

Supplementary Materials

1. Spectroscopic Data of the Known Compounds

Taxifolin (7). Pale yellow needles; $[\alpha]_D^{20} +42.5$ (c 1.30, acetone); $^1\text{H-NMR}$ (400 MHz, CD_3OD) δ : 6.95 (1H, d, $J = 1.2$ Hz, H-2'), 6.83 (1H, dd, $J = 8.0, 1.6$ Hz, H-6'), 6.79 (1H, d, $J = 8.0$ Hz, H-5'), 5.87 (2H, s, H-6, 8), 4.90 (1H, d, $J = 11.6$ Hz, H-2), 4.49 (1H, d, $J = 11.5$ Hz, H-3); $^{13}\text{C-NMR}$ (100 MHz, CD_3OD) δ : 198.4 (C-4), 168.8 (C-7), 165.3 (C-5), 164.5 (C-9), 147.1 (C-4'), 146.3 (C-3'), 129.9 (C-1'), 120.9 (C-6'), 116.1 (C-2'), 115.9 (C-5'), 101.8 (C-10), 97.3 (C-6), 96.3 (C-8), 85.1 (C-2), 73.7 (C-3).

Naringenin (8). Pale yellow needles; $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ : 7.30 (2H, d, $J = 8.0$ Hz, H-2', 6'), 6.78 (2H, d, $J = 8.0$ Hz, H-3', 5'), 5.87 (1H, s, H-6, 8), 5.43 (1H, dd, $J = 12.4, 2.9$ Hz, H-2), 3.28 (1H, dd, $J = 13.2, 16.8$ Hz, H-3b), 2.67 (1H, dd, $J = 16.8, 2.9$ Hz, H-3a); $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ : 196.4 (C-4), 166.6 (C-7), 163.4 (C-5), 162.9 (C-9), 157.7 (C-4'), 128.8 (C-1'), 128.3 (C-2', 6'), 115.1 (C-3', 5'), 101.7 (C-10), 95.7 (C-6), 94.9 (C-8), 78.4 (C-2), 41.9 (C-3).

Dihydrokaempferol (9). White powder; $[\alpha]_D^{20} +22.8$ (c 1.32, MeOH); $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ : 11.89, 10.80, 9.53 (each 1H, s, OH), 7.30 (2H, d, $J = 8.0$ Hz, H-2', 6'), 6.77 (2H, d, $J = 7.6$ Hz, H-3', 5'), 5.90 (1H, d, $J = 2.0$ Hz, H-8), 5.85 (1H, d, $J = 2.0$ Hz, H-6), 5.74 (1H, d, $J = 4.4$ Hz, 3-OH), 5.04 (1H, d, $J = 11.6$ Hz, H-2), 4.57 (1H, dd, $J = 10.4, 6.0$ Hz, H-3); $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ : 197.9 (C-4), 166.7 (C-7), 163.3 (C-5), 162.6 (C-9), 157.7 (C-4'), 129.4 (C-2', 6'), 127.5 (C-1'), 114.9 (C-3', 5'), 100.5 (C-10), 96.0 (C-6), 95.0 (C-8), 82.9 (C-2), 71.4 (C-3).

Sakuranetin (10). Pale yellow solid; $[\alpha]_D^{20} -7$ (c 0.5, MeOH); $^1\text{H-NMR}$ (600 MHz, CD_3OD) δ : 7.31 (2H, d, $J = 8.4$ Hz, H-2', 6'), 6.82 (2H, d, $J = 8.4$ Hz, H-3', 5'), 6.06 (1H, d, $J = 2.4$ Hz, H-8), 5.89 (1H, s, H-6), 5.34 (1H, dd, $J = 12.6, 3.0$ Hz, H-2), 3.91 (3H, s, 7-OCH₃), 3.11 (1H, dd, $J = 17.4, 13.2$ Hz, H-3b), 2.70 (1H, dd, $J = 16.8, 3.0$ Hz, H-3a); $^{13}\text{C-NMR}$ (150 MHz, CD_3OD) δ : 197.9 (C-4), 168.8 (C-7), 165.7 (C-5), 165.1 (C-9), 159.2 (C-4'), 131.3 (C-1'), 129.2 (C-2', 6'), 116.5 (C-3', 5'), 103.5 (C-10), 96.4 (C-6), 93.9 (C-8), 80.7 (C-2), 57.1 (7-OCH₃), 44.2 (C-3).

Isoastilbin (11). White powder; $[\alpha]_D^{20} -144.6$ (c 0.87, MeOH); ESIMS (m/z): 449 $[\text{M-H}]^-$, 473 $[\text{M+Na}]^+$; CD (6.35×10^{-5} MeOH): $\Delta\epsilon$ (nm) +5.89 (342), -14.79 (300); $^1\text{H-NMR}$ (500 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 7.66 (1H, d, $J = 1.5$ Hz, H-2'), 7.30 (1H, dd, $J = 8.0, 2.0$ Hz, H-6'), 7.25 (1H, d, $J = 8.5$ Hz, H-5'), 6.40 (1H, d, $J = 2.0$ Hz, H-6), 6.39 (1H, d, $J = 2.0$ Hz, H-8), 5.88 (1H, d, $J = 1.5$ Hz, H-2), 5.81 (1H, d, $J = 2.5$ Hz, H-3), 4.91 (1H, d, $J = 2.5$ Hz, H-1''), 4.51 (1H, br. s, H-2''), 4.37 (1H, dd, $J = 9.5, 3.5$ Hz, H-5''), 4.14 (1H, m, H-3''), 3.41 (1H, m, H-4''), 1.45 (3H, d, $J = 6.0$ Hz, H-6''); $^{13}\text{C-NMR}$ (125 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 194.2 (C-4), 168.9 (C-7), 165.6 (C-5), 163.7 (C-9), 147.6 (C-4'), 147.4 (C-3'), 127.6 (C-1'), 118.9 (C-6'), 116.4 (C-5'), 115.5 (C-2'), 101.5 (C-1''), 100.6 (C-10), 97.5 (C-6), 96.4 (C-8), 81.7 (C-2), 74.4 (C-3), 73.2 (C-4''), 72.4 (C-3''), 71.9 (C-2''), 70.4 (C-5''), 18.4 (C-6'').

Astilbin (12). White powder; $[\alpha]_D^{20} -13.5$ (c 0.76, MeOH); ESIMS (m/z): 449 $[\text{M-H}]^-$, 473 $[\text{M+Na}]^+$; CD (3.98×10^{-5} MeOH): $\Delta\epsilon$ (nm) +5.89-15.46 (294), +5.66 (330); $^1\text{H-NMR}$ (500 MHz, CD_3OD) δ : 6.95 (1H, d, $J = 2.0$ Hz, H-2'), 6.82 (1H, dd, $J = 8.5, 2.0$ Hz, H-6'), 6.80 (1H, d, $J = 8.0$ Hz, H-5'), 5.91 (1H, d, $J = 2.5$ Hz, H-6), 5.89 (1H, d, $J = 2.5$ Hz, H-8), 5.07 (1H, d, $J = 10.5$ Hz, H-2), 4.55 (1H, d,

$J = 10.5$ Hz, H-3), 4.24 (1H, dq, $J = 10.0, 6.5$ Hz, H-5''), 4.04 (1H, s, H-1''), 3.65 (1H, dd, $J = 9.5, 3.5$ Hz, H-3''), 3.53 (1H, br. s, H-2''), 3.31 (1H, dd, $J = 9.6, 9.6$ Hz, H-4''), 1.17 (1H, d, $J = 6.0$ Hz, H-6''); ^{13}C -NMR (125 MHz, CD_3OD) δ : 196.0 (C-4), 168.6 (C-7), 165.5 (C-5), 164.1 (C-9), 147.4 (C-4'), 146.6 (C-3'), 129.2 (C-1'), 120.5 (C-6'), 116.3 (C-5'), 115.5 (C-2'), 102.5 (C-1''), 102.2 (C-10), 97.4 (C-6), 96.3 (C-8), 83.9 (C-2), 78.6 (C-3), 73.8 (C-4''), 72.2 (C-3''), 71.8 (C-2''), 70.5 (C-5''), 17.9 (C-6'').

