

Supplementary Materials

Semiconductor SERS Platform Enables Rapid Discrimination of Structurally Similar Flavonoids in Multicomponent Systems

Haisu Wang¹, Siqi Li¹, Yuting Song¹, Yanguo Guo¹, Junbo Li¹, Lei Sun^{1,*}, Yunfei Xie^{2,*}, and Wei Ji^{1,*}

¹ College of Chemistry, Chemical Engineering and Resource Utilization, Northeast Forestry University, Harbin 150040, China

² State Key Laboratory of Food Science and Resources, School of Food Science and Technology, Jiangnan University, Wuxi 214122, China

* Correspondence: slei@nefu.edu.cn (L.S.); xieyunfei@jiangnan.edu.cn (Y.X.); jiwei@nefu.edu.cn (W.J.)

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Table of Content

1. Figure S1. Comparison of the SERS spectra and powder Raman spectra of chrysin and luteolin.	S2
2. Figure S2. Comparison of the SERS spectra and powder Raman spectra of kaempferol, quercetin and isorhamnetin.	S2
3. Figure S3. Comparison of the SERS spectra and powder Raman spectra of naringenin and liquiritigenin.	S2
4. Figure S4. Comparison of the SERS spectra and powder Raman spectra of neohesperidin and linarin.	S2
5. Figure S5. Comparison of the SERS spectra and powder Raman spectra of isoliquiritigenin.	S3
6. Figure S6. Comparison of the SERS spectra and powder Raman spectra of L-epicatechin.	S3
7. Figure S7. Comparison of the SERS spectra and powder Raman spectra of genistein.	S4
8. Figure S8. Reproducibility evaluation of ZnO superstructure-based SERS measurements.	S4
9. Figure S9. Binary mixtures of chrysin and luteolin.	S4
10. Figure S10. Binary mixtures of rutin and quercetin.	S5
11. Figure S11. Extracted ion chromatogram and mass chromatograph of Northern Isatis Root.	S5
12. Figure S12. Extracted ion chromatogram and mass chromatograph of Southern Isatis Root.	S5
13. Figure S13. HPLC Chromatograms of Crude Extracts from Northern and Southern Isatis Root.	S6
14. Figure S14. Loading plots of principal components from LDA analysis of Isatis Root samples.	S6
15. Table S1. Regions and assignments of characteristic bands of flavones.	S7
16. Table S2. Regions and assignments of characteristic bands of isoflavones.	S7
17. Table S3. Regions and assignments of characteristic bands of flavanones.	S7
18. Table S4. Regions and assignments of characteristic bands of flavonols.	S7
19. Table S5. Regions and assignments of characteristic bands of flavanols.	S7
20. Table S6. Regions and assignments of characteristic bands of chalcones.	S8
21. References	S8



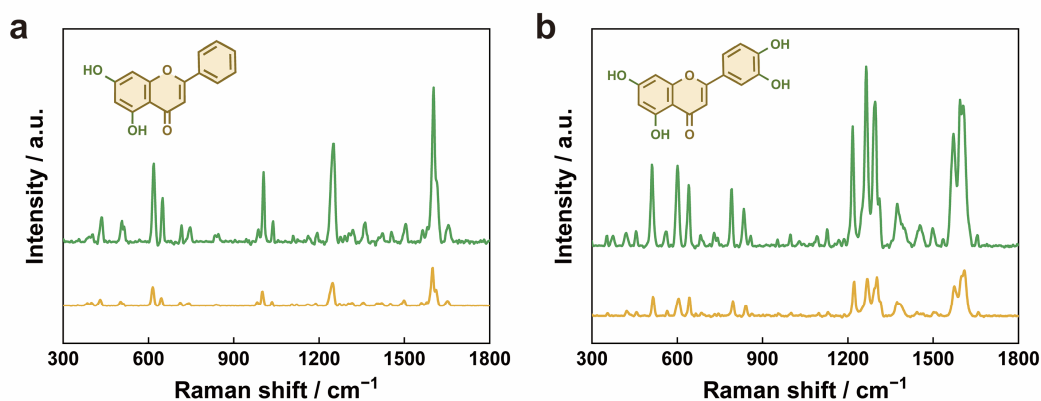


Figure S1. Comparison of the SERS spectra (green) and powder Raman spectra (yellow) of chrysin (a) and luteolin (b).

