

Supplementary materials

Scheme S1 Key fragmentation pathway of sennoside A

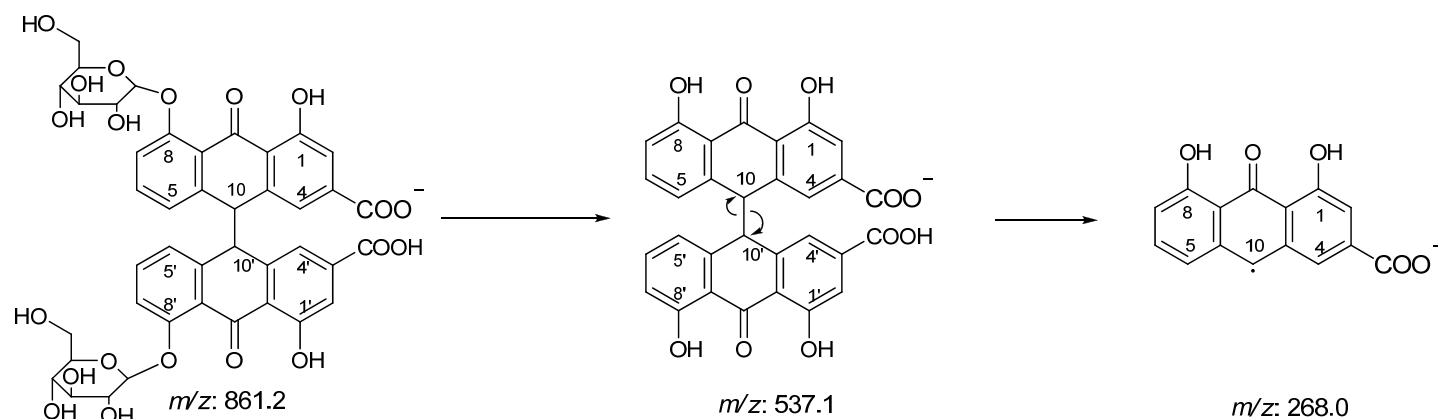


Figure S1 HPLC-DAD-ESI-MSⁿ chromatography: a. HPLC-UV (254 nm), b. (-) MS TIC, c. (+) MS TIC