Neoastilbin (13). White solid; $[\alpha]_{\text{D}}^{20} -85.6$ (c 0.85, MeOH); CD (2.05×10^{-5} MeOH): $\Delta\epsilon$ (nm) +0.76 (297), -1.43 (330); ^1H -NMR (600 MHz, CD_3OD) δ : 6.97 (1H, s, H-2'), 6.80 (2H, s, H-5', 6'), 5.92 (1H, d, $J = 2.4$ Hz, H-6), 5.89 (1H, d, $J = 2.4$ Hz, H-8), 5.16 (1H, s, H-2), 4.99 (1H, s, H-1'), 4.64 (1H, d, $J = 11.4$ Hz, H-3), 4.00 (1H, s, H-2''), 3.38 (1H, dd, $J = 9.6, 3.0$ Hz, H-3''), 3.20 (1H, t, H-4''), 2.31 (1H, m, H-5''), 0.90 (3H, d, $J = 6.0$ Hz, H-6''); ^{13}C -NMR (150 MHz, CD_3OD) δ : 197.9 (C-4), 168.9 (C-7), 165.7 (C-5), 164.5 (C-9), 147.6 (C-4'), 146.8 (C-3'), 130.2 (C-1'), 121.2 (C-6'), 116.5 (C-5'), 115.7 (C-2'), 103.0 (C-1''), 102.3 (C-10), 97.6 (C-6), 96.5 (C-8), 83.9 (C-2), 77.1 (C-3), 73.6 (C-4''), 72.1 (C-3''), 72.1 (C-2''), 70.5 (C-5''), 18.1 (C-6'').

Neoisostilbin (14). White solid; ESIMS (m/z): 449 $[\text{M}-\text{H}]^-$, 473 $[\text{M}+\text{Na}]^+$; CD (5.05×10^{-5} MeOH): $\Delta\epsilon$ (nm) +2.47 (297), -1.49 (340); ^1H -NMR (500 MHz, CD_3OD) δ : 6.99 (1H, d, $J = 2.0$ Hz, H-2'), 6.84 (1H, dd, $J = 6.0, 2.0$ Hz, H-6'), 6.79 (1H, d, $J = 8.5$ Hz, H-5'), 5.95 (1H, d, $J = 2.5$ Hz, H-6), 5.92 (1H, d, $J = 2.5$ Hz, H-8), 5.32 (1H, d, $J = 1.5$ Hz, H-2), 4.23 (1H, d, $J = 1.5$ Hz, H-1'), 4.06 (1H, d, $J = 2.0$ Hz, H-3), 3.59 (1H, s, H-2''), 3.49 (1H, dq, $J = 9.0, 6.5$ Hz, H-5''), 3.34 (1H, s, H-3''), 3.26 (1H, s, H-4''), 1.13 (3H, d, $J = 6.5$ Hz, H-6''); ^{13}C -NMR (125 MHz, CD_3OD) δ : 193.9 (C-4), 168.7 (C-7), 166.0 (C-5), 164.5 (C-9), 146.7 (C-4'), 146.3 (C-3'), 128.5 (C-1'), 119.4 (C-6'), 116.1 (C-5'), 115.3 (C-2'), 102.6 (C-1''), 102.1 (C-10), 97.2 (C-6), 96.0 (C-8), 82.3 (C-2), 78.4 (C-3), 73.7 (C-4''), 72.0 (C-3''), 71.6 (C-2''), 70.6 (C-5''), 17.5 (C-6'').

Engeletin (15). Yellow powder; $[\alpha]_{\text{D}}^{20} -14.2$ (c 0.32, MeOH); ^1H -NMR (500 MHz, CD_3OD) δ : 7.35 (2H, br. d, $J = 8.5$ Hz, H-2', 6'), 6.83 (2H, br. d, $J = 8.5$ Hz, H-3', 5'), 5.91 (1H, d, $J = 2.5$ Hz, H-8), 5.89 (1H, d, $J = 2.5$ Hz, H-6), 5.15 (1H, d, $J = 9.5$ Hz, H-2), 4.60 (1H, d, $J = 11.0$ Hz, H-3), 4.00 (1H, d, $J = 1.5$ Hz, H-1'), 3.64 (1H, dd, $J = 3.0, 1.5$ Hz, H-2''), 3.49 (1H, dd, $J = 9.5, 3.0$ Hz, H-3''), 3.29 (1H, m, H-4''), 2.25 (1H, m, H-5''), 1.17 (3H, d, $J = 6.5$ Hz, H-6''); ^{13}C -NMR (125 MHz, CD_3OD) δ : 196.0 (C-4), 168.7 (C-7), 165.5 (C-5), 164.1 (C-9), 159.5 (C-4'), 130.2 (C-2', 6'), 128.6 (C-1'), 116.4 (C-3', 5'), 102.5 (C-1''), 102.2 (C-10), 97.4 (C-8), 96.3 (C-6), 83.9 (C-2), 78.7 (C-3), 73.8 (C-4''), 72.2 (C-3''), 70.5 (C-5''), 18.0 (C-6'').

Arthromerin B (16). Pale yellow powder; $[\alpha]_{\text{D}}^{20} +28.3$ (c 0.90, MeOH); CD (2.16×10^{-5} MeOH): $\Delta\epsilon$ (nm) -19.41 (291), +3.99 (330); ^1H -NMR (500 MHz, CD_3OD) δ : 7.35 (2H, d, $J = 8.5$ Hz, H-2', 6'), 6.78 (2H, d, $J = 8.5$ Hz, H-3', 5'), 5.92 (1H, d, $J = 2.0$ Hz, H-8), 5.89 (1H, d, $J = 1.5$ Hz, H-6), 5.18 (1H, d, $J = 11.0$ Hz, H-2), 4.84 (1H, d, $J = 8.5$ Hz, H-3), 4.70 (1H, d, $J = 7.4$ Hz, H-1'), 3.89 (1H, dd, $J = 12.0, 2.4$ Hz, H-6''b), 3.76 (1H, dd, $J = 12.0, 6.0$ Hz, H-6''a), 3.55 (1H, m, H-2''), 3.52 (1H, m, H-5''), 3.35 (1H, m, H-3''), 3.29 (1H, m, H-4''); ^{13}C -NMR (125 MHz, CD_3OD) δ : 196.3 (C-4), 169.2 (C-7), 165.5 (C-5), 164.4 (C-9), 159.5 (C-4'), 130.3 (C-2', 6'), 128.4 (C-1'), 116.4 (C-3', 5'), 102.4

(C-1''), 101.5 (C-10), 97.4 (C-8), 96.4 (C-6), 83.7 (C-2), 77.6 (C-5''), 76.4 (C-3), 73.1 (C-3''), 71.1 (C-2''), 66.9 (C-4''), 63.5 (C-6'').

Sinensin (**17**). Yellow solid; CD (2.10×10^{-5} MeOH): $\Delta\epsilon$ (nm) -4.58 (298), +1.17 (336); ESIMS (m/z): 449 [M-H]⁻, 473 [M+Na]⁺; ¹H-NMR (600 MHz, CD₃OD) δ : 7.35 (2H, d, J = 8.4 Hz, H-2', 6'), 6.83 (2H, d, J = 8.5 Hz, H-3', 5'), 6.47 (1H, d, J = 2.4 Hz, H-8), 6.09 (1H, d, J = 1.8 Hz, H-6), 4.87 (1H, d, J = 11.4 Hz, H-2), 4.39 (1H, d, J = 11.4 Hz, H-3), 4.80 (1H, d, J = 7.4 Hz, H-1''), 3.94 (1H, dd, J = 12.0, 1.8 Hz, H-6''b), 3.76 (1H, dd, J = 12.0, 5.4 Hz, H-6''a), 3.45-3.58 (4H, m, H-2''-5''); ¹³C-NMR (150 MHz, CD₃OD) δ : 193.9 (C-4), 167.5 (C-5), 166.1 (C-9), 162.2 (C-7), 159.4 (C-4'), 130.5 (C-2', 6'), 129.5 (C-1'), 116.3 (C-3', 5'), 105.1 (C-1''), 104.4 (C-10), 100.2 (C-8), 99.3 (C-6), 84.5 (C-2), 78.8 (C-5''), 77.6 (C-3), 74.8 (C-3''), 71.4 (C-2''), 67.0 (C-4''), 62.7 (C-6'').

