Supplementary Material

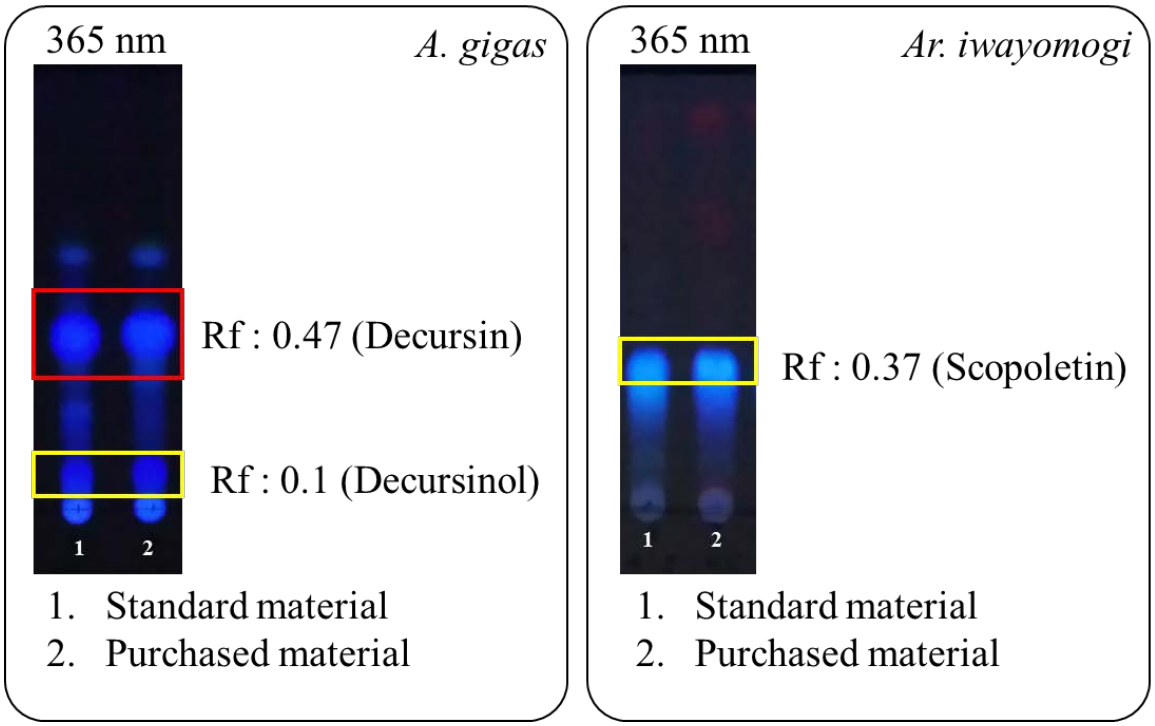
1. Verifications of two medicinal plants

1.1. Analysis of roots of *Angelica gigas* Nakai

Weigh 1 g of standard material, add 5 mL of ethanol, heat it in a water bath for 10 minutes, cool it, and use the filtered solution as the standard solution. It is dropped on normal-phase thin-layer chromatography (TLC) plate. Next, a *n*-hexane/ethyl acetate mixture (2:1) is used as a developing solvent. Among the spots obtained by irradiation with ultraviolet (365 nm), two spots with the same color and retention factor (Rf) value are identified (decursinol at Rf: 0.1 and decursin at Rf: 0.4).

1.2. Analysis of aerial parts of *Artemisia iwayomogi* Kitamura

The method of NHMI was used with some modifications. Brief, weigh 2 g of standard material, add 10 mL of methanol, perform ultrasonic extraction for 10 minutes, and use the filtered solution as the standard solution. It is dropped on the TLC plate. Next, a *n*-hexane/ethyl acetate mixture (2:1) is used as a developing solvent. Next, a petroleum ether/ethyl acetate/acetone mixture (4:5:0.5) is developed as a developing solvent. By irradiating ultraviolet (365 nm), the composition and color of the spots between the standard material and the purchased material are compared (scopoletin at Rf: 0.37).



2. Analytical conditions of LC-ion trap MS

An LC-MS/MS equipped with electrospray ionization (ESI) interface and an ion trap mass analyzer (ThermoFinnigan LCQ Advantage MAX ion trap mass spectrometer) was applied to the MS and multistage mass spectrometry (MS^n) analysis. Separation was carried out on ThermoFinnigan surveyor MS Pump using a Kinetex C18 column (150 × 4.6 mm, 5 μm; Phenomenex®, USA). The column was maintained at room temperature and flow rate was 1 mL/min (LC-MS post column flow splitters fixed, split ratio = 4:1). The mobile phase consisted of 0.1% formic acid in water (A) and 100% acetonitrile (B). The gradient profile was 0 to 30 min linear increase in B from 20% to 100%; 10 min held at 100% B. The ESI source was used and operated in both positive and negative ion mode. Mass analyzer scanned from 50 to 2,000 m/z. Collision induced dissociation spectra were obtained with a fragmentation amplitude of 40 V using helium as the collision gas.

Table S1. Analytical conditions of each compound

Compounds	Rt (min)	Q1 mass (m/z)	Q3 mass (m/z)	CE (eV)	Solvent condition	
					Time (min)	Methanol (%)
Decursinol angelate (1)	40.98	329	247, 229.1	20	0	20
					30	65
					45	65
Decursin (2)	40.15	329	247, 229.1	20	45.1	100
					60	100