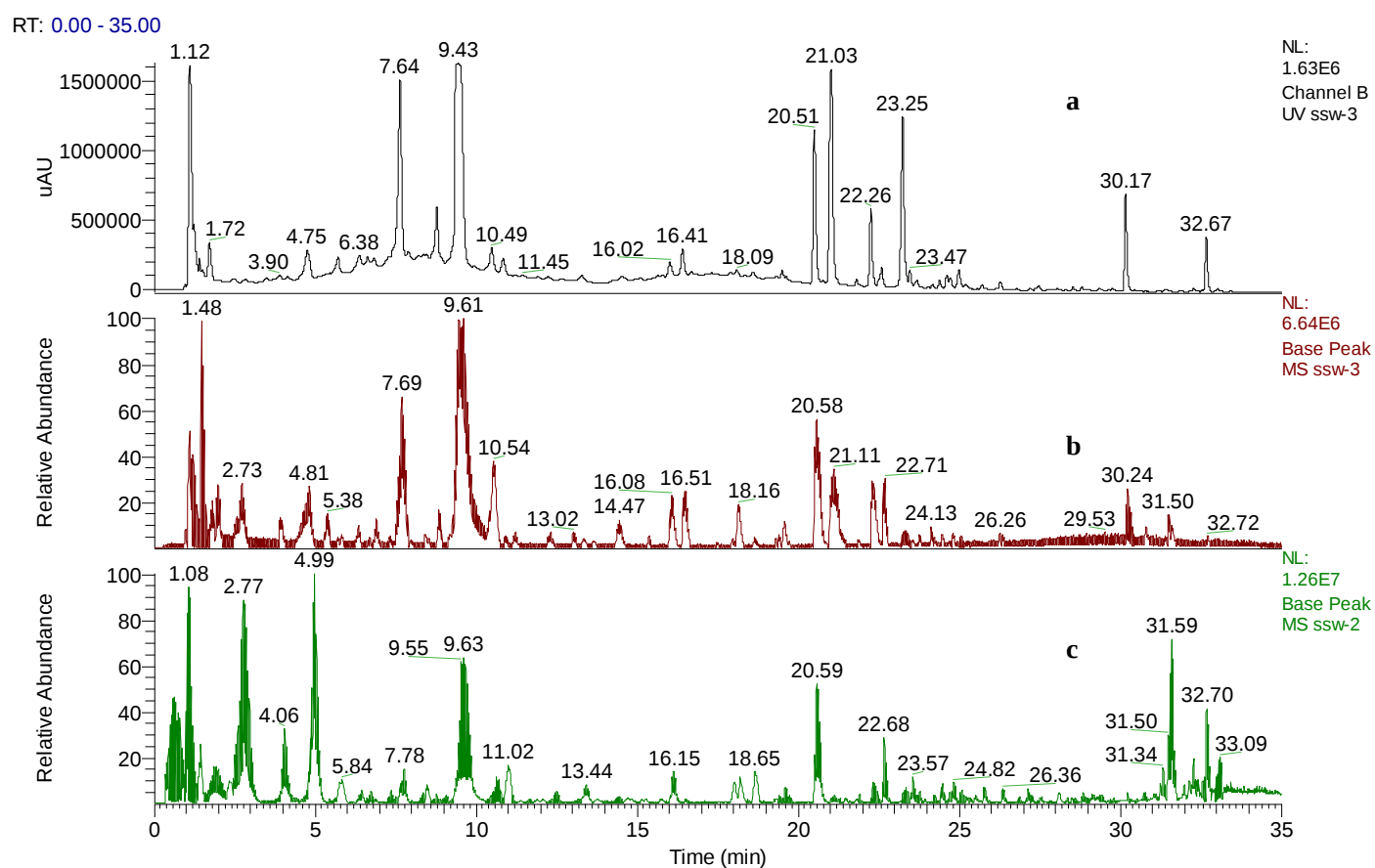


Figure S2 Extracted ion chromatography (EIC) of *P. multiflorum* for dianthrone glycosides ($R_t = 20.1\text{--}30.9\text{ min}$)

1: Total ion chromatography of *P. multiflorum*

2-8: Extracted ion chromatography for m/z 833, 919, 847, 933, 671, 757, and 685.

