Supporting information

Prenylated flavonoids from roots of *Glycyrrhiza uralensis* induce differentiation of B16-F10 melanoma cells

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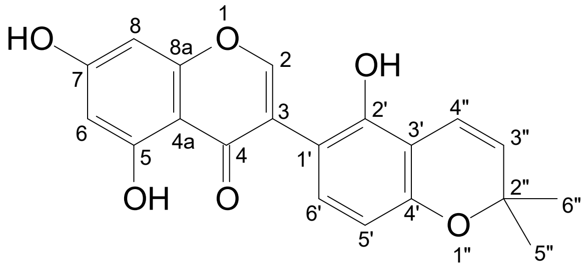
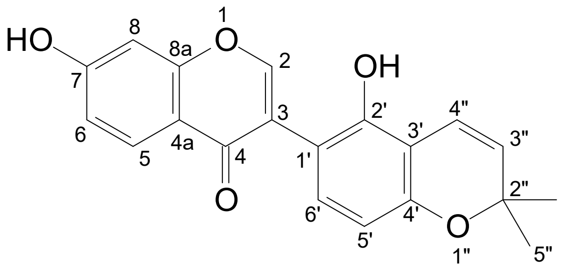
Part 1. The MS and ^{1}H NMR data of 10 flavonoid compounds

GF-1: faint yellow needle crystal; HR-ESI/MS: *m/z* 353.1024 $[M+H]^+$; molecular formula: $C_{20}H_{16}O_6$; ^{1}H NMR (DMSO-d_6, δ, ppm): 1.38 (6H, s, 5''-H and 6''-H), 5.68(1H, d, *J*=10.0, 3''-H), 6.23(1H, d, *J*=1.9, 6-H), 6.33(1H, d, *J*=8.3, 5'-H), 6.40(1H, d，*J*=1.9, 8-H), 6.67(1H, d, *J*=10.0, 4''-H), 6.89(1H, d, *J*=8.3, 6'-H), 8.18(1H, s, 2-H), 8.85(1H, s, 2'-OH), 10.83(1H, s, 7-OH), 12.85(1H, s, 5-OH). ^{1}H and ^{13}C NMR data were identical with the literature values of Licoisoflavone B [1].



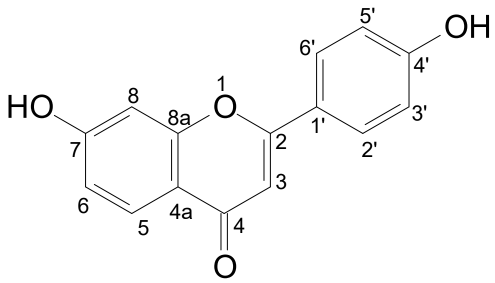
Licoisoflavone B

GF-2: faint yellow needle crystal; HR-ESI/MS: *m/z* 337.1071 $[M+H]^+$; molecular formula: $C_{20}H_{16}O_5$; ^{1}H NMR (DMSO-d_6, δ, ppm): 1.38 (6H, s, 5''-H and 6''-H), 5.68 (1H, d, *J*=10.0, 3''-H), 6.34 (1H, d, *J*=8.3, 5'-H), 6.68 (1H, d, *J*=10.0, 4''-H), 6.91 (1H, d, *J*=1.9, 8-H), 6.93 (1H, d, *J*=8.3, 6'-H), 6.97 (1H, dd, *J*=8.8, 1.9, 6-H), 7.98 (1H, d, *J*=8.8, 5-H), 8.25 (1H, s, 2-H), 9.11 (1H, s, 2'-OH), 10.85 (1H, s, 7-OH). ^{1}H and ^{13}C NMR data were identical with the literature values of glabrone [2].