(2*R*, 3*R*)-*Taxifolin 3'-O-β-D-glucopyranoside* (**18**). Pale yellow solid; CD (2.20×10^{-5} MeOH): $\Delta\epsilon$ (nm) -4.89 (292), +0.45 (326); ¹H-NMR (600 MHz, CD₃OD) δ : 7.38 (1H, d, J = 1.8 Hz, H-2'), 7.10 (1H, dd, J = 8.4, 2.4 Hz, H-6'), 6.90 (1H, d, J = 7.8 Hz, H-5'), 5.93 (1H, d, J = 2.4 Hz, H-6), 5.89 (1H, d, J = 2.4 Hz, H-8), 4.98 (1H, d, J = 11.4 Hz, H-2), 4.83 (1H, d, J = 7.4 Hz, H-1''), 4.57 (1H, d, J = 11.4 Hz, H-3), 3.89 (1H, dd, J = 12.0, 2.4 Hz, H-6''), 3.68 (1H, dd, J = 12.0, 6.0 Hz, H-2''), 3.64 (1H, s, H-5''), 3.51 (1H, dd, J = 9.6, 10.2 Hz, H-3''), 3.43 (1H, m, H-4''); ¹³C-NMR (150 MHz, CD₃OD) δ : 198.8 (C-4), 168.7 (C-7), 164.8 (C-5), 164.0 (C-9), 149.3 (C-4'), 146.9 (C-3'), 129.7 (C-1'), 124.9 (C-6'), 118.5 (C-2'), 117.1 (C-5'), 104.3 (C-1''), 101.2 (C-10), 97.6 (C-6), 96.5 (C-8), 85.1 (C-2), 78.6 (C-5''), 77.9 (C-3''), 75.1 (C-2''), 73.7 (C-3), 71.7 (C-4''), 62.8 (C-6'').

(2*S*, 3*S*)-*Glucodistylin* (**19**). Pale yellow solid; CD (3.62×10^{-5} MeOH): $\Delta\epsilon$ (nm) +1.51 (295), -3.24 (327); ¹H-NMR (600 MHz, CD₃OD) δ : 6.95 (1H, d, J = 1.8 Hz, H-2'), 6.79 (1H, dd, J = 8.0, 1.8 Hz, H-6'), 6.75 (1H, d, J = 8.4 Hz, H-5'), 5.90 (1H, d, J = 1.2 Hz, H-6), 5.89 (1H, d, J = 1.8 Hz, H-8), 5.26 (1H, d, J = 9.0 Hz, H-2), 4.90 (1H, d, J = 7.4 Hz, H-1''), 4.68 (1H, d, J = 7.8 Hz, H-3), 3.80 (1H, dd, J = 12.0, 2.4 Hz, H-6''b), 3.70 (1H, dd, J = 12.0, 6.0 Hz, H-6''a), 3.43 (1H, m, H-2''), 3.35 (1H, s, H-5''), 3.19 (1H, m, H-3''), 3.13 (1H, m, H-4''); ¹³C-NMR (150 MHz, CD₃OD) δ : 195.9 (C-4), 170.1 (C-7), 166.9 (C-5), 165.9 (C-9), 147.5 (C-3'), 146.3 (C-3'), 129.3 (C-1'), 121.3 (C-6'), 116.4 (C-2'), 116.2 (C-5'), 104.8 (C-1''), 102.7 (C-10), 97.7 (C-6), 96.5 (C-8), 83.7 (C-2), 78.1 (C-5''), 77.9 (C-3''), 75.6 (C-2''), 72.5 (C-3), 71.7 (C-4''), 63.1 (C-6'').

(-)-*Epicatechin* (**20**). White powder; $[\alpha]_D^{20}$ -70.50 (c 0.20, MeOH); ¹H-NMR (400 MHz, DMSO-*d*₆) δ : 6.88 (1H, s, H-2'), 6.65 (1H, d, J = 8.0 Hz, H-6'), 6.64 (1H, d, J = 8.0 Hz, H-5'), 5.88 (1H, d, J = 2.4 Hz, H-8), 5.70 (1H, d, J = 2.0 Hz, H-6), 4.64 (1H, s, H-2), 3.98 (1H, m, H-3), 2.67 (1H, dd, J = 16.4, 4.4 Hz, H-4a), 2.44 (1H, dd, J = 16.4, 3.6 Hz, H-4b); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ : 156.9 (C-9), 156.7 (C-7), 156.2 (C-5), 144.9 (C-3'), 144.8 (C-4'), 131.0 (C-1'), 118.4 (C-6'), 115.3 (C-5'), 115.2 (C-2'), 98.9 (C-10), 95.5 (C-6), 94.5 (C-8), 78.5 (C-2), 65.3 (C-3), 28.6 (C-4).

(+)-*Catechin* (**21**). White powder; $[\alpha]_D^{20}$ +25.5 (c 0.08, MeOH); ¹H-NMR (400 MHz, DMSO-*d*₆) δ : 6.70 (1H, d, J = 2.0 Hz, H-2'), 6.67 (1H, dd, J = 8.0, 1.6 Hz, H-6'), 6.58 (1H, d, J = 6.4 Hz, H-5'), 5.87 (1H, d, J = 2.0 Hz, H-8), 5.67 (1H, d, J = 2.0 Hz, H-6), 4.46 (1H, d, J = 7.6 Hz, H-2), 3.79 (1H, m, H-3), 2.64 (1H, dd, J = 16.0, 5.2 Hz, H-4a), 2.33 (1H, dd, J = 16.4, 7.6 Hz, H-4b); ¹³C-NMR (100

MHz, DMSO- d_6) δ : 156.4 (C-7), 156.1 (C-5), 155.3 (C-9), 144.8 (C-3', 4'), 130.6 (C-1'), 118.4 (C-6'), 115.0 (C-5'), 114.5 (C-2'), 99.0 (C-10), 95.1 (C-6), 93.8 (C-8), 81.0 (C-2), 66.3 (C-3), 27.8 (C-4).

Cinchonain Ib (**22**). Pale yellow solid; CD (6.20×10^{-4} MeOH): $\Delta\epsilon$ (nm) +7.12 (232); ESIMS (m/z): 451 [M-H]⁻, 488 [M+Na]⁺; ¹H-NMR (600 MHz, CD₃OD) δ : 6.83 (1H, d, J = 1.8 Hz, H-2'), 6.69 (1H, d, J = 7.8 Hz, H-5''), 6.67 (1H, dd, J = 8.0, 2.0 Hz, H-6'), 6.63 (1H, d, J = 8.0 Hz, H-5'), 6.61 (1H, d, J = 1.8 Hz, H-2''), 6.54 (1H, dd, J = 8.2, 2.0 Hz, H-6''), 6.21 (1H, s, H-6), 4.98 (1H, s, H-2), 4.46 (1H, br. d, J = 5.4 Hz, H-7''), 4.21 (1H, m, H-3), 3.01 (1H, dd, J = 15.6, 7.2 Hz, H-8''a), 2.94 (1H, dd, J = 16.8, 4.2 Hz, H-4a), 2.87 (1H, dd, J = 16.2, 1.8 Hz, H-8''b), 2.83 (1H, dd, J = 17.4, 2.4 Hz, H-4b); ¹³C-NMR (150 MHz, CD₃OD) δ : 170.7 (C-9''), 157.3 (C-5), 153.5 (C-9), 152.0 (C-7), 146.4 (C-3''), 145.9 (C-4'), 145.8 (C-4''), 145.3 (C-3'), 135.3 (C-1''), 131.7 (C-1'), 119.4 (C-6'), 119.3 (C-6''), 116.5 (C-5''), 115.9 (C-5'), 115.3 (C-2''), 115.0 (C-2'), 106.2 (C-8), 105.3 (C-10), 96.4 (C-6), 79.9 (C-2), 67.0 (C-3), 38.3 (C-8''), 35.2 (C-7''), 29.3 (C-4).

Cinchonain Ia (**23**). Pale yellow solid; CD (3.5×10^{-4} MeOH): $\Delta\epsilon$ (nm) -12.48 (235); ESIMS (m/z): 451 [M-H]⁻, ¹H-NMR (600 MHz, CD₃OD) δ : 6.97 (1H, d, J = 1.8 Hz, H-2'), 6.78 (1H, dd, J = 8.0, 1.8 Hz, H-6'), 6.77 (1H, d, J = 8.0 Hz, H-5'), 6.61 (1H, d, J = 8.2 Hz, H-6''), 6.52 (1H, d, J = 1.8 Hz, H-2''), 6.45 (1H, dd, J = 7.8, 1.8 Hz, H-5''), 6.21 (1H, s, H-6), 4.87 (1H, s, H-2), 4.55 (1H, br. d, J = 6.0 Hz, H-7''), 4.25 (1H, m, H-3), 3.07 (1H, dd, J = 15.6, 7.2 Hz, H-8''a), 2.91 (1H, dd, J = 16.8, 4.2 Hz, H-4a), 2.87 (1H, dd, J = 15.6, 2.0 Hz, H-8''b), 2.84 (1H, dd, J = 16.8, 2.0 Hz, H-4b); ¹³C-NMR (150 MHz, CD₃OD) δ : 170.7 (C-9''), 157.3 (C-5), 153.4 (C-9), 152.1 (C-7), 146.3 (C-3''), 146.0 (C-4'), 145.8 (C-4''), 145.1 (C-3'), 135.4 (C-1''), 131.9 (C-1'), 119.2 (C-6'), 119.2 (C-6''), 116.5 (C-5''), 116.0 (C-5'), 115.1 (C-2''), 115.1 (C-2'), 106.0 (C-8), 105.2 (C-10), 96.2 (C-6), 79.7 (C-2), 66.6 (C-3), 38.6 (C-8''), 35.4 (C-7''), 29.5 (C-4).