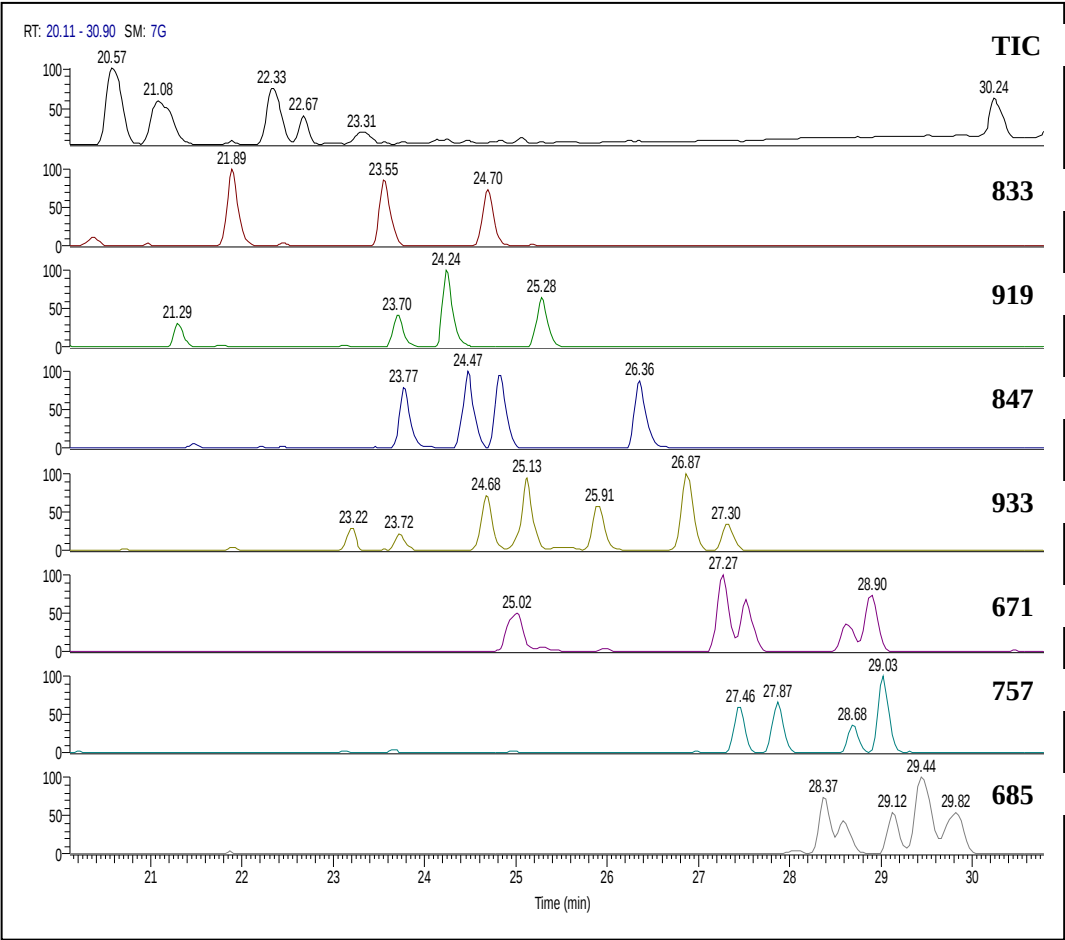
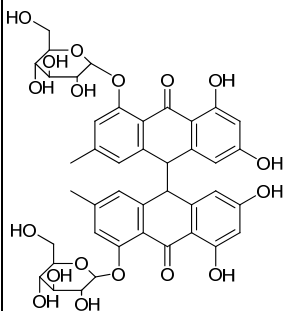
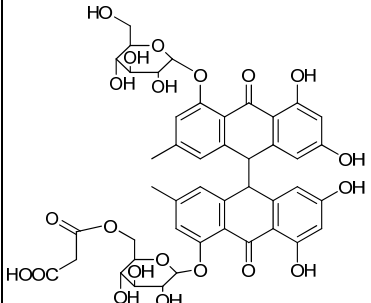
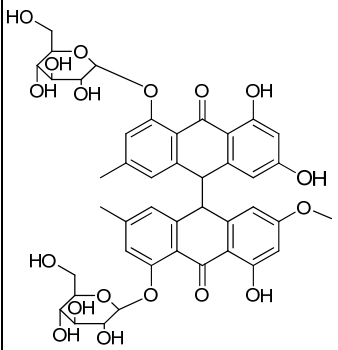
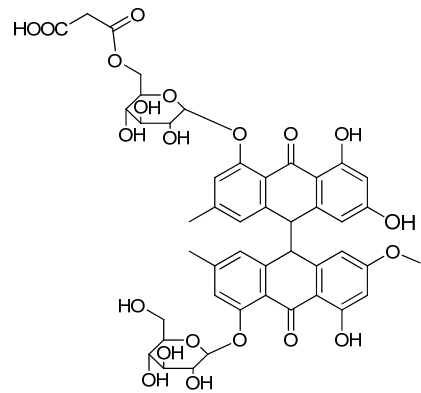
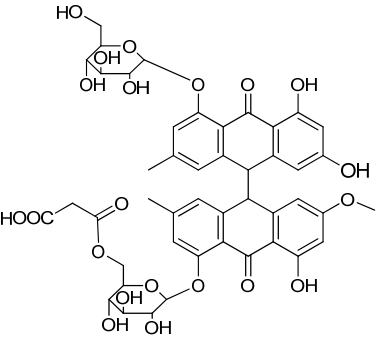
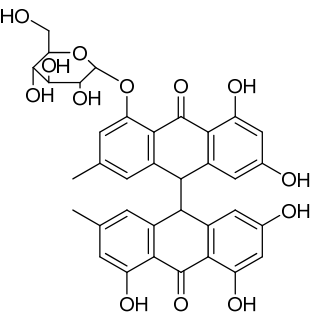


Table S-1 identification of dianthrone glucosides in *Polygonum multiflorum* Thunb.

