**) with identified peaks of aesculin (1) and aesculetin (2). LC separation conditions: Agilent InfinityLab Poroshell 120 EC-$C_{18}$ (2.1 mm × 30 mm, 2.7 μm); column temperature, 40 °C;

injection volume, 1 μL. MS detection mode: selected ion monitor; monitoring ions: *m*/*z* 339 (aesculin) and *m*/*z* 355 (aesculetin).

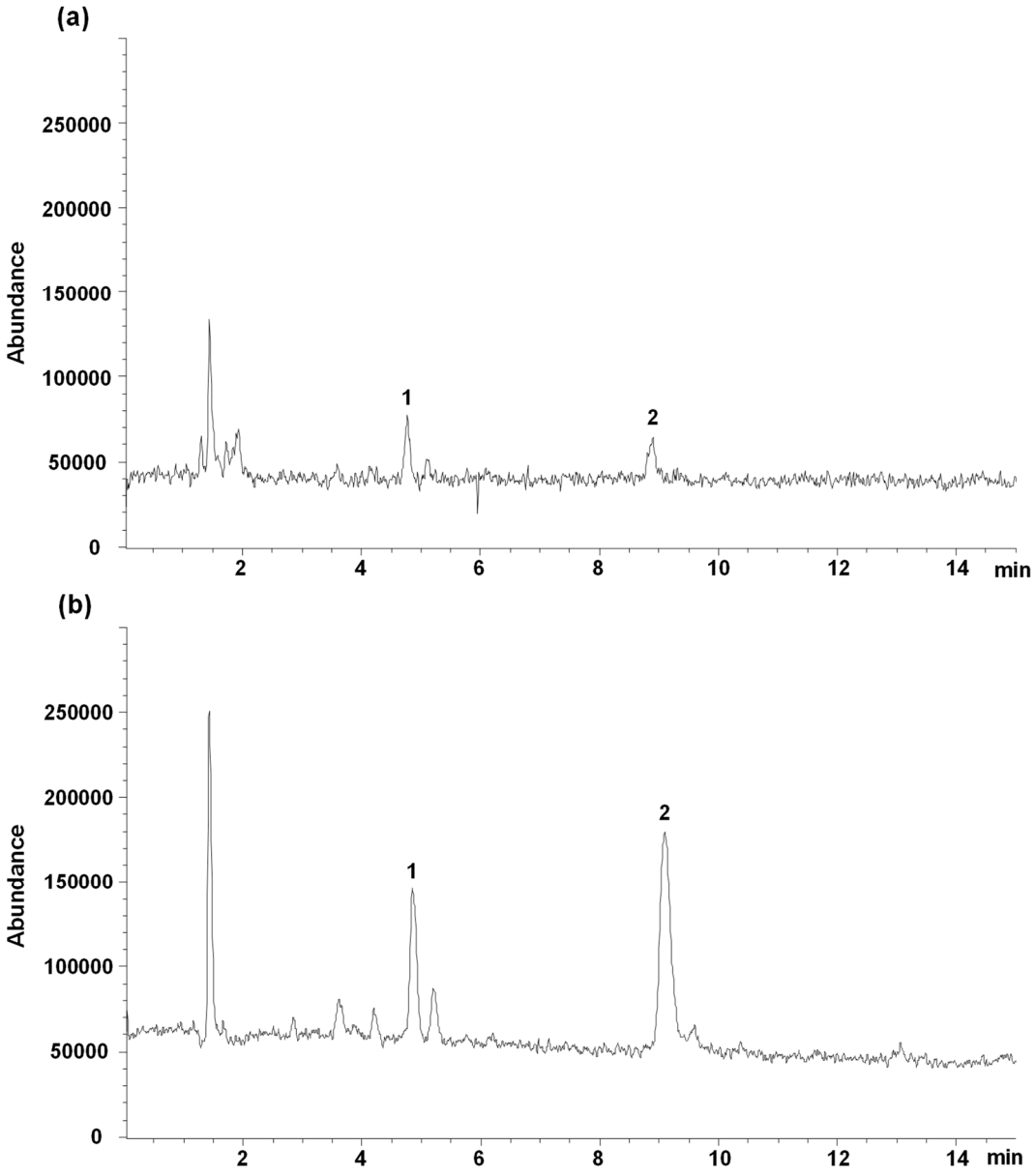


**Figure S3.** MS chromatograms of the sample extraction solution detected in the positive ion mode (**a**) and negative ion mode (**b**) with identified peaks of aesculin (1) and aesculetin (2). LC separation conditions: Agilent InfinityLab Poroshell 120 EC-$C_{18}$ column (4.6 mm × 50 mm, 2.7 μm); mobile phase, 0.1% formic acid aqueous solution–acetonitrile (94:6, *v*/*v*); column temperature, 40 °C; injection volume, 5 μL. MS detection mode: scan; scan range: 100–1000 *m*/*z*.