Apigenin (**24**). Yellow powder; ESIMS (m/z): 269 [M-H]⁻, 271 [M+H]⁺; ¹H-NMR (500 MHz, DMSO- d_6) δ : 10.03 (1H, s, 4'-OH), 7.73 (2H, d, J = 8.5 Hz, H-2', 6'), 6.84 (2H, d, J = 8.5 Hz, H-3', 5'), 6.77 (1H, s, H-3), 6.51 (1H, d, J = 2.0 Hz, H-8), 6.16 (1H, d, J = 2.0 Hz, H-6); ¹³C-NMR (125 MHz, DMSO- d_6) δ : 179.0 (C-4), 167.5 (C-2), 167.1 (C-7), 163.7 (C-5), 163.0 (C-4'), 158.7 (C-9), 132.7 (C-2', 6'), 123.3 (C-1'), 115.9 (C-3', 5'), 105.1 (C-10), 104.3 (C-3), 97.7 (C-6), 93.9 (C-8).

Quercetin (**25**). Yellow powder; ¹H-NMR (600 MHz, DMSO- d_6) δ : 12.48 (s, 1H, C5-OH), 10.78 (s, 1H, C7-OH), 9.58 (s, 1H, C4'-OH), 9.35 (s, 1H, 3-OH), 9.29 (s, 1H, C3'-OH), 7.66 (1H, d, J = 1.2 Hz, H-2'), 7.53 (1H, dd, J = 8.4, 1.8 Hz, H-6'), 6.87 (1H, d, J = 8.4 Hz, H-5'), 6.39 (1H, d, J = 1.8 Hz, H-8), 6.17 (1H, d, J = 1.8 Hz, H-6); ¹³C-NMR (150 MHz, DMSO- d_6) δ : 175.8 (C-4), 163.9 (C-7), 160.7 (C-5), 156.1 (C-9), 147.7 (C-4'), 146.8 (C-2), 145.0 (C-3'), 135.7 (C-3), 121.9 (C-1'), 119.9 (C-6'), 115.6 (C-5'), 115.0 (C-2'), 102.9 (C-10), 98.2 (C-6), 93.3 (C-8).

Luteolin (**26**). Yellow powder; ESIMS (m/z): 285 [M-H]⁻, 287 [M+H]⁺; ¹H-NMR (600 MHz, CD₃OD) δ : 7.48 (1H, d, J = 1.8 Hz, H-2'), 7.19 (1H, dd, J = 8.4, 1.8 Hz, H-6'), 6.83 (1H, d, J = 8.4 Hz, H-5'), 6.73 (1H, s, H-3), 6.57 (1H, br. s, H-8), 6.21 (1H, br. s, H-6); ¹³C-NMR (150 MHz, CD₃OD) δ : 182.9 (C-4), 169.6 (C-7), 169.5 (C-2), 166.5 (C-5), 159.9 (C-9), 148.9 (C-4'), 147.9 (C-3'), 125.9 (C-1'), 125.7 (C-6'), 118.6 (C-5'), 116.6 (C-2'), 104.7 (C-10), 103.6 (C-3), 98.5 (C-6), 91.6 (C-8).

Myricetin (27). Yellow powder; $^1\text{H-NMR}$ (600 MHz, CD_3OD) δ : 6.97 (2H, s, H-2', 6'), 6.49 (1H, s, H-8), 6.20 (1H, d, $J = 1.8\text{ Hz}$, H-6); $^{13}\text{C-NMR}$ (150 MHz, CD_3OD) δ : 182.8 (C-4), 169.7 (C-7), 169.5 (C-5), 159.9 (C-9), 148.0 (C-2), 147.0 (C-3', 5'), 137.2 (C-3), 136.5 (C-4'), 124.6 (C-1'), 111.8 (C-2', 6'), 104.7 (C-10), 99.3 (C-6), 91.6 (C-8).

Kukulkanin B (28). Yellow solid; ESIMS (m/z): 285 $[\text{M-H}]^-$, 287 $[\text{M+H}]^+$; $^1\text{H-NMR}$ (500 MHz, CD_3OD) δ : 7.98 (1H, d, $J = 9.5\text{ Hz}$, H-6'), 7.96 (2H, d, $J = 8.5\text{ Hz}$, H-2, 6), 7.64 (1H, d, $J = 16.0\text{ Hz}$, H- β), 7.22 (1H, d, $J = 9.0\text{ Hz}$, H- α), 6.88 (2H, d, $J = 8.5\text{ Hz}$, H-3, 5), 6.64 (1H, d, $J = 9.0\text{ Hz}$, H-5'), 3.84 (3H, s, 3'- OCH_3); $^{13}\text{C-NMR}$ (125 MHz, CD_3OD) δ : 191.3 (C=O), 163.7 (C-4'), 150.8 (C-4), 149.9 (C-3'), 141.1 (C- β), 139.7 (C-2'), 132.2 (C-2, 6), 131.3 (C-6'), 121.5 (C-1), 120.5 (C- α), 120.3 (C-3, 5), 116.4 (C-1'), 112.7 (C-5'), 61.8 (3'- OCH_3).

4,4',6-Trihydroxyaurone (29). Yellow powder; ESIMS (m/z): 269 $[\text{M-H}]^-$, 271 $[\text{M+H}]^+$; $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ : 10.83 (1H, s, OH), 10.79 (1H, s, OH), 10.00 (1H, s, OH), 7.74 (2H, d, $J = 8.5\text{ Hz}$, H-2', 6'), 6.85 (2H, d, $J = 9.0\text{ Hz}$, H-3', 5'), 6.53 (1H, s, -CH=), 6.19 (1H, d, $J = 2.0\text{ Hz}$, H-7), 6.05 (1H, d, $J = 1.5\text{ Hz}$, H-5); $^{13}\text{C-NMR}$ (125 MHz, $\text{DMSO-}d_6$) δ : 179.0 (C=O), 167.5 (C-4, 6), 158.7 (C-8), 158.1 (C-4'), 150.0 (C-2), 132.7 (C-2', 6'), 123.3 (C-1'), 115.9 (C-3', 5'), 109.0 (C-10), 102.8 (C-9), 97.6 (C-5), 90.4 (C-7).

Aureusidin (30). Yellow powder; ESIMS (m/z): 285 $[\text{M-H}]^-$, 287 $[\text{M+H}]^+$; $^1\text{H-NMR}$ (400 MHz, CD_3OD) δ : 7.49 (1H, d, $J = 1.2\text{ Hz}$, H-2'), 7.21 (1H, dd, $J = 8.0, 1.2\text{ Hz}$, H-6'), 6.85 (1H, d, $J = 8.0\text{ Hz}$, H-5'), 6.59 (1H, s, -CH=), 6.22 (1H, br. s, H-5), 6.02 (1H, br. s, H-7); $^{13}\text{C-NMR}$ (100 MHz, CD_3OD) δ : 182.9 (C=O), 169.6 (C-6), 169.4 (C-4), 160.0 (C-8), 148.9 (C-4'), 147.9 (C-2), 146.6 (C-3'), 125.9 (C-1'), 125.8 (C-6'), 118.7 (C-2'), 116.6 (C-5'), 112.8 (C-10), 104.8 (C-9), 98.5 (C-7), 91.6 (C-5).

(-)-Secoisolariciresinol (31). White powder; $[\alpha]_D^{20} -35.1$ (c 0.20, MeOH); ESIMS (m/z): 385 $[\text{M+Na}]^+$; $^1\text{H-NMR}$ (400 MHz, CD_3OD) δ : 6.65 (2H, d, $J = 8.0\text{ Hz}$, H-5, 5'), 6.58 (2H, d, $J = 1.6\text{ Hz}$, H-2, 2'), 6.53 (2H, dd, $J = 8.0, 2.0\text{ Hz}$, H-6, 6'), 3.73 (6H, s, 3, 3'- OCH_3), 3.58 (4H, m, H-9, 9'), 2.54 (2H, dd, $J = 13.6, 7.6\text{ Hz}$, H-7, 7'), 2.66 (2H, dd, $J = 13.6, 7.6\text{ Hz}$, H-7, 7'), 1.90 (2H, m, H-8, 8'); $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ : 147.2 (C-3, 3'), 144.3 (C-4, 4'), 132.2 (C-1, 1'), 121.1 (C-6, 6'), 115.0 (C-5, 5'), 112.9 (C-2, 2'), 60.2 (C-9, 9'), 55.4 (3, 3'- OCH_3), 42.4 (C-8, 8'), 33.9 (C-7, 7').