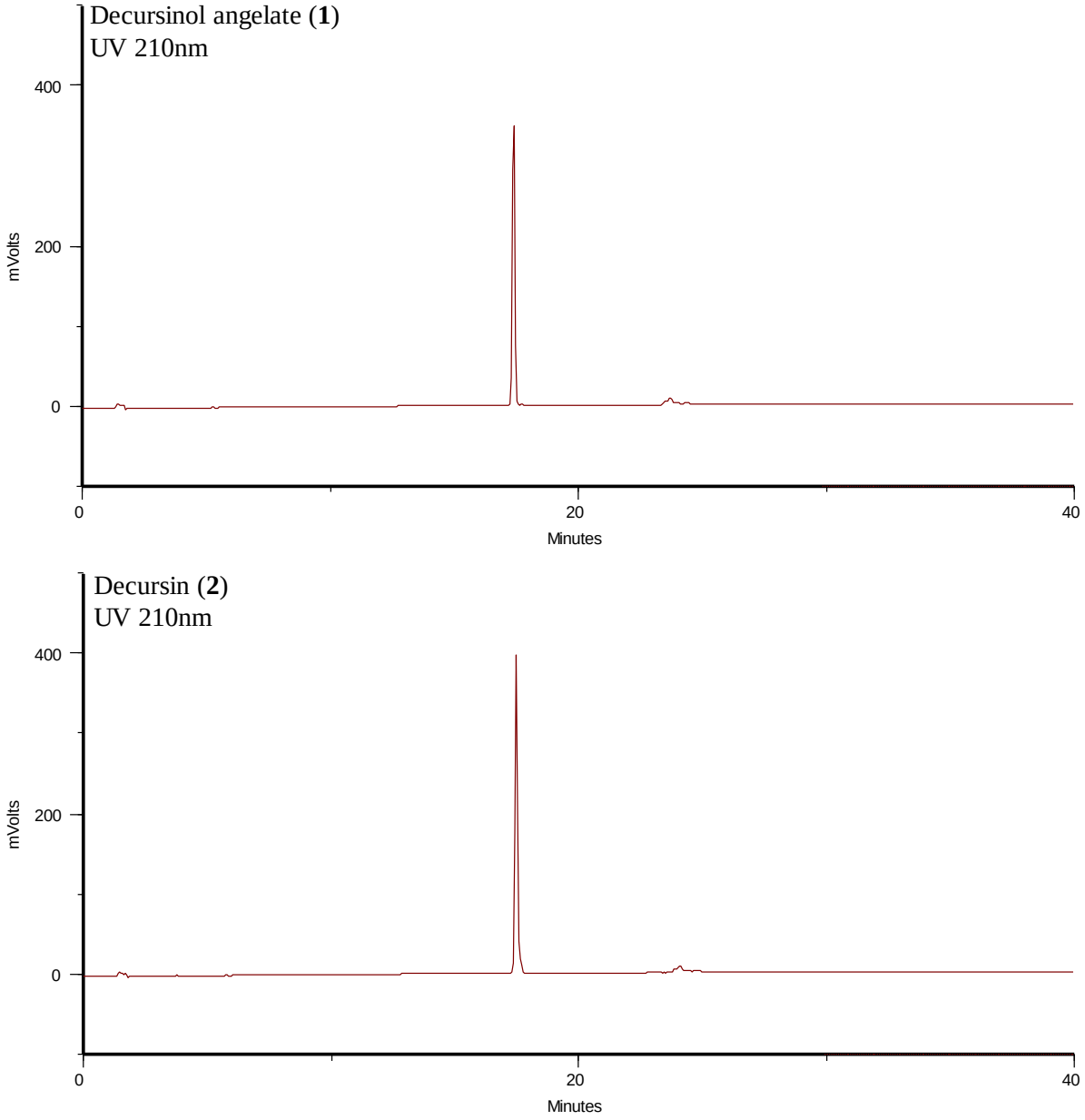


Fig. S1. HPLC chromatograms of decursinol angelate (1) and decursin (2) (purity > 98%). HPLC condition: HPLC analysis was carry out using a Gilson 151 UV-VIS detector and a 321 pump, and equipped with a Kinetex C18 column (150 × 4.6 mm, 5 µm; Phenomenex®, USA). The column was maintained at room temperature and flow rate was 1 mL/min. The mobile phase consisted of water (A) and 100% acetonitrile (B). The gradient profile was 0–30 min linear increase in B from 20% to 100%; 10 min held at 100% B.

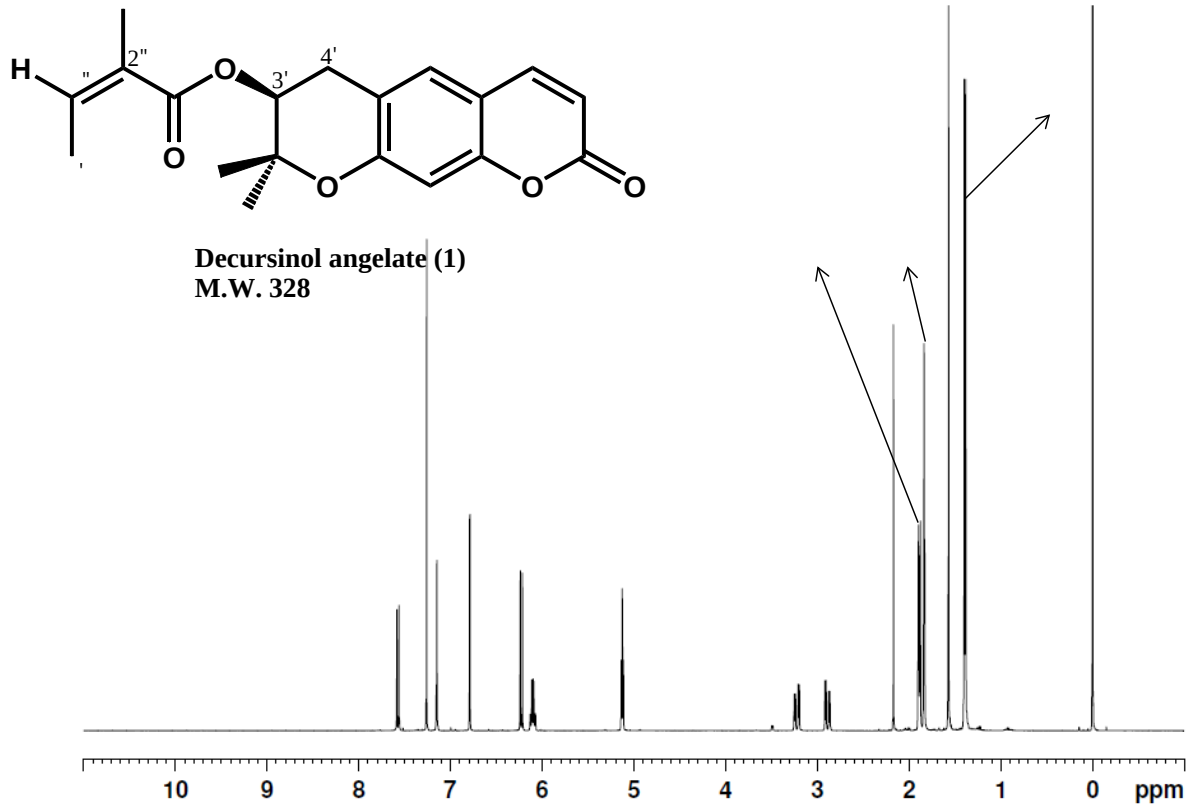


Fig. S2. ^{1}H-NMR spectrum of decursinol angelate (1).