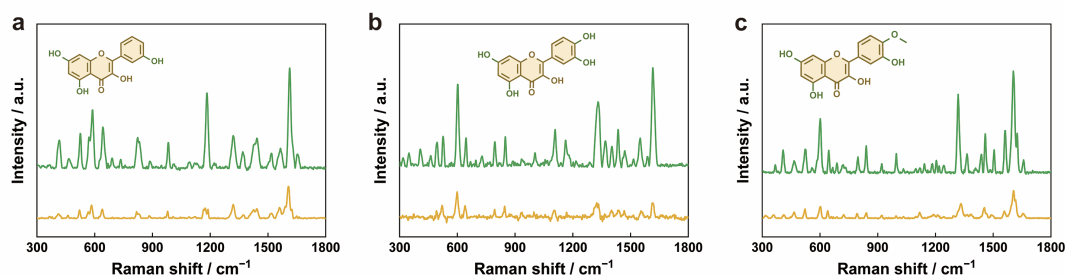


Figure S2. Comparison of the SERS spectra (green) and powder Raman spectra (yellow) of kaempferol (a), quercetin (b) and isorhamnetin (c).

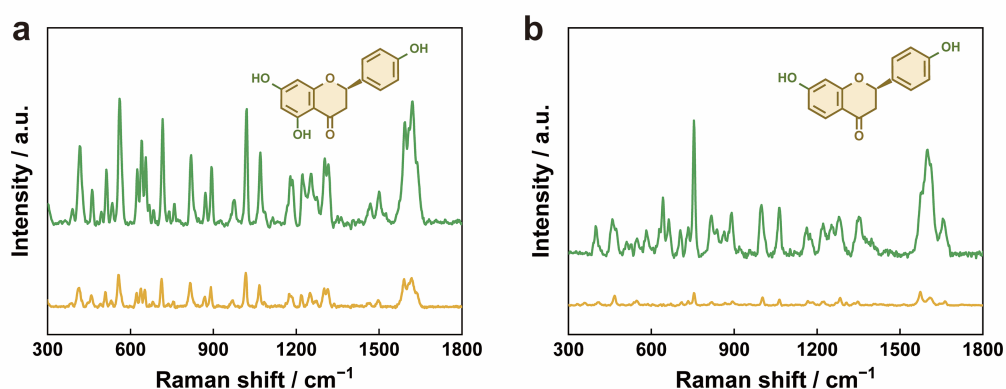


Figure S3. Comparison of the SERS spectra (green) and powder Raman spectra (yellow) of naringenin (a) and liquiritigenin (b).

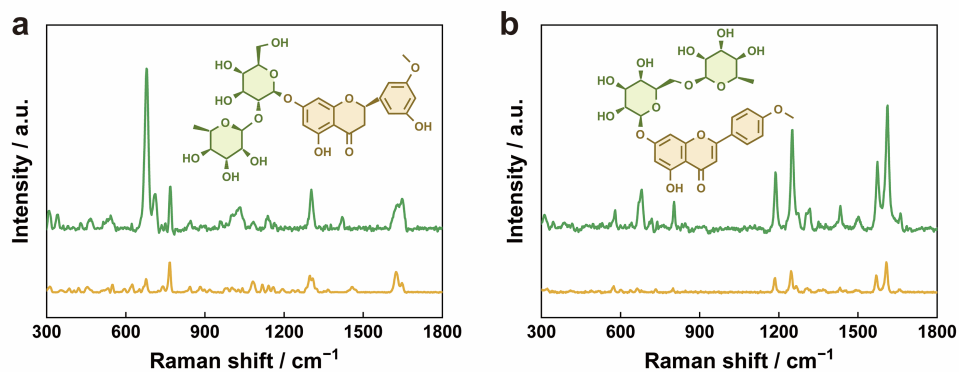


Figure S4. Comparison of the SERS spectra (green) and powder Raman spectra (yellow) of neohesperidin (a) and linarin (b).