No.	T_R	Precursor ions	MS ⁿ	Identification
A1	21.87	835 (C ₄₂ H ₄₃ O ₁₈) [M+H] ⁺	-MS ² [833]: 671(100) -MS ³ [671]: 416(100), 509(22), 254(13) + MS ² [511]: 256(100)	
A2	23.55	511 (C ₃₀ H ₂₈ O ₈) [M+H-2glu] ⁺		
A3	24.68	833 (C ₄₂ H ₄₁ O ₁₈) [M-H] ⁻		
B1	23.70	921 (C ₄₅ H ₄₅ O ₂₁) [M+H] ⁺	-MS ² [919]: 713(100), 671(78), 857(45) -MS ³ [713]: 458(100), 509(11), 254(11) +MS ² [759]: 504(100), 256(25), 486 (18), 511(16)	
B2	24.24	759 (C ₃₉ H ₃₅ O ₁₆) [M+H-gluc] ⁺		
B3	25.28	919 (C ₄₅ H ₄₃ O ₂₁) [M-H] ⁻		
C1	23.77	849 (C ₄₃ H ₄₅ O ₁₈) [M+H] ⁺	-MS ² [847]: 416(100), 685(35) -MS ³ [416]: 254(100), 255(15) +MS ² [525]: 270(100), 256(11)	
C2	24.47	525 (C ₃₁ H ₂₅ O ₈) [M+H-2glu] ⁺		
C3	24.81	847 (C ₄₃ H ₄₃ O ₁₈) [M-H] ⁻		
C4	26.34			

D1	23.19	935 (C ₄₆ H ₄₇ O ₂₁) [M+H] ⁺	-MS ² [933]: 889(100), 458(18), 727(17)	TYPE I 
D2	24.66	933 (C ₄₆ H ₄₅ O ₂₁) [M-H] ⁻	-MS ³ [889]: 458(100), 727(29)	
D3	26.87			
D4	25.88	935 (C ₄₆ H ₄₇ O ₂₁) [M+H] ⁺	-MS ² [933]: 889(100), 685(21), 416(10), 727 (10)	TYPE II 
D5	27.30	933 (C ₄₆ H ₄₅ O ₂₁) [M-H] ⁻	-MS ³ [889]: 416(100), 685(29)	
E1	27.24	673 (C ₃₆ H ₃₃ O ₁₃) [M+H] ⁺	-MS ² [671]: 416(100), 509(28), 254(12)	
E2	27.50	511 (C ₃₀ H ₂₃ O ₈) [M+H-glu] ⁺	-MS ³ [416]: 254(100)	
E3	28.61	671 (C ₃₆ H ₃₁ O ₁₃) [M-H] ⁻	+MS ² [511]: 256(100)	
E4	28.90			

F1	27.43	759 (C ₃₉ H ₃₅ O ₁₆) [M+H] ⁺	-MS ² [757]: 713(100), 458(18)	
F2	27.86	757 (C ₃₉ H ₃₃ O ₁₆) [M-H] ⁻	-MS ³ [713]: 458(100), 509(29), 254 (10)	
F3	28.68		+MS ² [759]: 504(100), 256(21), 489 (11), 511 (10)	
F4	29.03			
G1	28.38	687 (C ₃₇ H ₃₅ O ₁₃) [M+H] ⁺	-MS ² [685]: 254(100), 523(15)	TYPE I
G2	28.57	525 (C ₃₁ H ₂₅ O ₈) [M+H-gluc] ⁺	-MS ³ [254]: 226(100), 254(55)	
G3	29.17	685 (C ₃₇ H ₃₃ O ₁₃) [M-H] ⁻	+MS ² [525]: 270(100), 256(11)	
G4	29.41	687 (C ₃₇ H ₃₅ O ₁₃) [M+H] ⁺	-MS ² [685]: 416(100), 254(52)	TYPE II
G5	29.81	525 (C ₃₁ H ₂₅ O ₈) [M+H-gluc] ⁺ 685 (C ₃₇ H ₃₃ O ₁₃) [M-H] ⁻	-MS ³ [416]: 254(100) +MS ² [525]: 270(100), 256(11)	

Identification of new diantrone glycosides from *Polygonum multiflorum* Thunb. using high-performance liquid chromatography coupled with LTQ-Orbitrap mass spectrometry detection: A strategy for rapid detection of new low abundant metabolites from traditional Chinese medicines.

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