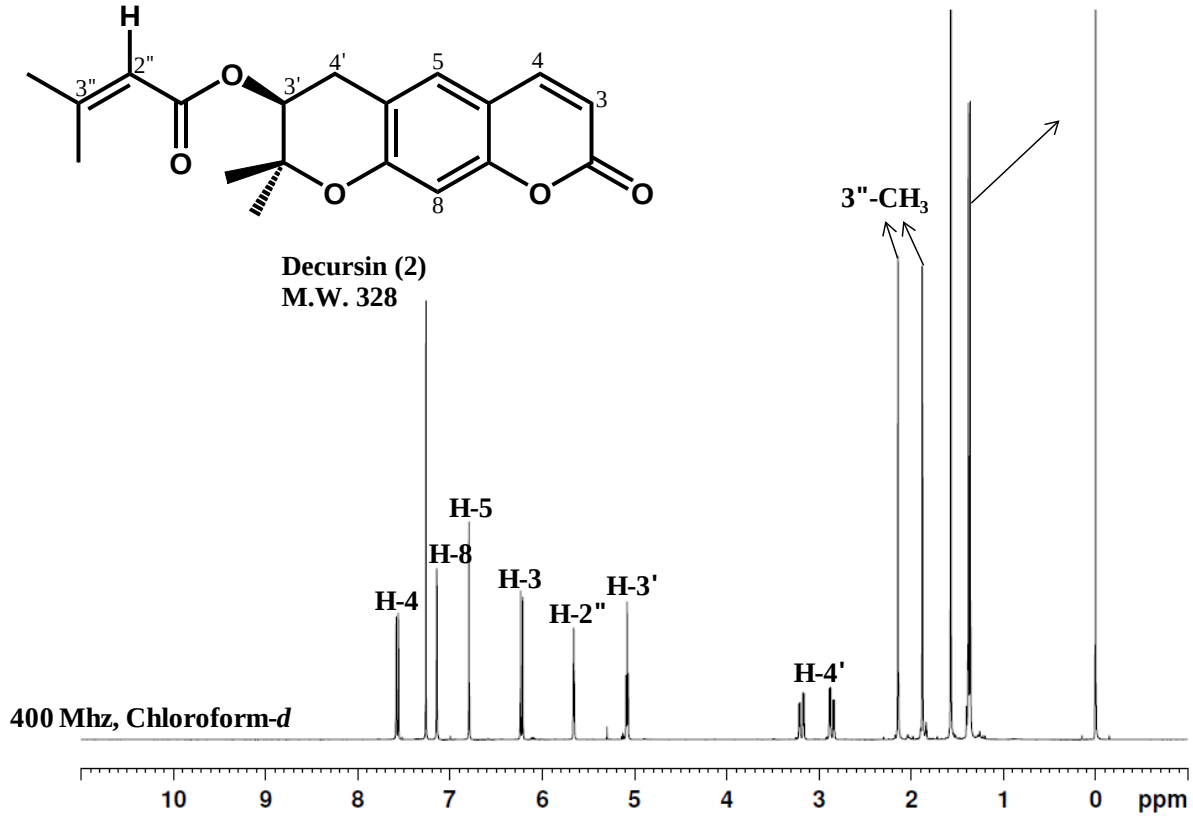


Fig. S3. ^{1}H-NMR spectrum of decursin (2).

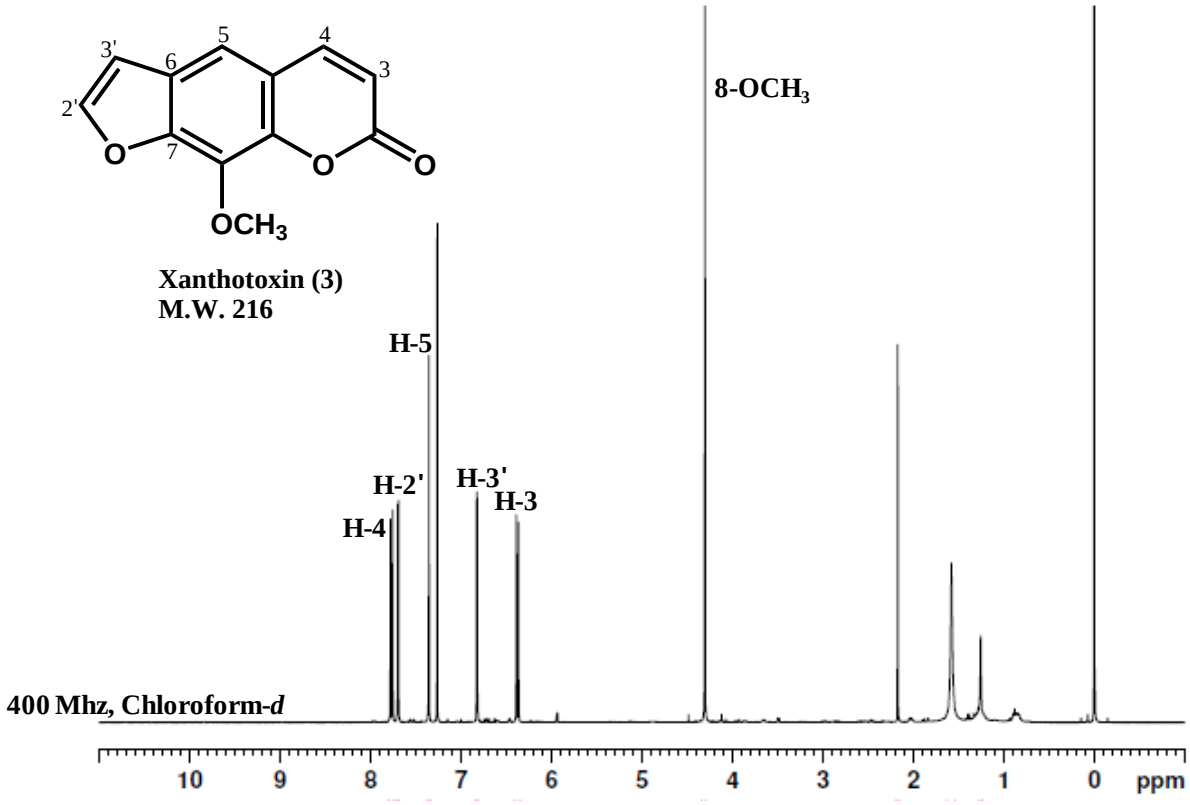


Fig. S4. ^{1}H-NMR spectrum of xanthotoxin (3).