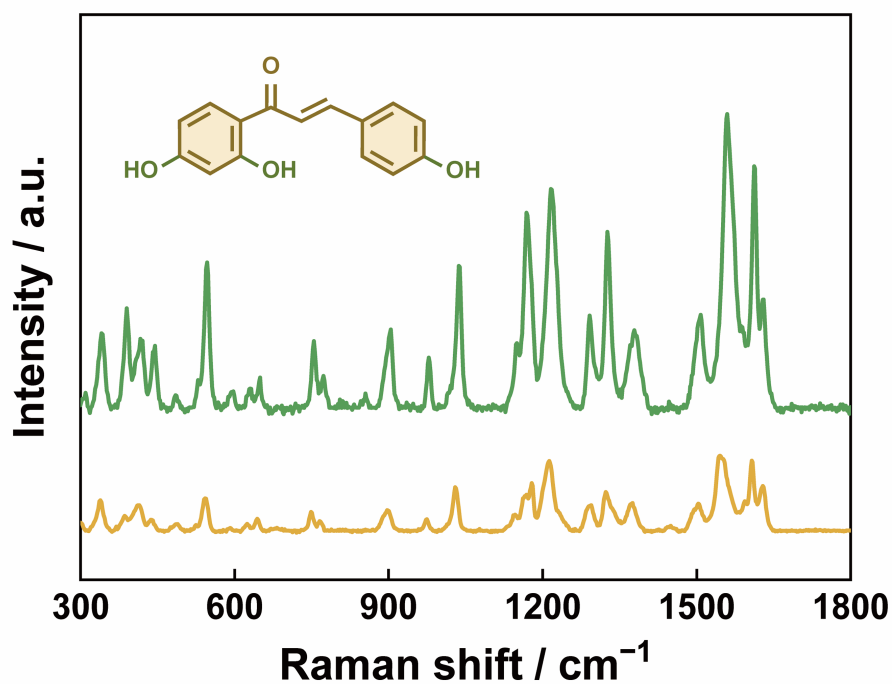


Figure S5. Comparison of the SERS spectra (green) and powder Raman spectra (yellow) of isoliquiritigenin.

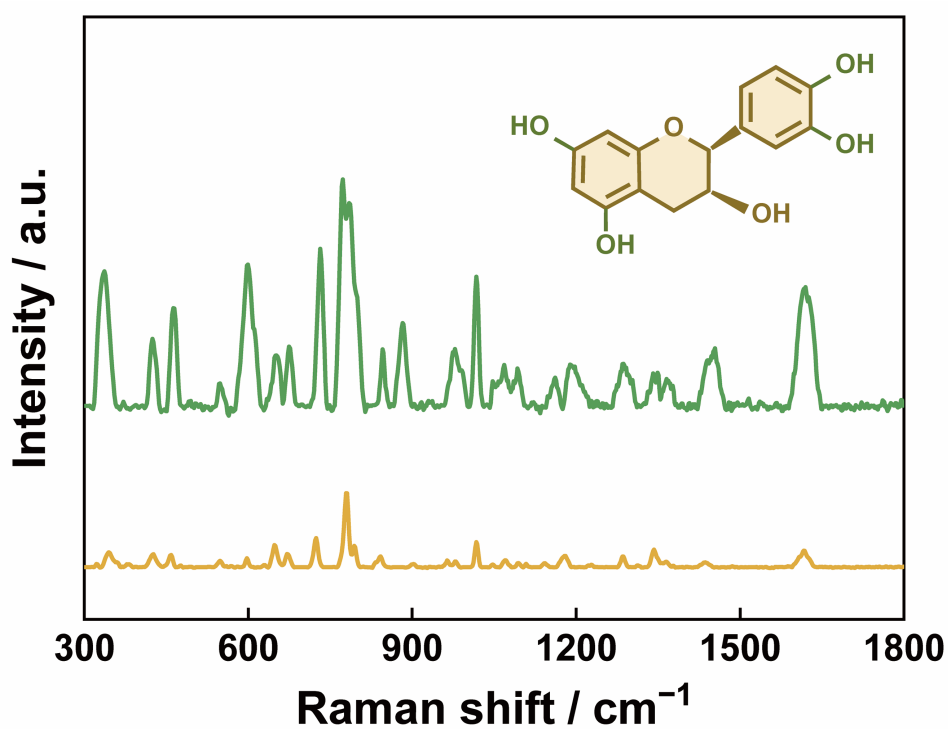


Figure S6. Comparison of the SERS spectra (green) and powder Raman spectra (yellow) of L-epicatechin.