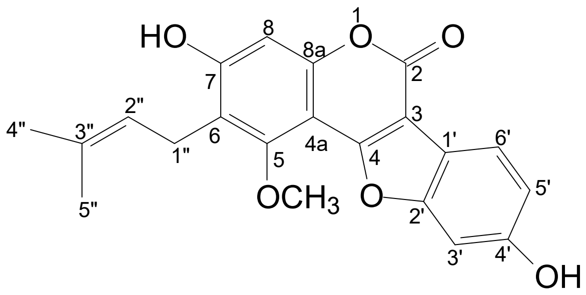
Glabrone

GF-3: yellow needle crystal; HR-ESI/MS: *m/z* 353.1012 $[M+H]^+$; molecular formula: $C_{20}H_{16}O_6$; ^{1}H NMR (DMSO-d_6, δ, ppm): 6.72 (1H, s, H-3), 7.87 (1H, *J*=9.0, H-5)，7.91 (2H, m, H-2', 6'), 6.97 (1H, d, *J* = 2.5 , H-8) , 6.93 (2H, m, H-3', 5'), 6.89 (1H, m, H-6), 10.73 (1H, br, 7-OH)，10.26 (1H, br, 4'-OH). ^{1}H and ^{13}C NMR data were in agreement with the literature values of 7, 4'-dihydroxyflavone [3].



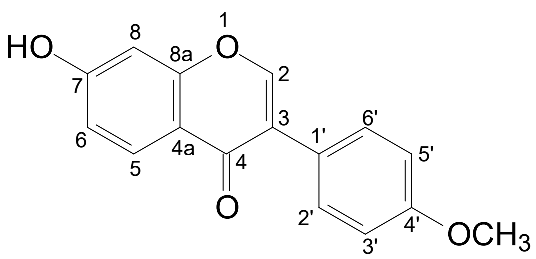
7, 4'-dihydroxyflavone

GF-4: faint yellow needle crystal; HR-ESI/MS: *m/z* 367.1187 $[M+H]^+$; molecular formula: $C_{21}H_{18}O_6$; ^{1}H NMR (DMSO-d_6, δ, ppm): 1.76 (6H, s, 4''-H and 5''-H), 3.32 (2H, d, *J* =6.8, 1''-H), 3.90 (3H, s, 5-OCH_3), 5.19 (1H, m, 2''-H), 6.77 (1H, s, 8-H), 6.95 (1H, dd, *J*=2.0, 8.4, 5'-H), 7.17(1H, d, *J*=1.6, 3'-H), 7.71 (1H, d, *J* =8.4, 6'-H), 7.71 (1H, d, *J*=8.4, 6'-H), 10.04 (1H, s, 4'-OH), 10.81 (1H, s, 7-OH). ^{1}H and ^{13}C NMR data were in agreement with the literature values of neoglycyrol [4].



Neoglycyrol

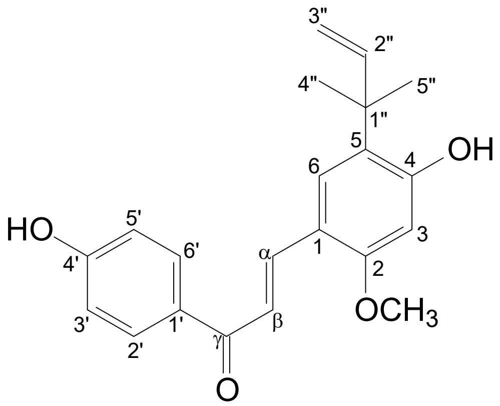
GF-5: yellow needle crystal; HR-ESI/MS: *m/z* 269.0808 $[M+H]^+$; molecular formula: $C_{16}H_{12}O_4$; ^{1}H NMR (DMSO-d_6, δ, ppm): 3.77 (3H, s, 4'-OCH_3), 6.97 (2H, d, *J*=8.7, 3'-H), 7.49 (2H, d, *J*=8.7, 2'-H), 8.31 (1H, s, 2-H), 7.96 (1H, d, *J*=8.8, 5-H)，6.92 (1H, dd, *J*=8.8, 2.0, 6-H), 6.87 (1H, d, *J*=2.0, 8-H), 10.75 (1H, s, 7-OH); ^{1}H and ^{13}C NMR data were in agreement with the literature values of formononetin [5].