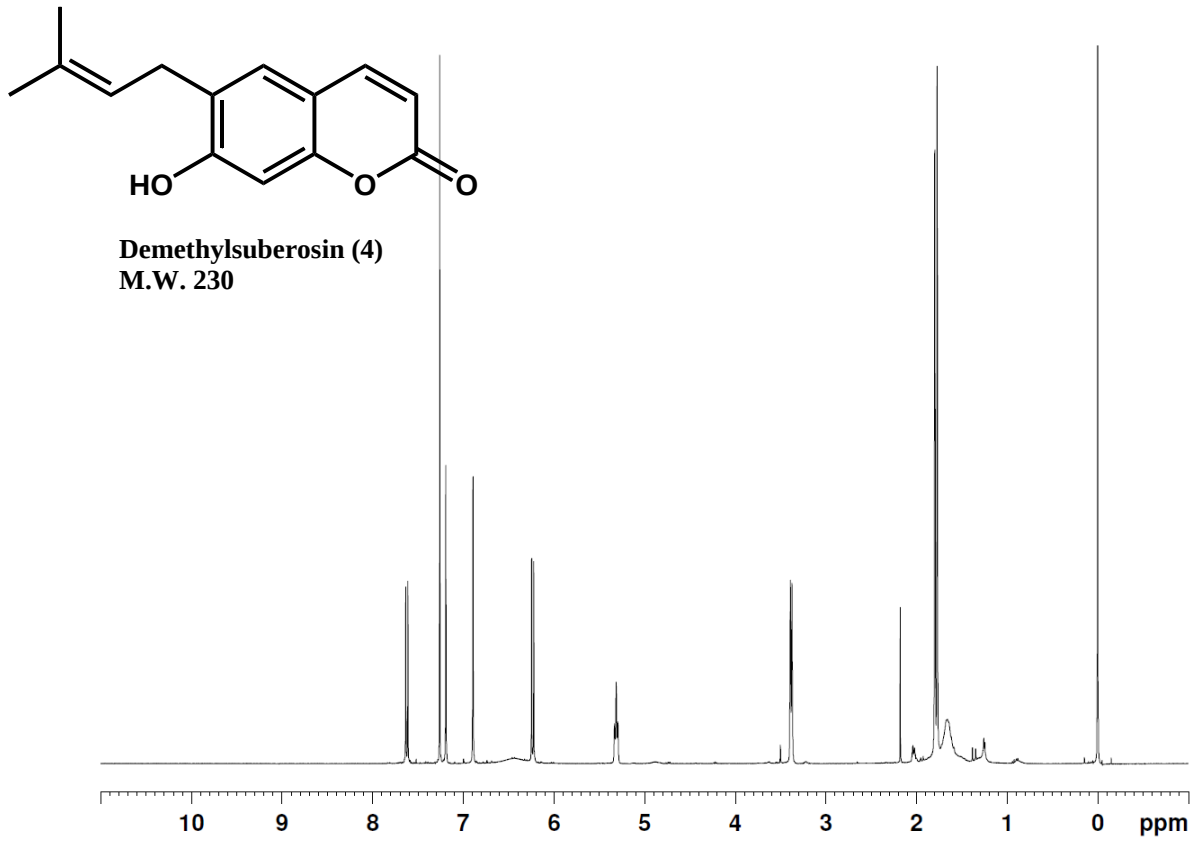


Fig. S5. ^{1}H-NMR spectrum of demethylsuberosin (4).

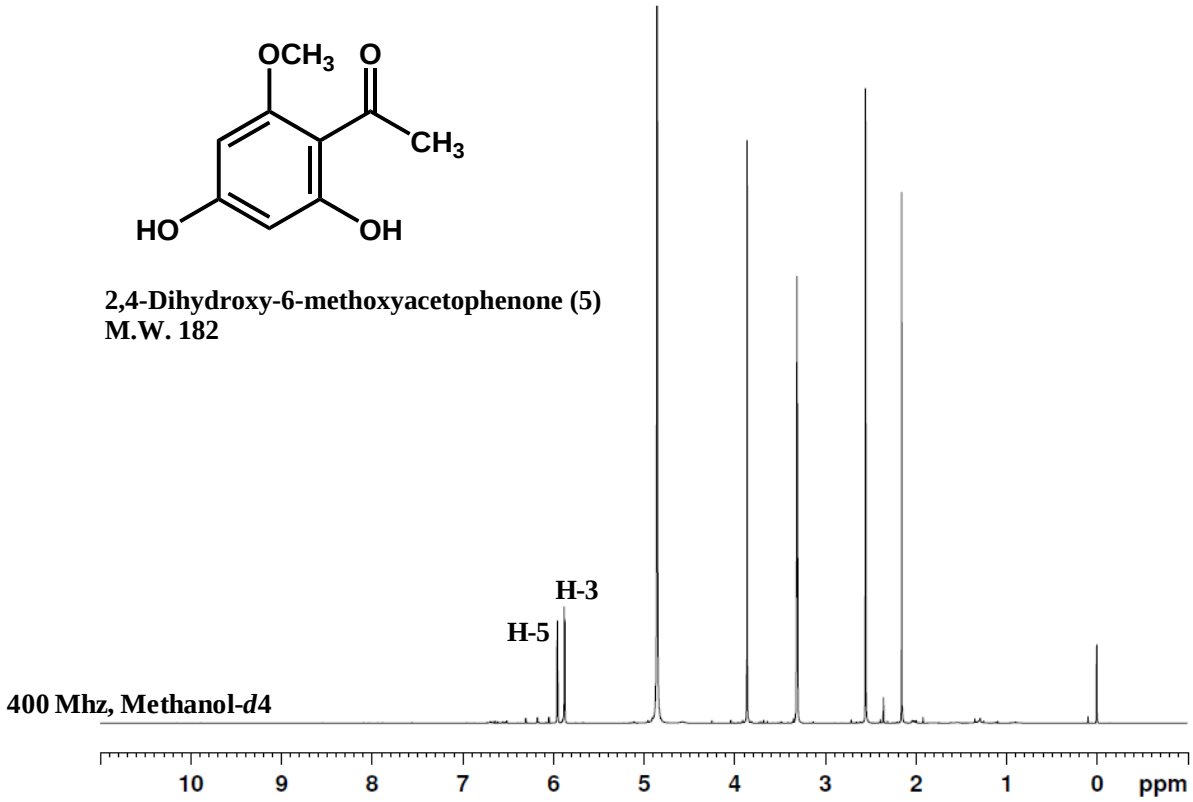


Fig. S6. ^{1}H-NMR spectrum of 2,4-Dihydroxy-6-methoxyacetophenone (5).

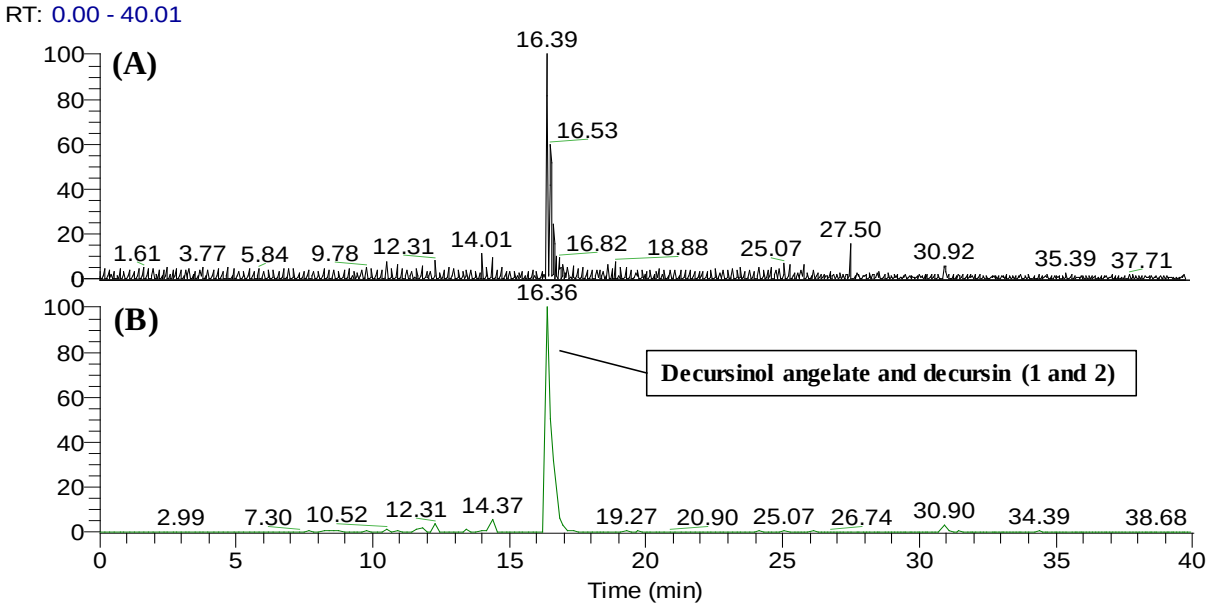


Fig. S7. LC-MS chromatograms of active sub-fraction MC-I. (A) Total ion chromatogram of MC-I. (B) Chromatogram of positive ESI-MS.