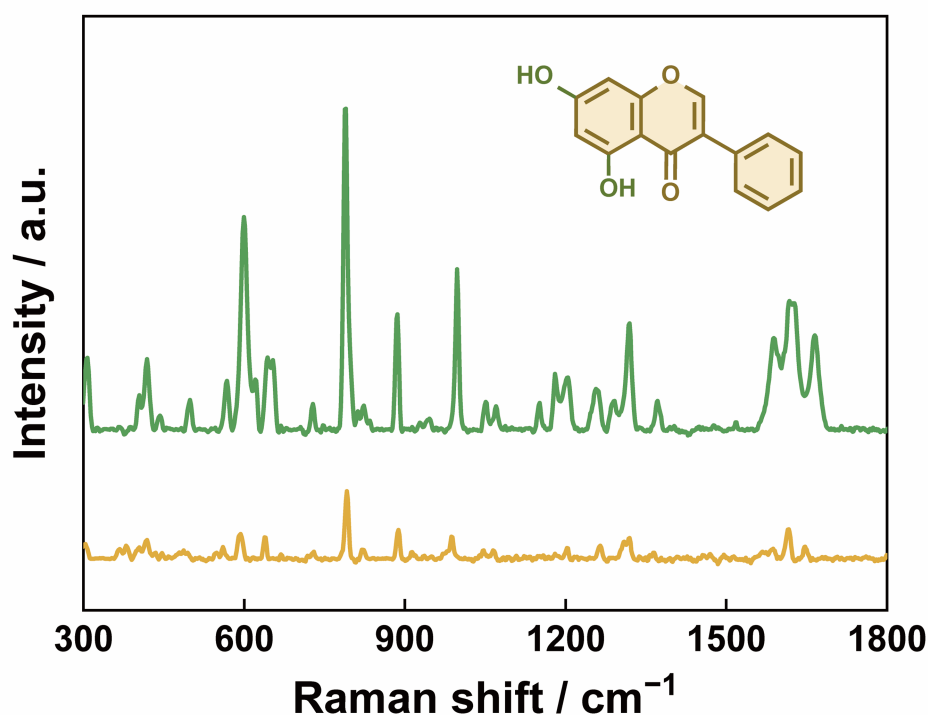


Figure S7. Comparison of the SERS spectra (green) and powder Raman spectra (yellow) of genistein.

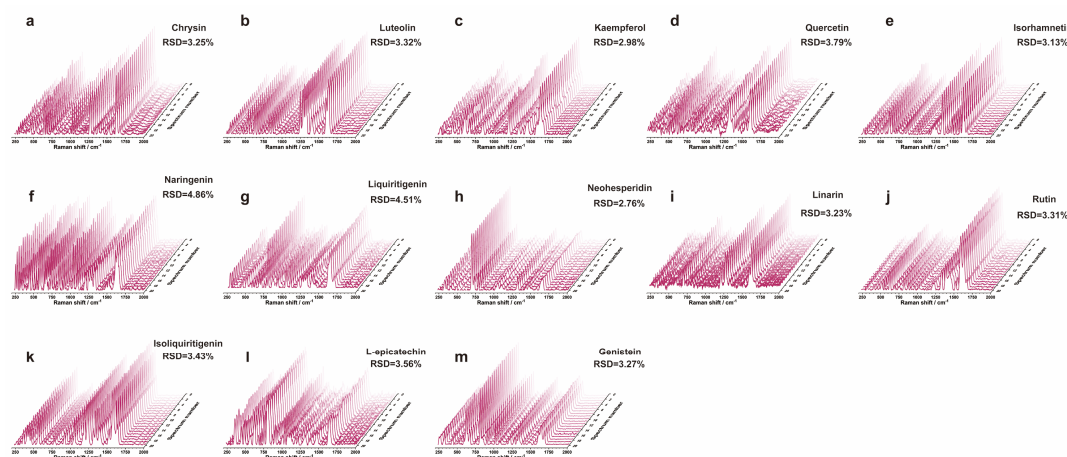


Figure S8. Reproducibility evaluation of ZnO superstructure-based SERS measurements. (a–m) Repeated SERS spectra and corresponding RSD values of 13 representative flavonoids, including chrysin, luteolin, kaempferol, quercetin, isorhamnetin, naringenin, liquiritigenin, neohesperidin, linarin, rutin, isoliquiritigenin, L-epicatechin, and genistein.

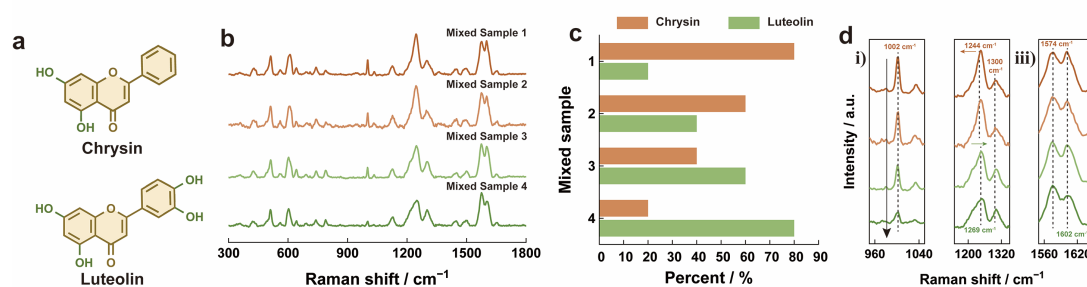


Figure S9. (a–d) Binary mixtures of chrysin and luteolin: (a) chemical structures; (b) SERS spectra (10^{-3} M); (c) composition ratios; (d) expanded spectral regions (950–1050, 1150–1350, and 1550–1650 cm^{-1}). Binary mixtures were prepared at molar ratios of 4:1, 3:2, 2:3, and 1:4, corresponding to individual concentrations of 8.0×10^{-4} and 2.0×10^{-4} M, 6.0×10^{-4} and 4.0×10^{-4} M, 4.0×10^{-4} and 6.0×10^{-4} M, and 2.0×10^{-4} and 8.0×10^{-4} M, respectively.