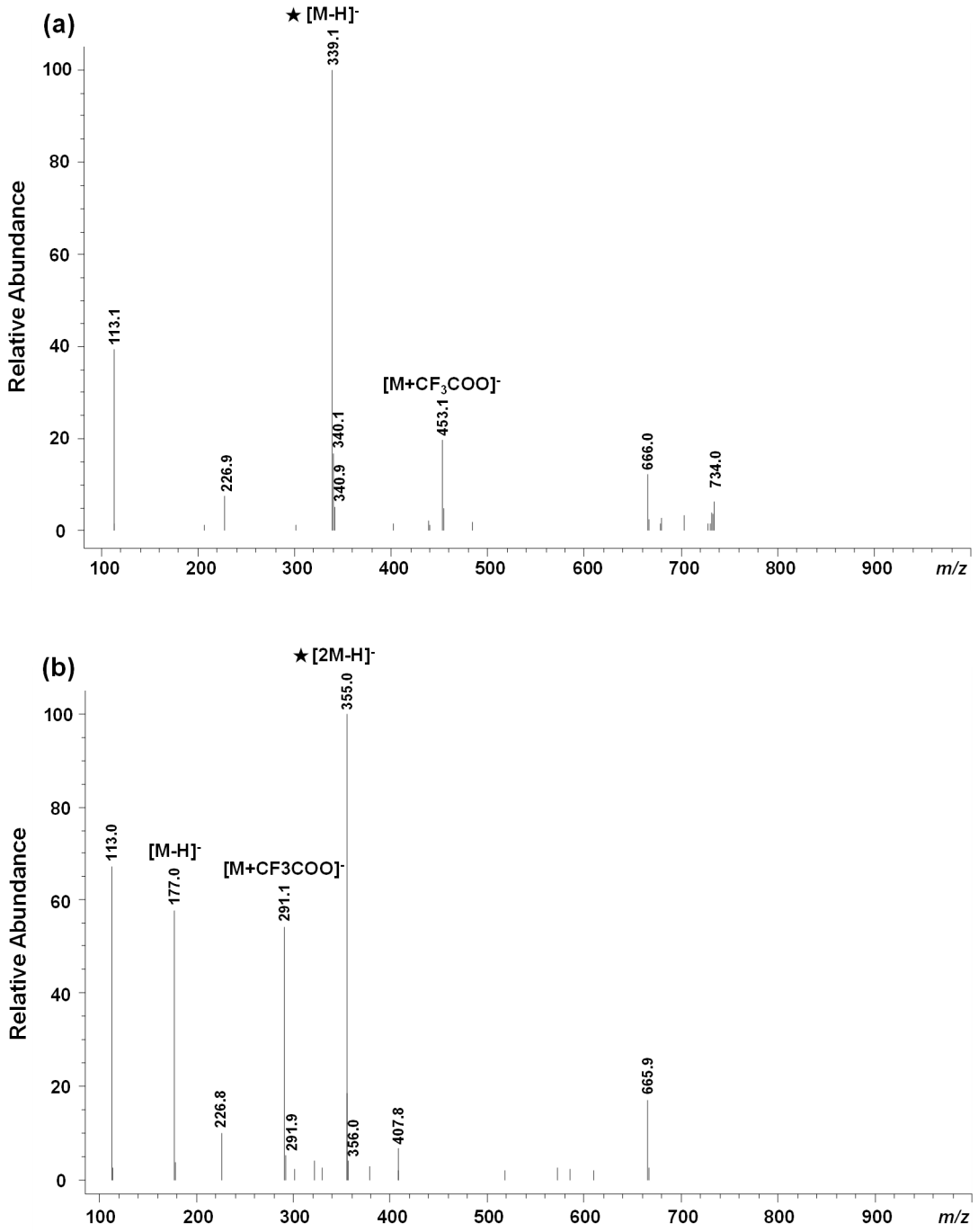


**Figure S4.** MS spectra of aesculin (**a**) and aesculetin (**b**) with selected *m*/*z* for the target component (★). LC separation conditions: Agilent InfinityLab Poroshell 120 EC-$C_{18}$ column (4.6 mm × 50 mm, 2.7 μm); mobile phase, 0.1% formic acid aqueous solution–acetonitrile (94:6, *v*/*v*); column temperature, 40 °C; injection volume, 5 μL. MS detection mode: scan; scan range: 100–1000 *m*/*z*.