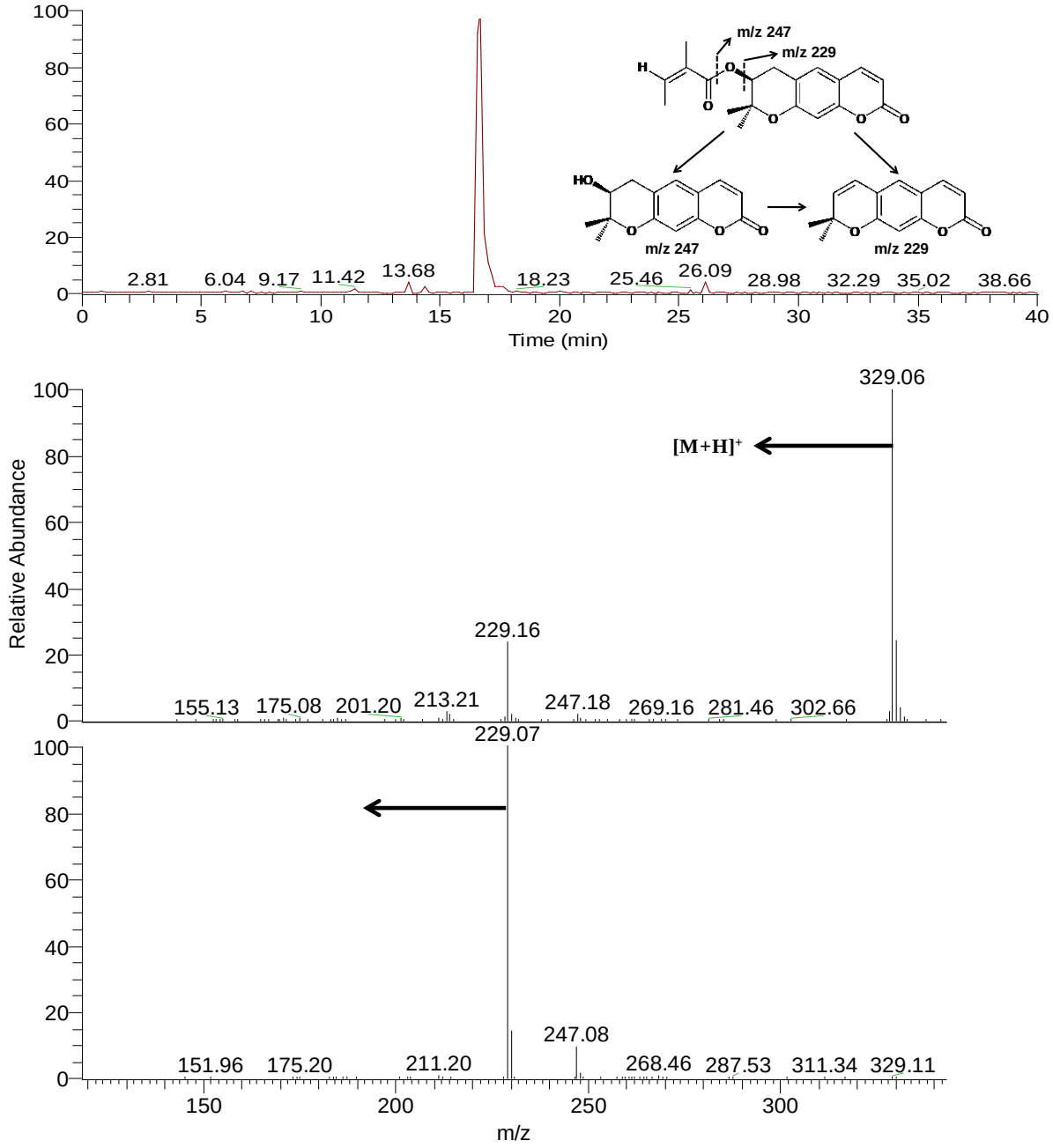


Fig. S8. MS fragmentation of decursinol angelate (1).