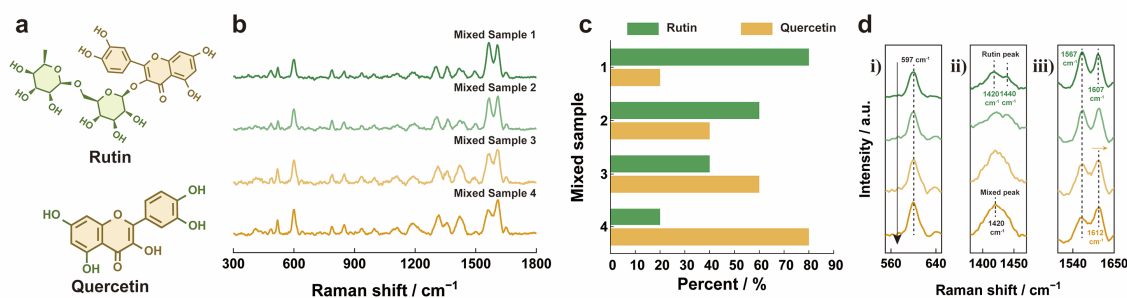


Figure S10. (a–d) Binary mixtures of rutin and quercetin: (a) chemical structures; (b) SERS spectra; (c) composition ratios; (d) expanded spectral regions (550–650, 1380–1470, and 1500–1650 cm^{-1}). Binary mixtures were prepared at molar ratios of 4:1, 3:2, 2:3, and 1:4, corresponding to individual concentrations of 8.0×10^{-4} and 2.0×10^{-4} M, 6.0×10^{-4} and 4.0×10^{-4} M, 4.0×10^{-4} and 6.0×10^{-4} M, and 2.0×10^{-4} and 8.0×10^{-4} M, respectively.

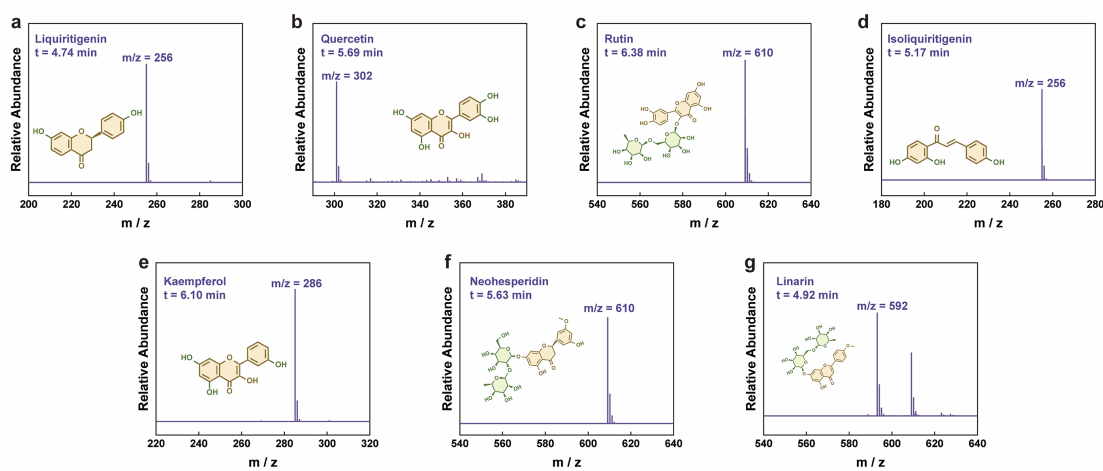


Figure S11. Extracted ion chromatogram and mass chromatogram of Northern Isatis Root (Heilongjiang).