Formononetin

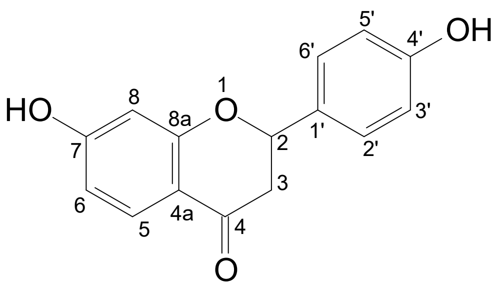
GF-6: yellow needle crystal; HR-ESI/MS: *m/z* 339.1590 $[M+H]^+$; molecular formula: $C_{21}H_{22}O_4$; ^{1}H

NMR (DMSO-d_6, δ, ppm): 1.45 (6H, s, 4''-H and 5''-H), 3.83 (3H, s, 2-OCH_3), 4.95 (1H, d, *J*=17.8, 3''a-H), 4.92 (1H, d, *J*=10.3, 3''b-H), 6.24 (1H, dd, *J*=17.8, 10.3, 2''-H), 6.52 (1H, s, 3-H), 6.88 (2H, d, *J*=8.5, 3'-H and 5'-H), 7.52 (1H, s, 6-H), 7.58 (1H, d, *J*=15.0, α-H), 7.89 (1H, d, *J*=15.0, β-H), 7.97 (2H, d, *J*=8.5, 2'-H and 6'-H), 10.28 (1H, s, 4'-OH), 10.10 (1H, s, 4-OH). ^{1}H and ^{13}C NMR data were identical with the literature values of licochalcone A [6].



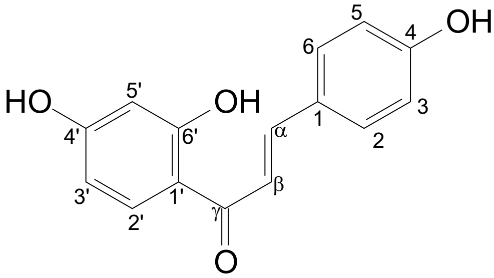
Licochalcone A

GF-7: white needle crystal; HR-ESI/MS: *m/z* 257.0809 $[M+H]^+$; molecular formula: $C_{15}H_{12}O_4$; ^{1}H NMR (DMSO-d_6, δ, ppm): 2.63 (1H, dd, *J*=16.8, 2.8, 3a-H), 3.10 (1H, dd, *J*=12.8, 16.7, 3b-H), 5.44 (1H, dd, *J*=12.8，2.7, 2-H), 6.33 (1H, d, *J*=2.1, 8-H)，6.50 (1H, dd, *J*=2.1, 8.6, 6-H), 6.79 (2H, d, *J*=8.5, 3'-H and 5'-H), 7.32 (2H, d, *J*=8.5, 2'-H and 6'-H), 7.64 (1H, d, *J*=8.7, 5-H), 10.51 (1H, s, 7-OH)，9.52 (1H, s, 4'-OH). ^{1}H and ^{13}C NMR data were identical with the literature values of liquiritigenin [5].



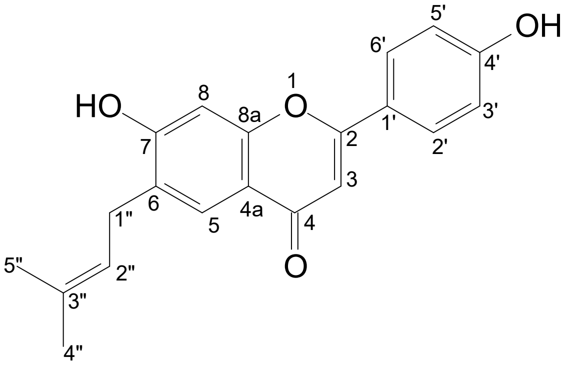
Liquiritigenin

GF-8: yellow needle crystal; HR-ESI/MS: *m/z* 257.0805 $[M+H]^+$; molecular formula: $C_{15}H_{12}O_4$; ^{1}H NMR (DMSO-d_6, δ, ppm): 6.42 (1H, d, *J*=8.6, 6'-H), 6.84 (2H, dd, *J*=8.6, 2.2, 5'-H), 7.51 (1H, d, *J*=15.0, α-H), 7.74 (2H, m, 3-H and 5-H)， 7.72 (2H, m, 2-H, and 6-H), 7.82 (1H, d, *J*=15.0, β-H), 8.15 (1H, d, *J*=2.2, 3'-H), 10.10 (1H, s, 4-OH), 10.60 (1H, s,2'-OH), 13.57 (1H, s, 4'-OH). ^{1}H and ^{13}C NMR data were identical with the literature values of isoliquiritigenin [7].