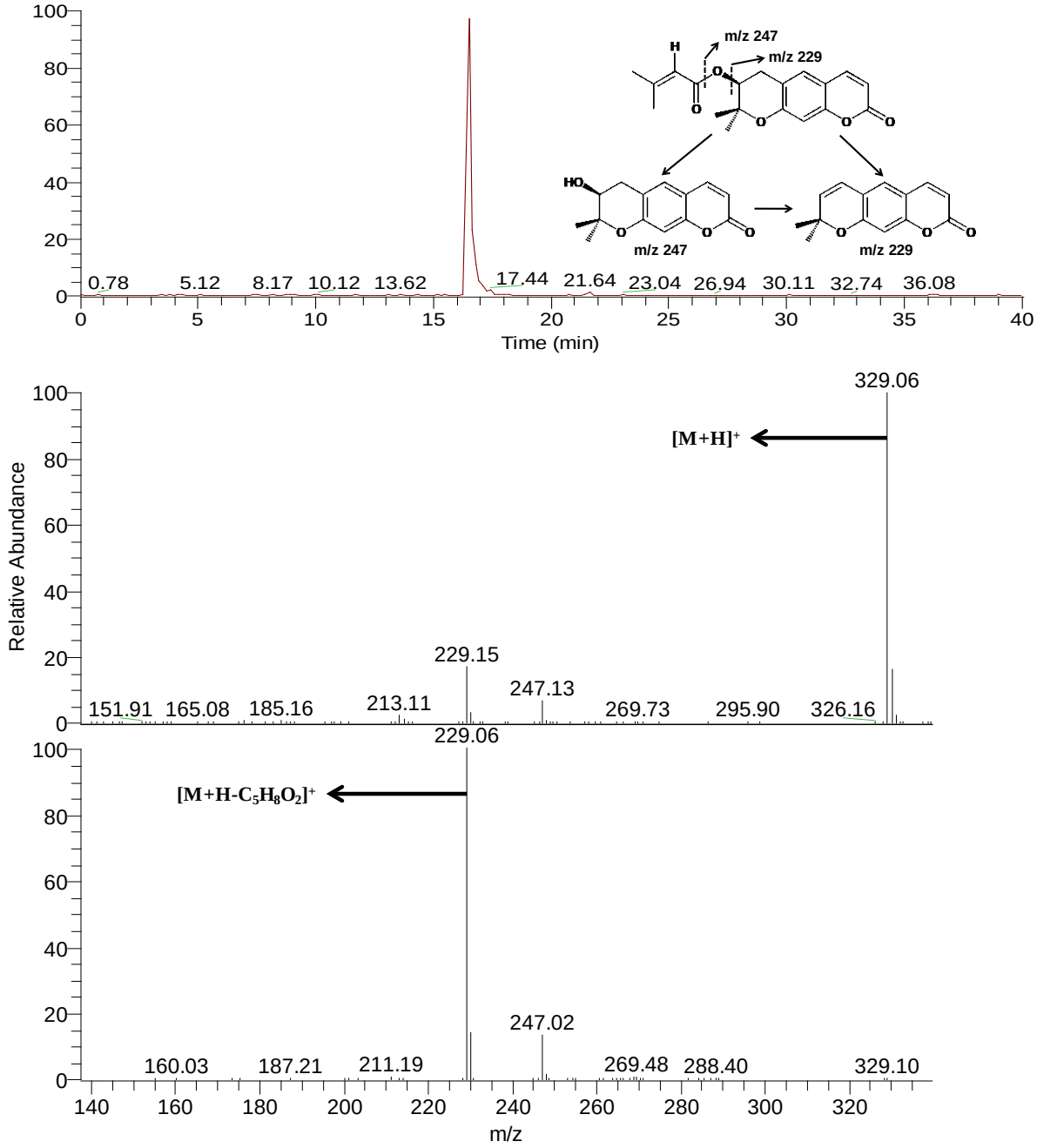


Fig. S9. MS fragmentation of decursin (2).

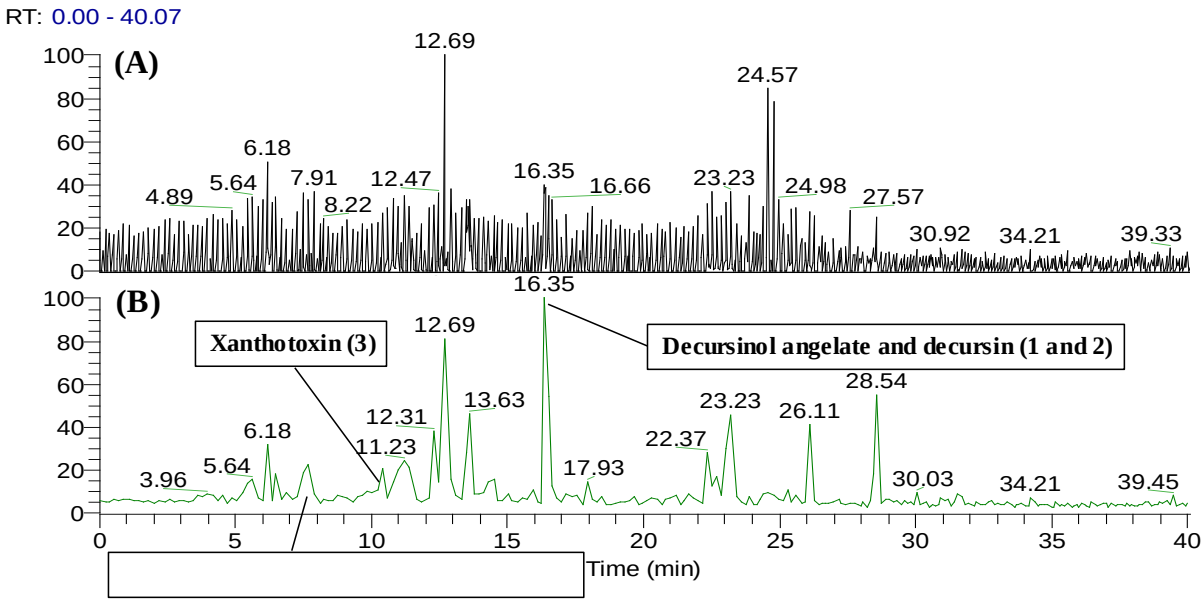


Fig. S10. LC-MS chromatograms of active sub-fraction MC-II. (A) Total ion chromatogram of MC-II. (B) Chromatogram of positive ESI-MS.