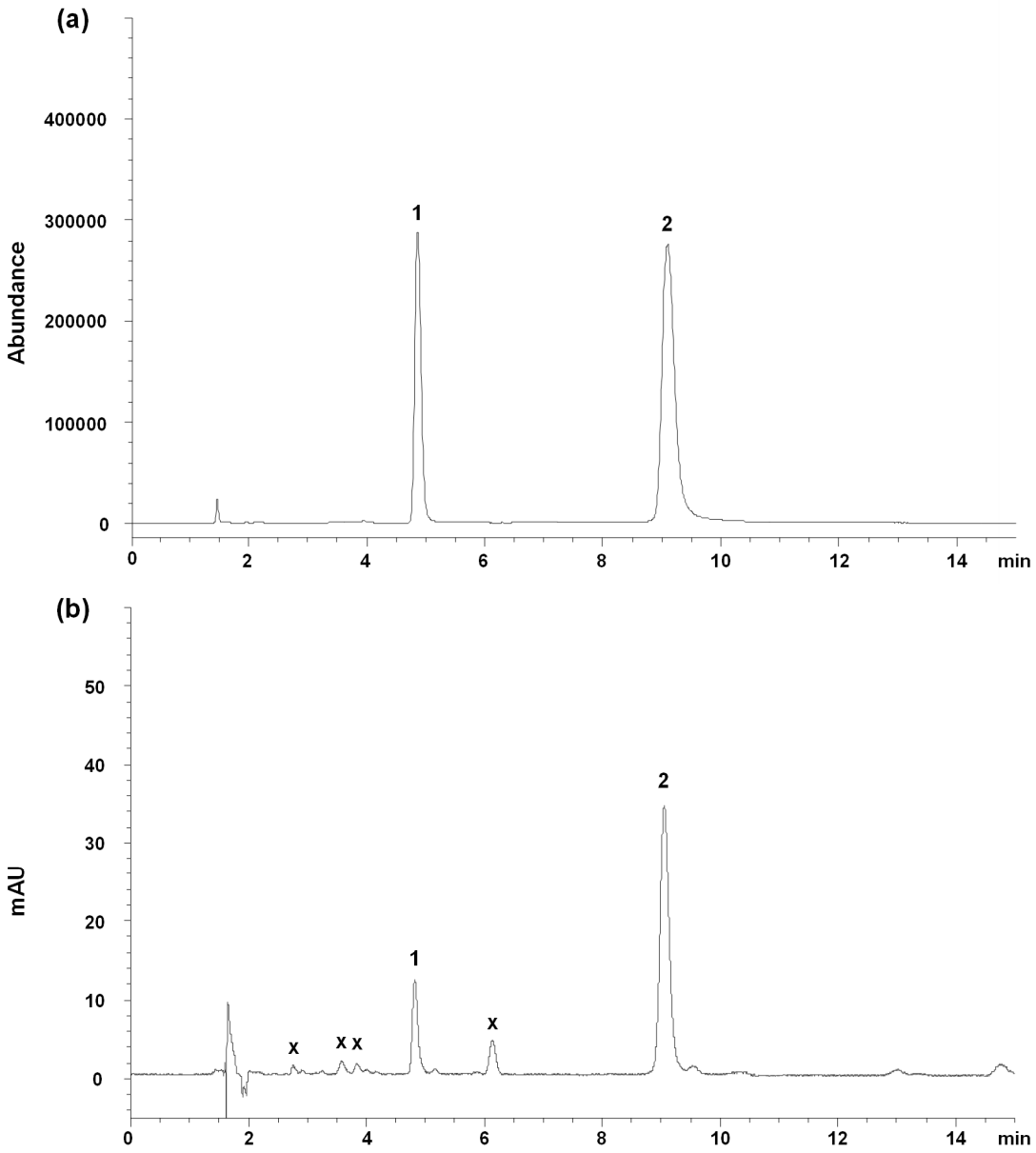


**Figure S5.** LC–MS (**a**) and LC–ultraviolet detection (**b**) chromatograms of sample extraction solution aesculin (1), aesculetin (2), and interference peak (x). LC separation conditions: Agilent InfinityLab Poroshell 120 EC-$C_{18}$ column (4.6 mm × 50 mm, 2.7 μm); mobile phase, 0.1% formic acid aqueous solution–acetonitrile (94:6, *v*/*v*); column temperature, 40 °C; injection volume, 5 μL. MS detection mode: selected ion monitor; monitoring ions: *m*/*z* 339 (aesculin) and *m*/*z* 355 (aesculetin). Ultraviolet detection conditions: detection wavelength, 236 nm.