**Data S1**

**CA purity testing method**

An appropriate amount of extracted CA was dissolved in methanol (>99%) and filtered through a 2.5 $\mu$m microporous membrane. CA purity was then determined by HPLC using an LC-2050C 3D high-performance liquid chromatography system (Shimadzu, Japan) equipped with a C18 column (Hypersil GOLD C18 column, Thermo Fisher Scientific, Lot No.: 12169, USA). The analysis was carried out at 25°C with a mobile phase of 10% acetic acid-water/methanol (72:28, v/v) at a flow rate of 1.0 ml/min. The chromatographic results are shown below, and the main peak was identified as CA.

**Data S2**

**Nuclear magnetic resonance (NMR) spectroscopic analysis and identification of CA**

Weigh approximately 10 mg of CA powder, dissolve it in 0.5 ml of deuterated dimethyl sulfoxide (DMSO-d6), and transfer the solution to a 5-mm NMR sample tube. Using a Bruker DRX-600M NMR spectrometer, measure the $^{1}$H-NMR (600 MHz) and $^{13}$C-NMR (150 MHz) spectra at 25˚C. The $^{1}$H-NMR scan count was 16, the $^{13}$C-NMR scan count was 1024, and the sample tube rotation speed was 20 Hz.

**Data S3**

**Determination of the three-dimensional structure of CA via single-crystal X-ray diffraction**

An appropriate amount of CA powder was dissolved in dimethyl sulfoxide (DMSO) and stirred continuously with a stirring rod under heated conditions until the solid was completely dissolved, forming a saturated or supersaturated solution. The solution was then filtered to remove impurities and allowed to stand to allow the solvent to evaporate slowly, promoting crystal precipitation. A single crystal sample of suitable size and high quality was selected. Data were collected at a low temperature of 150(2) K using an X-ray single-crystal diffractometer equipped with a Cu Kα radiation source (λ=1.54178 Å). Diffraction points were acquired via ω-ϕ scanning, and independent diffraction points were obtained after absorption correction and data reduction. The crystal structure was solved using the direct method (SHELXT) and refined using the full-matrix least-squares method based on $F^2$ (SHELXL). All non-hydrogen atoms were refined using anisotropic displacement parameters, while hydrogen atoms were refined via theoretical hydrogenation and the riding model. The final crystal structure was validated using the Flack parameter 0.01(12), and the absolute configuration was determined.

Table SI. Statistics of chromatographic peaks for 6'-O-Caffeoylarbutin purity determination.

| Number | Retention time (min) | Area | Area % (concentration) |
|---|---|---|---|
| 1 | 4.783 | 3270 | 0.02 |
| 2 | 5.477 | 3683 | 0.023 |
| 3 | 7.125 | 1915 | 0.012 |
| 4 | 7.408 | 3010 | 0.019 |
| 5 | 9.527 | 36345 | 0.224 |
| 6 | 15.657 | 77473 | 0.478 |
| 7 | 18.018 | 15960795 | 98.409 |
| 8 | 34.415 | 132276 | 0.816 |