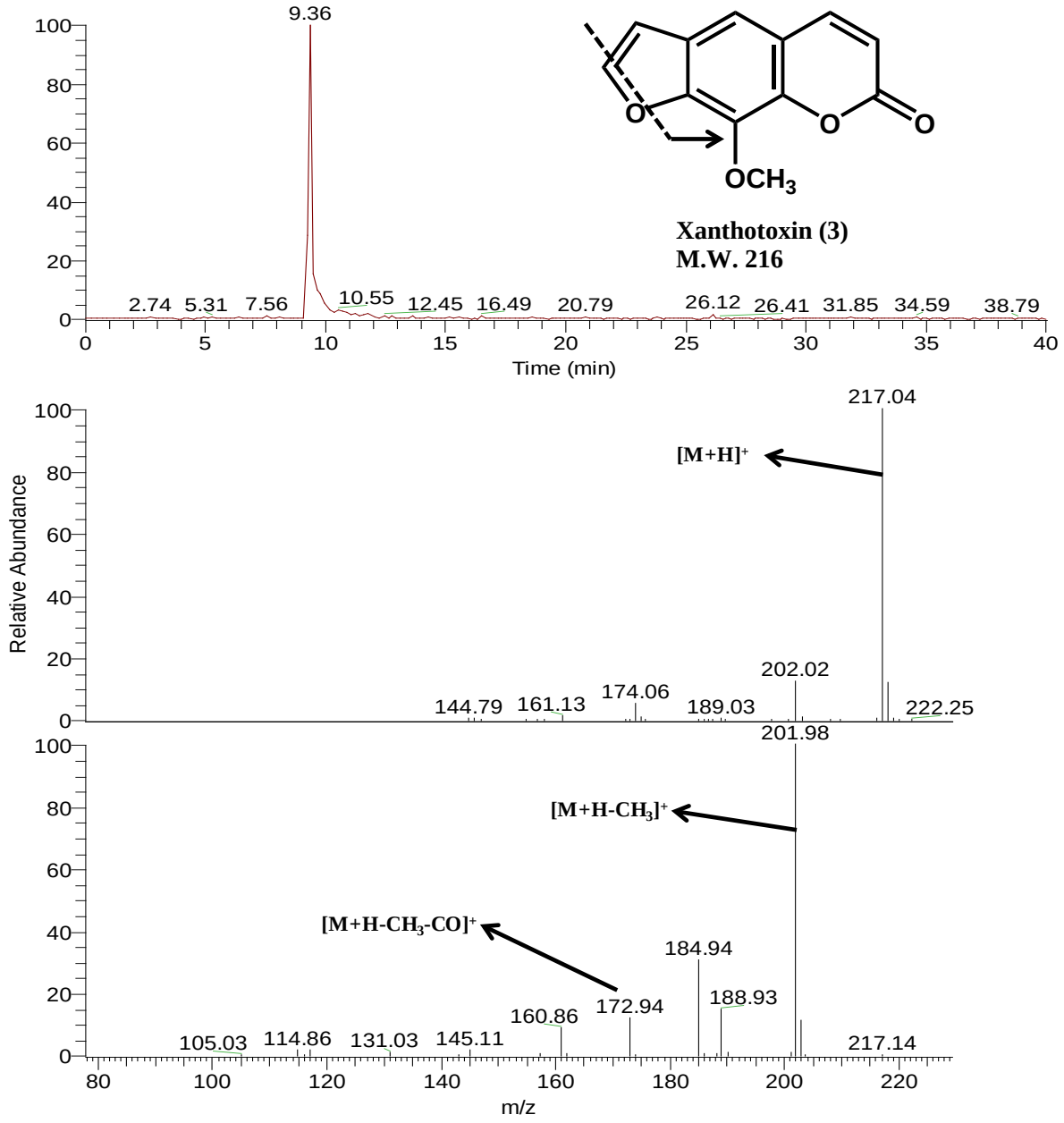


Fig. S11. MS fragmentation of xanthotoxin (3).

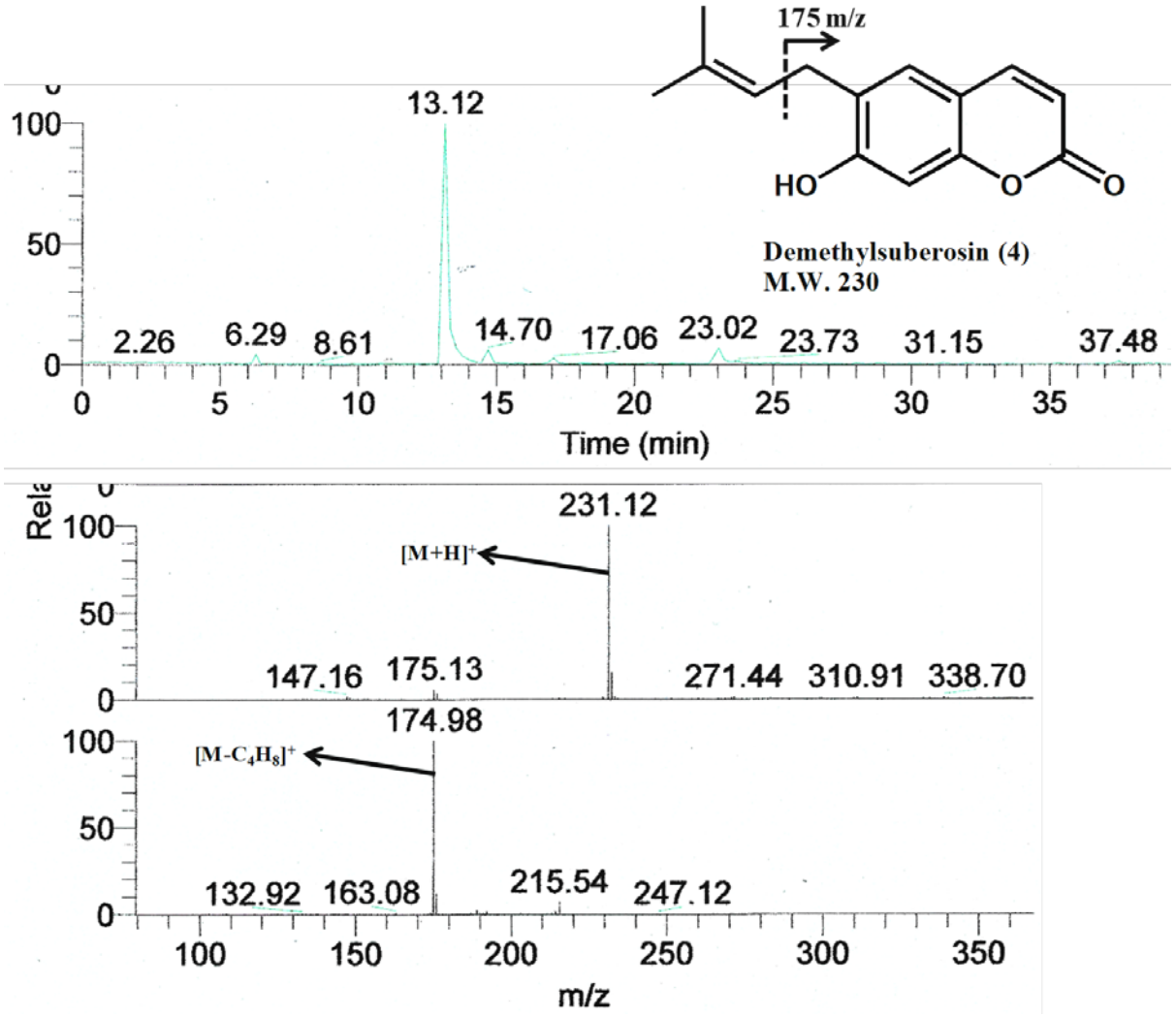


Fig. S12. MS fragmentation of demethylsuberosin (4).