4-Ketopinioresinol (32). Colorless solid; ESIMS (m/z): 371 $[\text{M-H}]^-$, 395 $[\text{M+Na}]^+$; $^1\text{H-NMR}$ (600 MHz, CD_3OD) δ : 6.78–6.97 (6H, m, ArH), 5.39 (1H, d, $J = 4.2\text{ Hz}$, H-6), 5.23 (1H, d, $J = 4.2\text{ Hz}$, H-2), 4.29 (1H, dd, $J = 9.6, 7.2\text{ Hz}$, H-8'), 4.03 (1H, dd, $J = 9.6, 4.8\text{ Hz}$, H-8), 3.87 (6H, s, $2 \times \text{OCH}_3$), 3.66 (2H, m, H-1, 5); $^{13}\text{C-NMR}$ (150 MHz, CD_3OD) δ : 179.9 (C-4), 149.6 (C-4''), 149.4 (C-4'), 148.4 (C-3''), 147.7 (C-3'), 133.4 (C-1''), 132.6 (C-1'), 119.9 (C-6''), 119.7 (C-6'), 116.6 (C-5''), 116.4 (C-5'), 110.8 (C-2''), 109.9 (C-2'), 85.3 (C-6), 82.6 (C-2), 74.0 (C-8), 56.7 (OCH_3), 56.6 (OCH_3), 51.2 (C-1), 46.8 (C-5).

1,4-Bis(4-hydroxy-3,5-dimethoxyphenyl)-2,3-bis(hydroxymethyl)-1,4-butanediol (Smiglabranol) (33). Pale yellow solid; EIMS m/z : 418 $[\text{M-2H}_2\text{O}]^+$, 319 (100), 210 (50), 226(41), 320(20), 436 (15); $^1\text{H-NMR}$ (500 MHz, CD_3OD) δ : 6.74 (4H, s, H-2, 2', 6, 6'), 4.95 (2H, d, $J = 8.5\text{ Hz}$, H-7, 7'), 3.86

(12H, s, 4 × -OCH₃), 3.71 (2H, dd, J = 8.5, 2.5 Hz, H-9b, 9'b), 3.62 (2H, dd, J = 11.5, 5.0 Hz, H-9a, 9'a), 2.31 (2H, m, H-8, 8'); ¹³C-NMR (125 MHz, CD₃OD) δ : 149.3 (C-3, 3', 5, 5'), 136.2 (C-1, 1'), 134.2 (C-4, 4'), 104.8 (C-2, 2', 6, 6'), 84.6 (C-7, 7'), 61.7 (C-9, 9'), 56.8 (C-8, 8'), 55.2 (3, 3'-OCH₃).

(+)-*Lyoniresinol* (**34**). Colorless solid; ESIMS (m/z): 419 [M-H]⁻, 443 [M+Na]⁺; ¹H-NMR (600 MHz, CD₃OD) δ : 6.59 (1H, s, H-6), 6.38 (2H, s, H-2', 6'), 4.31 (1H, d, J = 5.4 Hz, H-7'), 3.87 (3H, s, 5-OCH₃), 3.74 (6H, s, 3', 5'-OCH₃), 3.60 (2H, m, H-9b, 9b'), 3.50 (2H, d, J = 5.4 Hz, H-9a, 9a'), 3.38 (3H, s, 3-OCH₃), 2.70 (1H, dd, J = 4.8, 15.0 Hz, H-7b), 2.57 (1H, dd, J = 11.4, 14.4 Hz, H-7a), 1.97 (1H, m, H-8'), 1.63 (1H, m, H-8); ¹³C-NMR (150 MHz, CD₃OD) δ : 149.2 (C-3', 5'), 148.9 (C-5), 147.9 (C-3), 139.5 (C-4, 1'), 134.8 (C-4'), 130.4 (C-1), 126.5 (C-2), 108.0 (C-6), 107.1 (C-2', 6'), 67.0 (C-9), 64.4 (C-9'), 60.4 (3-OCH₃), 57.0 (3', 5'-OCH₃), 56.8 (5-OCH₃), 49.8 (C-8'), 42.5 (C-7'), 41.1 (C-8), 33.8 (C-7).

Kompasinol A (**35**). Pale yellow solid; ESIMS (m/z): 451 [M-H]⁻, 453 [M+H]⁺; ¹H-NMR (600 MHz, CD₃OD) δ : 6.85 (1H, d, J = 1.8 Hz, H-10), 6.78 (1H, d, J = 7.8 Hz, H-13), 6.75 (1H, dd, J = 7.8, 1.8 Hz, H-14), 6.33 (1H, s, H-2'), 6.33 (1H, s, H-6'), 6.24 (1H, d, J = 1.7 Hz, H-6), 6.19 (1H, d, J = 1.8 Hz, H-4), 4.65 (1H, d, J = 4.2 Hz, H-8), 4.47 (1H, dd, J = 8.4, 7.8 Hz, H-9'a), 4.13 (1H, br. s, H-7'), 3.77 (1H, m, H-7), 3.73 (6H, s, 3', 5'-OCH₃), 3.54 (1H, t, J = 8.6 Hz, H-9'b), 3.04 (1H, ddd, J = 8.4, 8.4, 1.2 Hz, H-8'); ¹³C-NMR (150 MHz, CD₃OD) δ : 160.5 (C-5), 156.3 (C-3), 149.1 (C-3', 5'), 148.5 (C-1), 146.5 (C-12), 146.0 (C-11), 137.9 (C-1'), 135.2 (C-9), 134.6 (C-4'), 123.0 (C-2), 119.1 (C-14), 116.3 (C-13), 114.5 (C-10), 105.4 (C-2', 6'), 103.2 (C-6), 102.8 (C-4), 89.4 (C-8), 75.0 (C-9'), 59.8 (C-7), 56.6 (3', 5'-OCH₃), 56.5 (C-8'), 52.1 (C-7').

Aiphanol (**36**). Pale yellow powder; ESIMS (m/z): 451 [M-H]⁻; ¹H-NMR (600 MHz, CD₃OD) δ : 7.09 (1H, s, H-8), 7.04 (1H, d, J = 8.4 Hz, H-6), 6.93 (1H, d, J = 15.0 Hz, H-10), 6.83 (1H, d, J = 16.2 Hz, H-9), 6.78 (1H, d, J = 8.0 Hz, H-5), 6.75 (2H, s, H-2'), 6.45 (2H, s, H-12), 6.17 (1H, s, H-14), 4.87 (1H, d, J = 8.0 Hz, H-2), 4.08 (1H, m, H-3), 3.87 (6H, s, 3', 5'-OCH₃), 3.71 (1H, d, J = 12.0 Hz, CH₂OH), 3.49 (1H, dd, J = 12.0, 4.2 Hz, CH₂OH); ¹³C-NMR (150 MHz, CD₃OD) δ : 159.7 (C-13), 149.4 (C-3'), 145.4 (C-8a), 144.7 (C-4a), 141.0 (C-11), 137.2 (C-4'), 132.5 (C-7), 129.0 (C-10), 128.6 (C-1'), 128.4 (C-9), 121.1 (C-6), 118.1 (C-5), 115.6 (C-8), 105.9 (C-2'), 105.9 (C-12), 102.9 (C-14), 80.1 (C-3), 78.0 (C-2), 62.1 (CH₂OH), 56.8 (3', 5'-OCH₃).

Trans-resveratrol (**37**). White powder; ¹H-NMR (600 MHz, CD₃OD) δ : 7.35 (2H, d, J = 8.4 Hz, H-2', 6'), 6.95 (1H, d, J = 16.2 Hz, H-8), 6.80 (1H, d, J = 16.8 Hz, H-7), 6.76 (2H, d, J = 8.4 Hz, H-3', 5'), 6.45 (2H, d, J = 1.8 Hz, H-2, 6), 6.16 (1H, t, H-4); ¹³C-NMR (150 MHz, CD₃OD) δ : 159.6 (C-3, 5), 158.3 (C-4'), 141.3 (C-1), 130.4 (C-1'), 129.4 (C-2', 6'), 128.8 (C-8), 127.0 (C-7), 116.5 (C-3', 5'), 105.8 (C-2, 6), 102.6 (C-4).