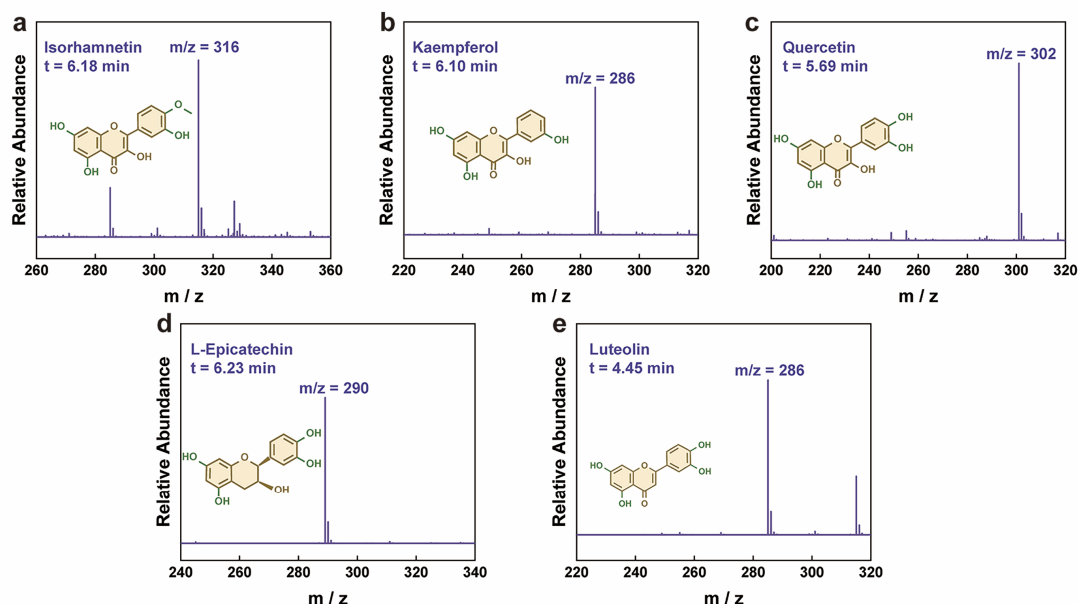


Figure S12. Extracted ion chromatogram and mass chromatogram of Southern Isatis Root (Sichuan).

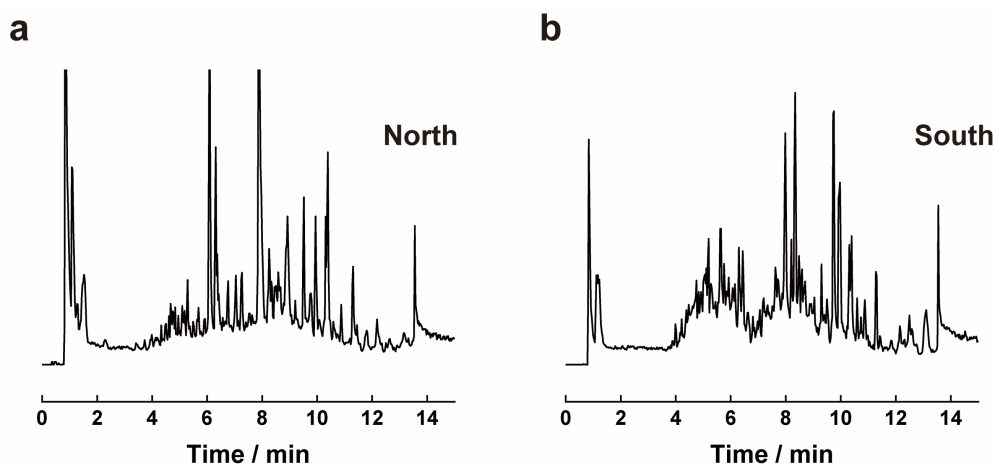


Figure S13. HPLC Chromatograms of Crude Extracts from Northern (Heilongjiang) and Southern (Sichuan) Isatis Root.