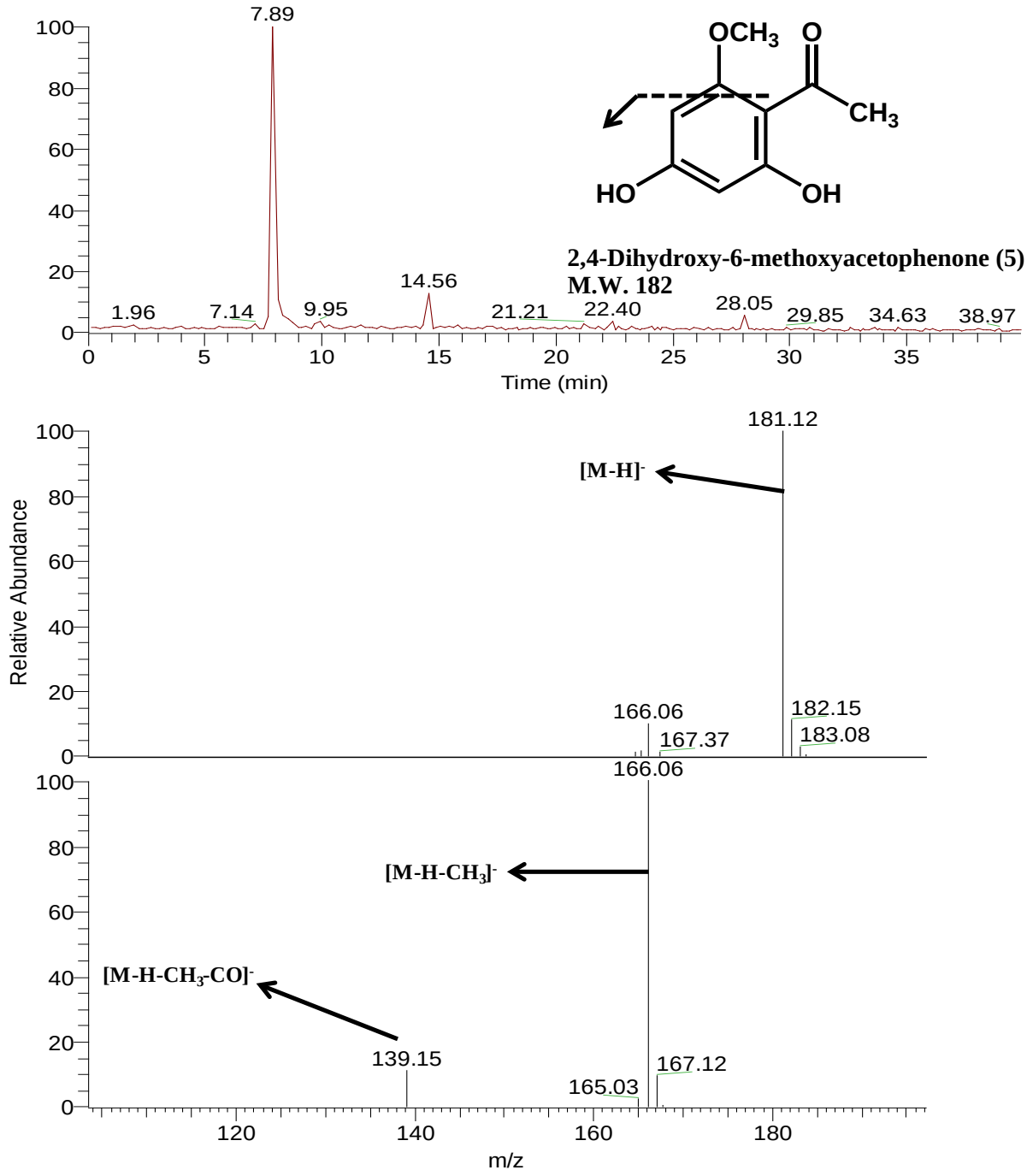


Fig. S13. MS fragmentation of 2,4-Dihydroxy-6-methoxyacetophenone (5).

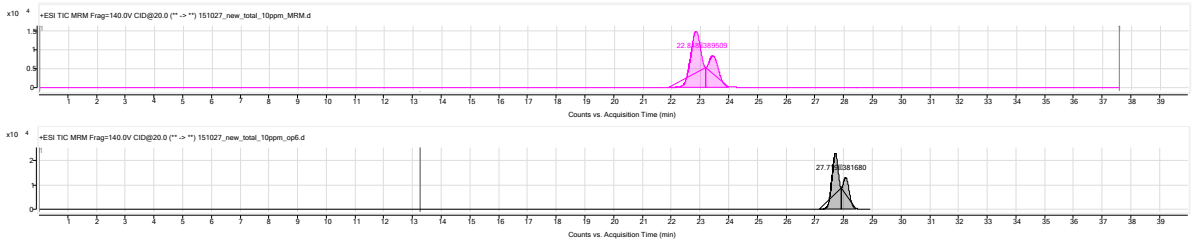


Fig. S14. LC-MS chromatogram for decursinol angelate (1) and decursin (2) in CE in two different C_{18} columns (50 or 150 × 4.6 mm, solvent conditions are the same as in Table S1).

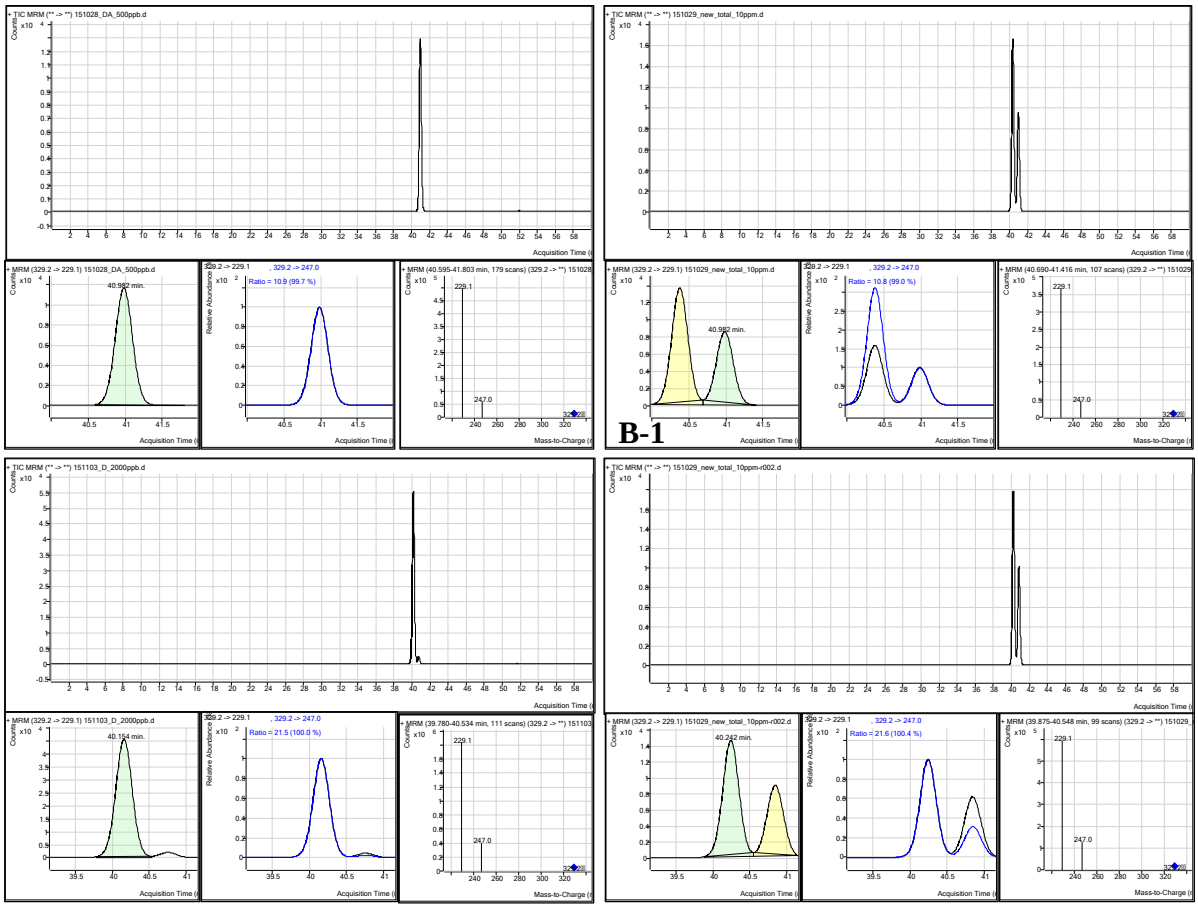


Fig. S15. Specificity of decursinol angelate (1) and decursin (2). (A) MRM chromatogram of each standard compound; A-1, 2: peak area and retention time of each standard compound; (B) MRM chromatogram of CE; B-1, 2: peak area and retention time of each active compound in CE.