Trans-piceid (**38**). White powder; ESIMS (m/z): 413 [M+Na]⁺; ¹H-NMR (400 MHz, CD₃OD) δ : 7.36 (2H, d, J = 8.4 Hz, H-2', 6'), 7.01 (1H, d, J = 16.0 Hz, H-8), 6.84 (1H, d, J = 16.0 Hz, H-7), 6.77 (2H, d, J = 6.4 Hz, H-3', 5'), 6.74 (1H, t, J = 1.6 Hz, H-2), 6.60 (1H, t, J = 1.6 Hz, H-6), 6.44 (1H, t, J = 2.0 Hz, H-4), 4.82 (1H, d, J = 7.5 Hz, H-1'); ¹³C-NMR (100 MHz, CD₃OD) δ : 160.5 (C-3), 159.6 (C-5), 158.5 (C-4'), 141.4 (C-1), 130.3 (C-1'), 129.9 (C-8), 128.9 (C-2', 6'), 126.7 (C-7), 116.5 (C-3', 5'), 108.3

(C-6), 106.9 (C-2), 104.0 (C-4), 102.4 (C-1'), 78.3 (C-3'), 78.1 (C-5'), 74.9 (C-2'), 71.5 (C-4'), 62.6 (C-6').

Piceatannol (39). Pale yellow solid; 243 [M-H]⁻; ¹H-NMR (400 MHz, CD₃OD) δ: 6.99 (1H, d, *J* = 2.0 Hz, H-2), 6.93 (1H, d, *J* = 16.0 Hz, H-8), 6.85 (1H, dd, *J* = 8.0, 2.0 Hz, H-6), 6.78 (1H, d, *J* = 16.0 Hz, H-7), 6.75 (1H, d, *J* = 1.6 Hz, H-5), 6.46 (2H, d, *J* = 2.0 Hz, H-2', 6'), 6.18 (1H, t, *J* = 2.0 Hz, H-4'); ¹³C-NMR (100 MHz, CD₃OD) δ: 159.6 (C-3', 5'), 146.5 (C-3), 146.5 (C-4), 141.3 (C-1'), 131.1 (C-1), 129.7 (C-7), 127.0 (C-8), 120.2 (C-6), 116.5 (C-2), 113.9 (C-5), 105.8 (C-2', 6'), 102.7 (C-4').

Trans-caffeic acid (40). Pale yellow powder; ¹H-NMR (500 MHz, CD₃OD) δ: 7.52 (1H, d, *J* = 15.5 Hz, H-7), 7.03 (1H, d, *J* = 2.0 Hz, H-2), 6.92 (1H, dd, *J* = 2.0, 8.0 Hz, H-6), 6.77 (1H, d, *J* = 8.5 Hz, H-5), 6.21 (1H, d, *J* = 16.0 Hz, H-8); ¹³C-NMR (125 MHz, CD₃OD) δ: 171.1 (COOH), 149.4 (C-4), 147.0 (C-7), 146.8 (C-3), 127.8 (C-1), 122.8 (C-6), 116.5 (C-5), 115.5 (C-8), 115.1 (C-2).

5-O-Caffeoylshikimic acid (41). Pale yellow solid; [α]_D²⁰ -97 (*c* 0.09, MeOH); ESIMS (*m/z*): 335 [M-H]⁻, 359 [M+Na]⁺; ¹H-NMR (600 MHz, CD₃OD) δ: 7.56 (1H, d, *J* = 15.6 Hz, H-9), 7.04 (1H, d, *J* = 2.4 Hz, H-2'), 6.95 (1H, dd, *J* = 7.8, 1.8 Hz, H-6'), 6.86 (1H, m, H-2), 6.77 (1H, d, *J* = 7.8 Hz, H-5'), 6.28 (1H, d, *J* = 15.6 Hz, H-8), 5.24 (1H, dt, H-5), 4.40 (1H, br. t, H-3), 3.91 (1H, dd, *J* = 7.2, 4.2 Hz, H-4), 2.85 (1H, dd, *J* = 18.2, 5.0 Hz, H-6b), 2.31 (1H, dd, *J* = 18.2, 5.2 Hz, H-6a); ¹³C-NMR (150 MHz, CD₃OD) δ: 169.8 (COOH), 168.8 (C-7), 149.9 (C-4'), 147.5 (C-9), 147.0 (C-3'), 139.1 (C-2), 130.5 (C-1), 127.9 (C-1'), 123.2 (C-6'), 116.7 (C-5'), 115.4 (C-2'), 115.3 (C-8), 71.6 (C-5), 70.2 (C-4), 67.5 (C-3), 29.4 (C-6).

3-O-p-Coumaroylshikimic acid (42). Pale yellow solid; ESIMS (*m/z*): 319 [M-H]⁻, 343 [M+Na]⁺; ¹H-NMR (600 MHz, CD₃OD) δ: 7.63 (1H, d, *J* = 15.6 Hz, H-8'), 7.47 (2H, br. d, *J* = 9.0 Hz, H-3', 5'), 6.81 (2H, br. d, *J* = 7.2 Hz, H-2', 6'), 6.75 (1H, s, H-2), 6.35 (1H, d, *J* = 15.6 Hz, H-7'), 5.28 (1H, br. s, H-3), 4.40 (1H, m, H-5), 3.91 (1H, dd, *J* = 6.5, 4.0 Hz, H-4), 2.86 (1H, dd, *J* = 18.0, 4.8 Hz, H-6b), 2.32 (1H, dd, *J* = 18.0, 5.4 Hz, H-6a); ¹³C-NMR (150 MHz, CD₃OD) δ: 168.6 (C-7, 9'), 161.3 (C-1'), 146.9 (C-7'), 134.5 (C-2), 133.6 (C-4'), 131.2 (C-3'/C-5'), 127.2 (C-1), 116.8 (C-3'/C-5'), 115.1 (C-8'), 71.4 (C-4), 70.1 (C-5), 67.4 (C-3), 29.4 (C-6).

(2S)-1,2-O-Di-trans-p-coumaroylglycerol (Smiglycerol) (43). Pale yellow powder; mp 183–185 °C; [α]_D²⁰ +164.7 (*c* 0.17, MeOH); CD (3.02 × 10⁻⁴ MeOH): Δε(nm) -6.68 (287), +5.04 (326); UV λ_{max} (MeOH): 210, 228, 310 nm; IR ν_{max}^{KBr} cm⁻¹: 3448, 2926, 1686, 1634, 1516, 1438, 1342, 1287, 1150, 1052, 829; HR-ESI-MS *m/z*: 383.1133 [M-H]⁻ (calcd. for C₂₁H₁₉O₇ 383.1131); 407.1103 [M+Na]⁺ (calcd. for C₂₁H₂₀O₇Na 407.1107); ¹H-NMR (600 MHz, DMSO-*d*₆) δ: 10.02 (2H, s, -OH), 7.57 (1H, d, *J* = 16.2 Hz, H-6), 7.541 (2H, d, *J* = 8.4 Hz, H-8, 12), 7.540 (1H, d, *J* = 15.6 Hz, H-3'), 7.53 (2H, d, *J* = 8.4 Hz, H-5', 9'), 6.77 (2H, d, *J* = 8.4 Hz, H-9, 11), 6.76 (2H, d, *J* = 8.4 Hz, H-6', 8'), 6.39 (1H, d, *J* = 16.2 Hz, H-5), 6.38 (1H, d, *J* = 15.6 Hz, H-2'), 5.11 (1H, m, H-2), 4.40 (1H, dd, *J* = 11.4, 3.0 Hz, H-1a), 4.25 (1H, dd, *J* = 12.0, 6.6 Hz, H-1b), 3.60 (2H, t, H-3a, H-3b); ¹³C-NMR (150 MHz, DMSO-*d*₆) δ: 166.41 (C-1'), 166.19 (C-4), 159.92 (C-10), 159.89 (C-7'), 145.21 (C-6), 145.16 (C-3'), 130.44 (C-8, 12),

130.40 (C-5',9'), 125.02 (C-4'), 124.97 (C-7), 115.77 (C-9,11), 115.75 (C-6',8'), 114.03 (C-5), 113.68 (C-2'), 72.13 (C-2), 62.54 (C-1), 59.67(C-3).

Juncusyl ester B (44). White powder; ESIMS (m/z): 237 $[M-H]^-$; 1H -NMR (600 MHz, CD_3OD) δ : 7.67 (1H, d, $J = 16.2$ Hz, H-6), 7.46 (2H, d, $J = 8.4$ Hz, H-8, 12), 6.81 (2H, d, $J = 9.0$ Hz, H-9, 11), 6.37 (1H, d, $J = 15.6$ Hz, H-5), 4.99 (1H, m, H-2), 3.75 (4H, m, H-3), 3.75 (4H, m, H-1); ^{13}C -NMR (150 MHz, CD_3OD) δ : 168.9 (C-4), 161.2 (C-12), 146.6 (C-6), 131.1 (C-8), 131.1 (C-10), 127.2 (C-7), 116.8 (C-9), 116.8 (C-11), 115.4 (C-5), 76.6 (C-2), 61.7 (C-1), 61.7(C-3).