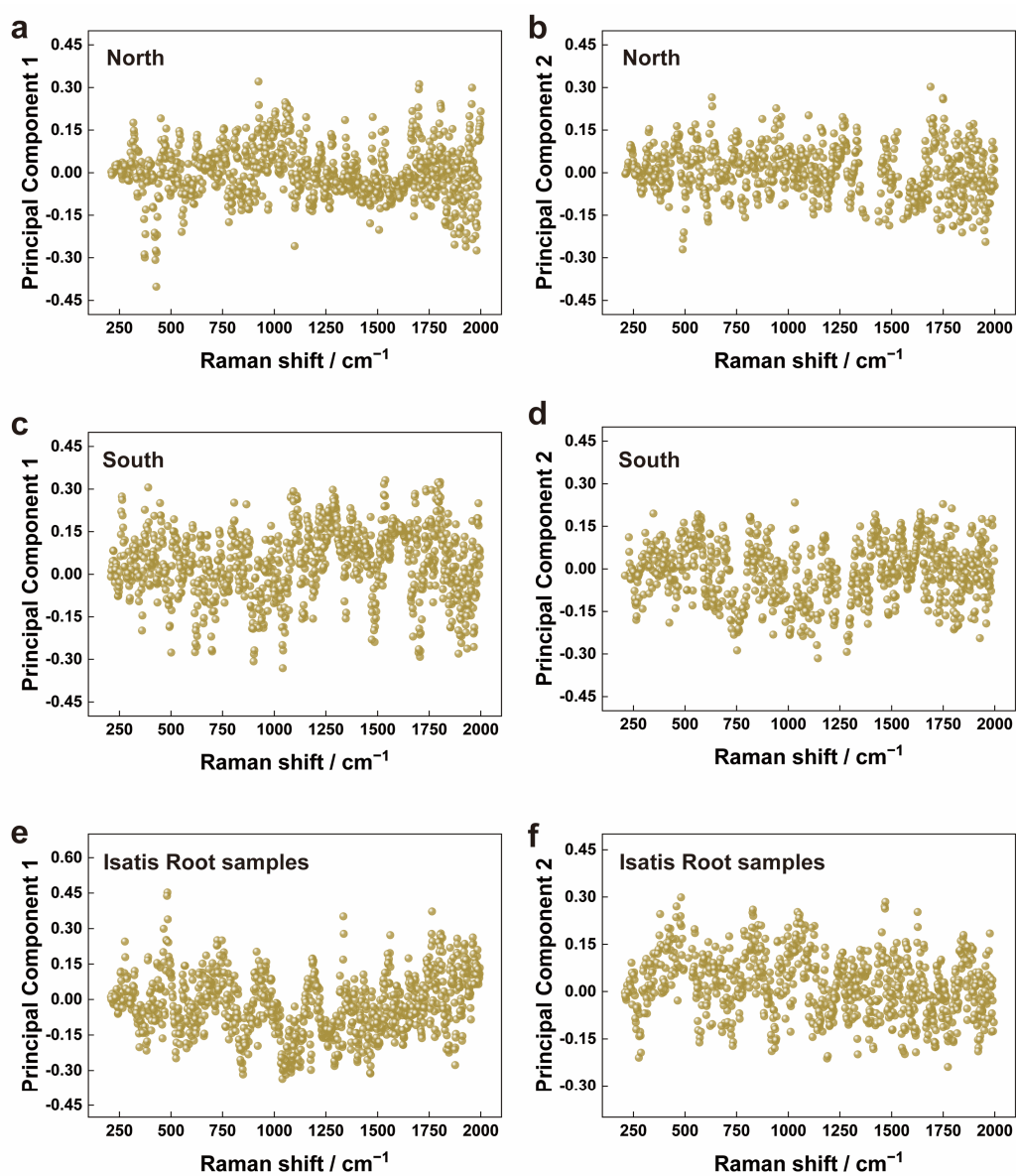


Figure S14. Loading plots of principal components from LDA analysis of Isatis Root samples. (a,b) Loading plots for northern Isatis Root samples. (c,d) Loading plots for southern Isatis Root samples. (e,f) Loading plots for Isatis Root samples with different geographical origins.

Table S1. Regions and assignments of characteristic bands of flavones [1–3].

Band	Raman Shift cm^{-1}
$\nu(\text{C}=\text{O})$	1660–1590 cm^{-1}
$\nu(\text{C}=\text{C})$	1620–1605 cm^{-1}
$\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{O})$	1490–1450 cm^{-1}
$\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{O})$	1380–1350 cm^{-1}
$\nu(\text{C}=\text{C})$	1250–1200 cm^{-1}
$\delta(\text{CCC})$ of ring	640–620 cm^{-1}

δ —bending vibration; ν —stretching vibration; τ —torsion vibration.

Table S2. Regions and assignments of characteristic bands of isoflavones [4,5].

Band	Raman Shift cm^{-1}
$\nu(\text{C}=\text{O})$ of ring B	1649–1694 cm^{-1}
$\nu(\text{C}=\text{C})$ of ring	1623–1608 cm^{-1}
$\nu(\text{C}=\text{O}) + \nu(\text{C}=\text{C})$	1200–1160 cm^{-1}
$\nu(\text{C}=\text{C})$	1185–1179 cm^{-1}
$\nu(\text{C}=\text{C})$	991–970 cm^{-1}
$\delta(\text{C}-\text{C}-\text{C})$ ring C + $\nu(\text{C}=\text{C})$ ring A	890–880 cm^{-1}
$\delta(\text{C}-\text{C}-\text{O})$ of ring B + $\delta(\text{C}-\text{O})$	566–547 cm^{-1}

δ —bending vibration; ν —stretching vibration; τ —torsion vibration.