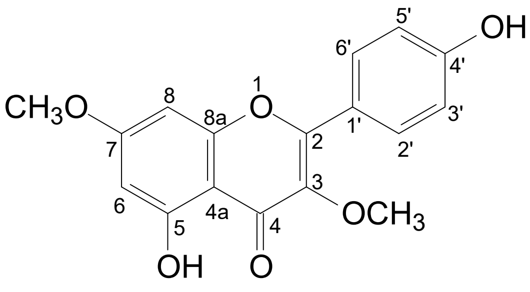
Isoliquiritigenin

GF-9: faint yellow needle crystal; HR-ESI/MS: *m/z* 323.1278 $[M+H]^+$; molecular formula: $C_{20}H_{18}O_4$; ^{1}H NMR (DMSO-d_6, δ, ppm): 1.68 (3H, s, 5''-H), 1.73 (3H, s, 4''-H), 3.29 (1H,d, *J*=7.3, 1''-H), 5.32 (1H, t, *J*=7.3, 2''-H), 6.69 (1H, s, 3-H), 6.92 (2H, d, *J*=8.7, 3'-H and 5'-H), 6.97 (1H, s, 8-H), 7.66 (1H, s, 5-H), 7.88 (2H, d, *J*=8.7, 2'-H and 6'-H), 10.21 (1H, s, 4'-OH), 10.81(1H, s, 7-OH). ^{1}H and ^{13}C NMR data were identical with the literature values of licoflavone [8].

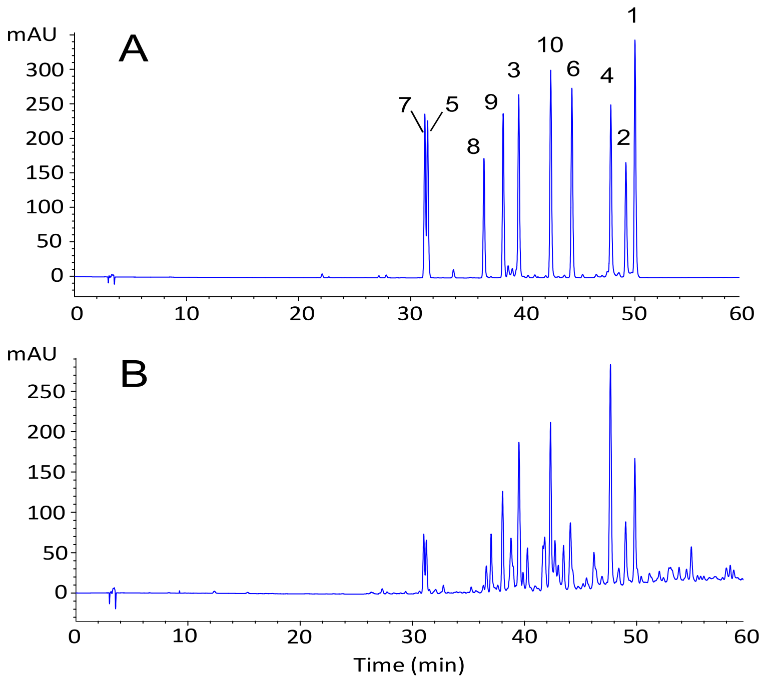


Licoflavone

GF-10: yellow needle crystal; HR-ESI/MS: *m/z* 315.0866 $[M+H]^+$; molecular formula: $C_{17}H_{14}O_6$; ^{1}H NMR (DMSO-d_6, δ, ppm): 3.86 (3H, s, 7-OCH_3), 3.80 (3H, s, 3-OCH_3), 6.36 (1H, d, *J*=1.8, 8-H), 6.72 (1H, d, *J*=1.8, 6-H), 6.95 (2H, d, *J*=8.7, 3'-H and 5'-H), 7.97 (2H, d, *J*=8.7, 2'-H and 6'-H), 10.25 (1H, s, 4'-OH), 12.66 (1H, s, 5-OH);. ^{1}H and ^{13}C NMR data were identical with the literature values of kumatakenin A [9].



Kumatakenin A



Part 2. HPLC of isolated flavonoids and dichloromethane extract of *G. uralensis*

(A) 10 flavonoids isolated from CH_2Cl_2 extract of *G. uralensis*; (B) CH_2Cl_2 extract of *G. uralensis*

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