1-O-p-Coumaroylglycerol (45). Colorless solid; ESIMS (m/z): 237 $[M-H]^-$, 261 $[M+Na]^+$; 1H -NMR (600 MHz, CD_3OD) δ : 7.66 (1H, d, $J = 16.2$ Hz, H-7'), 7.46 (2H, d, $J = 9.5$ Hz, H-2', 6'), 6.81 (2H, d, $J = 9.0$ Hz, H-3', 5'), 6.36 (1H, d, $J = 15.6$ Hz, H-8'), 4.26 (1H, dd, $J = 11.4, 4.2$ Hz, H-1a), 4.17 (1H, dd, $J = 11.4, 6.6$ Hz, H-1b), 3.90 (1H, $J = 6.0$ Hz, H-2), 3.61 (2H, d, $J = 5.4$ Hz, H-3); ^{13}C -NMR (150 MHz, CD_3OD) δ : 169.2 (C-9'), 161.3 (C-4'), 145.3 (C-7'), 131.2 (C-2'), 131.2 (C-6'), 127.2 (C-1'), 116.4 (C-3'), 116.4 (C-5'), 115.8 (C-8'), 71.3 (C-2), 66.6 (C-1), 64.1 (C-3).

Vanillin (46). Pale yellow oil; 1H -NMR (500 MHz, CD_3OD) δ : 9.71 (1H, s, H-7), 7.42 (1H, s, H-2), 7.41 (1H, d, $J = 7.0$ Hz, H-6), 6.90 (1H, d, $J = 7.5$ Hz, H-5), 3.90 (3H, s, OCH_3); ^{13}C -NMR (125 MHz, CD_3OD) δ : 192.7 (C-7), 156.0 (C-4), 150.0 (C-3), 130.1 (C-1), 128.3 (C-6), 116.6 (C-5), 111.1 (C-2), 56.3 (OCH_3).

p-Hydroxy-benzaldehyde (47). Pale yellow powder; 1H -NMR (500 MHz, CD_3OD) δ : 9.75 (1H, s, CHO), 7.76 (2H, d, $J = 8.8$ Hz, H-2, 6), 6.89 (2H, d, $J = 8.4$ Hz, H-3, 5); ^{13}C -NMR (125 MHz, CD_3OD) δ : 192.8 (CHO), 165.4 (C-4), 133.4 (C-2, 6), 130.2 (C-1), 116.9 (C-3, 5).

Acetovanillone (48). White powder; EIMS (m/z): 166 $[M]^+$; 1H -NMR (600 MHz, $DMSO-d_6$) δ : 7.50 (1H, dd, $J = 1.8, 8.4$ Hz, H-6), 7.43 (1H, d, $J = 1.8$ Hz, H-2), 6.86 (1H, d, $J = 8.4$ Hz, H-5), 3.82 (3H, s, OCH_3), 2.50 (3H, s, H-8); ^{13}C -NMR (150 MHz, $DMSO-d_6$) δ : 196.0 (C-7), 153.8 (C-4), 147.5 (C-3), 128.8 (C-1), 123.4 (C-6), 114.9 (C-5), 111.1 (C-2), 55.6 (OCH_3), 26.2(C-8).

(+)-Scytalone (49). Pale yellow powder; $[\alpha]_D^{20} +10.6$ (c 0.08, MeOH); 1H -NMR (400 MHz, CD_3OD) δ : 6.22 (1H, br. s, H-5), 6.09 (1H, br. s, H-7), 4.25 (1H, m, H-3), 3.07 (1H, d, $J = 16.0$ Hz, H-4a), 2.84 (1H, d, $J = 16.0$ Hz, H-4b), 2.84 (1H, dd, $J = 16.8, 3.2$ Hz, H-2a), 2.61 (1H, dd, $J = 17.2, 7.6$ Hz, H-2b), ^{13}C -NMR (100 MHz, CD_3OD) δ : 202.4 (C-1), 166.7 (C-6), 166.5 (C-8), 146.0 (C-10), 111.7 (C-9), 109.4 (C-5), 101.7 (C-7), 66.9 (C-3), 47.4 (C-2), 39.2 (C-4).

Glucosyringic acid (50). White powder; 1H -NMR (500 MHz, $DMSO-d_6$) δ : 12.87 (1H, s, COOH), 7.23 (2H, s, H-2, 6), 5.11 (1H, d, $J = 7.5$ Hz, H-1'), 3.79 (6H, s, $2 \times OCH_3$); ^{13}C -NMR (125 MHz, $DMSO-d_6$) δ : 166.9 (C-7), 152.2 (C-3, 5), 138.2 (C-4), 125.6 (C-1), 107.3 (C-2, 6), 101.9 (C-1'), 77.4 (C-5'), 76.6 (C-3'), 74.1 (C-2'), 69.8 (C-4'), 60.8 (C-6'), 56.3($2 \times OCH_3$).

Protocatechuic acid (51). White powder; EIMS m/z : 154 (M^+); 1H -NMR (600 MHz, CD_3OD) δ : 7.43 (1H, s, H-2), 7.41 (1H, s, H-6), 6.79 (1H, d, $J = 7.8$ Hz, H-5); ^{13}C -NMR (150 MHz, CD_3OD) δ : 170.3 (COOH), 151.5 (C-4), 146.1 (C-3), 123.9 (C-6), 123.2 (C-3), 117.7 (C-2), 115.7(C-5).

3-Methoxygallic acid (52). White powder; $^1\text{H-NMR}$ (500 MHz, CD_3OD) δ : 7.18 (2H, s, H-2, 6), 3.86 (3H, s, OCH_3); $^{13}\text{C-NMR}$ (125 MHz, CD_3OD) δ : 170.2 (COOH), 149.1 (C-5), 146.2 (C-3), 140.4 (C-4), 122.0 (C-1), 112.2 (C-6), 106.3 (C-2), 56.6 (OCH_3).

Vanillic acid 1-O- β -D-glucopyranosyl ester (53). Pale yellow oil; $[\alpha]_{\text{D}}^{20}$ -16.5 (c0.07, MeOH); $^1\text{H-NMR}$ (500 MHz, CD_3OD) δ : 7.63 (1H, dd, $J = 8.0, 2.0$ Hz, H-6), 7.61 (1H, d, $J = 2.0$ Hz, H-2), 7.20 (1H, d, $J = 8.5$ Hz, H-5), 5.02 (1H, d, $J = 7.5$ Hz, GlcH-1'), 3.90 (3H, s, OCH_3), 3.68 (1H, dd, $J = 12.0, 5.4$ Hz, GlcH-6'), 3.54-3.38 (4H, m, GlcH-2', 3', 4', 5'); $^{13}\text{C-NMR}$ (125 MHz, CD_3OD) δ : 169.5 (C-7), 152.0 (C-4), 150.4 (C-3), 126.0 (C-6), 124.8 (C-1), 116.4 (C-5), 114.4 (C-2), 101.9 (C-1'), 77.9 (C-5'), 78.3 (C-3'), 74.8 (C-2'), 71.3 (C-4'), 62.4 (C-6'), 56.6 (OCH_3).

Hydroxytyrosol (54). Pale yellow solid; $^1\text{H-NMR}$ (600 MHz, CD_3OD) δ : 6.67 (1H, d, $J = 8.4$ Hz, H-5), 6.65 (1H, d, $J = 2.4$ Hz, H-2), 6.52 (1H, dd, $J = 8.4, 2.4$ Hz, H-6), 3.67 (2H, t, $J = 7.2$ Hz, H-2'), 2.66 (2H, t, $J = 7.2$ Hz, H-1'); $^{13}\text{C-NMR}$ (150 MHz, CD_3OD) δ : 146.1 (C-3), 144.6 (C-4), 131.8 (C-1), 121.2 (C-6), 117.1 (C-5), 116.3 (C-2), 64.6 (C-2'), 39.7 (C-1').