Table S3. Regions and assignments of characteristic bands of flavanones [6,7].

Band	Raman Shift cm^{-1}
$\nu(\text{AR}-\text{C}=\text{O})$	1660–1590 cm^{-1}
$\nu(\text{C}=\text{C})$ of ring A	1555–1575 cm^{-1}
$\delta(\text{HCC})$ of ring C	1500–1480 cm^{-1}
$\delta(\text{HCC})$ of ring C	1460–1445 cm^{-1}
$\nu(\text{C}=\text{C})$ of ring A and B	1300–1240 cm^{-1}
$\tau(\text{HCCC})$ of ring C	1010–990 cm^{-1}
$\tau(\text{HCCC})$ of ring A	780–770 cm^{-1}

δ —bending vibration; ν —stretching vibration; τ —torsion vibration

Table S4. Regions and assignments of characteristic bands of flavonols [8,9].

Band	Raman Shift cm^{-1}
$\nu(\text{C}=\text{O})$ and $\nu(\text{C}_2=\text{C}_3)$	1620–1600 cm^{-1}
$\nu(\text{C}=\text{O})$, $\delta(\text{OH})$ and $\nu(\text{C}_2=\text{C}_3)$	1570–1540 cm^{-1}
$\nu(\text{C}=\text{C})$ of A ring and $\delta(\text{CH})$	1515–1485 cm^{-1}
$\nu(\text{C}=\text{C})$ of B ring and $\delta(\text{OH})$	1475–1420 cm^{-1}
$\delta(\text{OH})$ and $\nu(\text{C}=\text{C})$ of A ring	1370–1350 cm^{-1}
$\nu(\text{C}=\text{C})$ of A and B ring and $\delta(\text{OH})$	1320–1275 cm^{-1}
$\nu(\text{C}=\text{C})$ of ring C	1230–1210 cm^{-1}
$\nu(\text{C}-\text{OH})$ and $\delta(\text{C}-\text{H})$ of ring B	1190–1180 cm^{-1}
$\delta(\text{C}-\text{H})$ of ring A	1140–1115 cm^{-1}
$\nu(\text{C}-\text{C})$ of ring A, B and C	1010–995 cm^{-1}
$\nu(\text{OH})$ and $\delta(\text{C}-\text{C})$ of ring A, B and C	900–880 cm^{-1}
$\nu(\text{C}-\text{C})$ of ring A, B and C	850–825 cm^{-1}
$\nu(\text{C}-\text{C})$ of ring A, B and C	695–670 cm^{-1}
$\nu(\text{C}-\text{C})$ of ring B	640–620 cm^{-1}
$\nu(\text{C}-\text{C})$ of ring A, B and C	600–575 cm^{-1}
$\nu(\text{C}-\text{C})$ of ring A, B and C	525–510 cm^{-1}

δ —bending vibration; ν —stretching vibration; τ —torsion vibration.

Table S5. Regions and assignments of characteristic bands of flavanols [10,11].

Band	Raman Shift cm^{-1}
$\nu(\text{C}=\text{O})$	1680–1690 cm^{-1}
$\nu(\text{C}=\text{C})$ of A and B ring	1630–1600 cm^{-1}
$\nu(\text{C}=\text{C})$ of B ring	1305–1215 cm^{-1}
$\nu(\text{C}=\text{C})$ of A and C ring	1210–1190 cm^{-1}
$\nu(\text{C}=\text{C})$ of A and B ring	1135–1120 cm^{-1}
$\nu(\text{C}=\text{C})$ of B ring and $\nu(\text{CH})$	1025–1000 cm^{-1}
δ of ring A, $\delta(\text{C}-\text{O}-\text{C})$, $\delta(\text{C}-\text{C}-\text{C})$	780–740 cm^{-1}

δ —bending vibration; ν —stretching vibration; τ —torsion vibration.

Table S6. Regions and assignments of characteristic bands of chalcones [12,13].

Band	Raman Shift cm^{-1}
$\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{C})$	1680–1645 cm^{-1}
$\nu(\text{C}-\text{C})$	1590–1585 cm^{-1}
$\nu(\text{C}-\text{C})$ and $\delta(\text{HCC})$	1420–1415 cm^{-1}
$\nu(\text{C}-\text{C})$ and $\nu(\text{C}-\text{O})$	1230–1210 cm^{-1}
$\nu(\text{C}=\text{C})$ and $\delta(\text{HCC})$	1160–1050 cm^{-1}
$\delta(\text{C}-\text{C}-\text{C})$	820–810 cm^{-1}

δ —bending vibration; ν —stretching vibration; τ —torsion vibration.

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