Acetyl-11-keto- β -boswellic acid (55). Pale yellow solid; EIMS m/z : 512 (4) $[\text{M}]^+$, 232 (100), 408 (53), 273 (45), 393 (28); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 5.56 (1H, s, H-12), 5.31 (1H, t, $J = 2.5$ Hz, H-3), 2.42 (1H, s, H-9), 2.09 (3H, s, CH_3CO), 1.35 (3H, s, CH_3 -23), 1.24 (3H, s, CH_3 -27), 1.20 (3H, s, CH_3 -26), 1.15 (3H, s, CH_3 -25), 0.95 (3H, s, CH_3 -30), 0.83 (3H, s, CH_3 -28), 0.81 (3H, d, $J = 6.5$ Hz, CH_3 -29); $^{13}\text{C-NMR}$ (125 MHz, CD_3OD) δ : 201.6 (C-11), 179.6 (C-24), 172.3 (COCH_3), 167.9 (C-13), 131.2 (C-12), 74.9 (C-3), 61.7 (C-9), 60.5 (C-18), 51.5 (C-5), 46.4 (C-4), 45.1 (C-14), 42.0 (C-8), 40.6 (C-22), 40.5 (C-19), 40.4 (C-20), 38.6 (C-10), 35.8 (C-1), 35.1 (C-17), 33.9 (C-7), 30.8 (C-21), 29.4 (C-28), 28.6 (C-15), 28.3 (C-16), 24.5 (C-23), 24.4 (C-2), 21.5 (COCH_3), 21.1 (C-27), 20.8 (C-30), 20.1 (C-6), 18.9 (C-26), 17.8 (C-29), 14.4 (C-25).

Stigmasterol (56). White powder; $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 5.35 (1H, br d, $J = 5.5$ Hz, H-6), 5.15 (1H, dd, $J = 8.5, 15.5$ Hz, H-22), 5.02 (1H, dd, $J = 8.5$ Hz, H-23), 3.52 (1H, m, H-3), 0.93 (3H, d, $J = 6.0$ Hz, H-21), 0.86 (3H, t, $J = 7.0$ Hz, H-29), 0.84 (3H, d, $J = 7.5$ Hz, H-26), 0.82 (3H, d, $J = 7.5$ Hz, H-27), 0.80 (3H, s, H-19), 0.68 (3H, s, H-18); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 140.8 (C-5), 138.3 (C-22), 129.3 (C-23), 121.7 (C-6), 71.8 (C-3), 56.9 (C-17), 55.9 (C-14), 51.2 (C-24), 50.2 (C-9), 42.2 (C-13), 40.5 (C-20), 39.7 (C-4), 39.7 (C-12), 36.5 (C-10), 33.2 (C-25), 31.9 (C-2), 31.9 (C-7), 31.9 (C-8), 31.7 (C-1), 28.9 (C-16), 25.4 (C-28), 24.4 (C-15), 21.2 (C-11), 21.1 (C-21), 21.1 (C-27), 19.4 (C-19), 19.0 (C-26), 12.2 (C-29), 12.0 (C-18).

β -Sitosterol (57). White powder; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 5.35 (1H, br d, $J = 5.2$ Hz, H-6), 3.55 (1H, m, H-3), 1.00 (3H, s, 19- CH_3), 0.93 (3H, d, $J = 8.0$ Hz, 21- CH_3), 0.91 (3H, d, $J = 8.0$ Hz, 29- CH_3), 0.86 (3H, d, $J = 7.6$ Hz, 26- CH_3), 0.84 (3H, d, $J = 7.6$ Hz, 27- CH_3), 0.79 (3H, s, 18- CH_3); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 140.8 (C-5), 121.7 (C-6), 71.8 (C-3), 56.8 (C-14), 56.1 (C-17), 50.1 (C-9), 45.8 (C-4), 42.3 (C-13), 39.7 (C-12), 37.3 (C-1), 36.5 (C-10), 36.1 (C-20), 34.0 (C-22), 31.9 (C-8), 31.7 (C-7), 29.2 (C-2), 28.2 (C-25), 26.1 (C-15), 24.3 (C-23), 23.1 (C-28), 21.1 (C-11), 19.8 (C-26), 19.4 (C-19), 19.0 (C-21), 18.8 (C-27), 12.0 (C-29), 11.9 (C-18).

Daucosterol (**58**). White powder; $^1\text{H-NMR}$ (400 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 5.34 (1H, m, H-6), 5.06 (1H, d, $J = 7.6$ Hz, Glc H-1'); $^{13}\text{C-NMR}$ (100 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 140.9 (C-5), 121.9 (C-6), 102.6 (Glc C-1'), 78.6 (C-3), 78.5 (Glc C-3'), 78.1 (Glc C-5'), 75.3 (Glc C-2'), 71.7 (Glc C-4'), 62.9 (Glc C-6'), 56.8 (C-14), 56.3 (C-17), 50.4 (C-9), 46.1 (C-24), 42.5 (C-13), 40.0 (C-4), 39.4 (C-12), 37.5 (C-1), 36.9 (C-20), 36.4 (C-10), 34.2 (C-22), 32.2 (C-8), 32.1 (C-7), 30.3 (C-2), 29.5 (C-25), 28.6 (C-16), 26.4 (C-23), 24.5 (C-15), 23.4 (C-28), 21.3 (C-11), 20.0 (C-27), 19.4 (C-19), 19.2 (C-26), 19.0 (C-21), 12.2 (C-18), 12.0 (C-29).

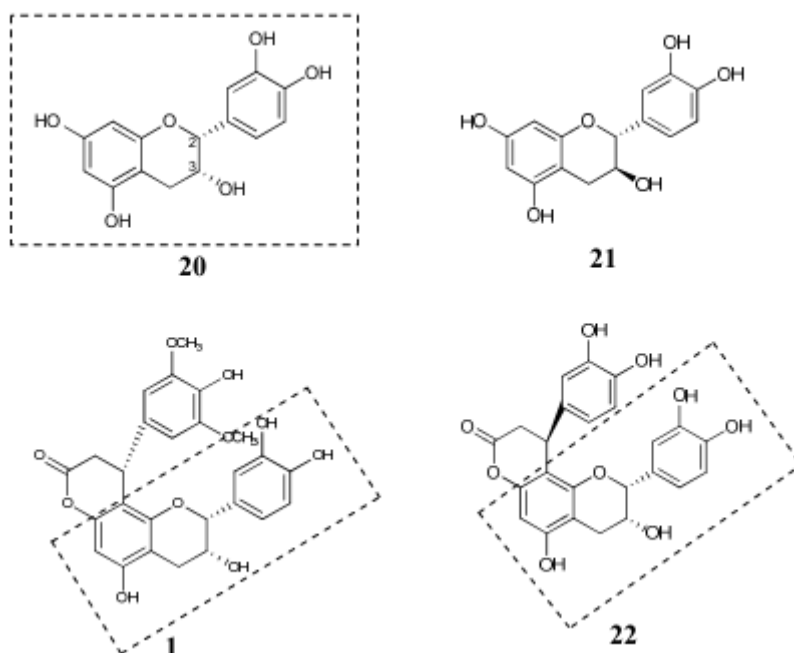
Smilagenin (**59**). White powder; ESIMS (m/z): 339 $[\text{M-H}]^-$, 363 $[\text{M+Na}]^+$; $^1\text{H-NMR}$ (500 MHz, CD_3OD) δ : 8.09 (1H, s, H-2), 6.32 (1H, d, $J = 2.0$ Hz, H-8), 6.20 (1H, d, $J = 2.0$ Hz, H-6), 5.31 (1H, d, $J = 1.5$ Hz, H-1'), 3.82 (1H, dd, $J = 3.5, 9.5$ Hz, H-2'), 3.76 (1H, dq, $J = 9.0, 6.0$ Hz, H-5'), 3.44 (1H, dd, $J = 1.5, 9.5$ Hz, H-3'), 3.30 (1H, s, H-4'), 1.27 (3H, d, $J = 6.0$ Hz, H-6'); $^{13}\text{C-NMR}$ (125 MHz, CD_3OD) δ : 178.7 (C-4), 166.5 (C-7), 163.5 (C-5), 159.3 (C-9), 147.9 (C-2), 140.4 (C-3), 106.4 (C-10), 102.1 (C-1'), 100.1 (C-6), 95.0 (C-8), 73.5 (C-4'), 71.9 (C-3'), 71.6 (C-2'), 71.2 (C-5'), 18.0 (C-6').

5-Hydroxymaltol (**60**). White powder; EIMS m/z : 142 $[\text{M}]^+$; $^1\text{H-NMR}$ (600 MHz, CD_3OD) δ : 7.85 (1H, s, H-2), 2.32 (3H, s, CH_3); $^{13}\text{C-NMR}$ (150 MHz, CD_3OD) δ : 170.3 (C-4), 151.8 (C-3), 145.8 (C-6), 142.9 (C-5), 140.4 (C-2), 14.5 (CH_3).

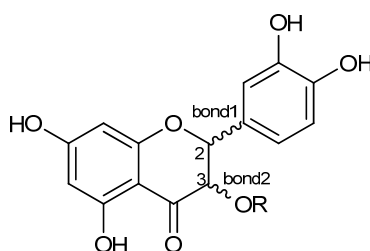
5-Hydroxyuridine (**61**). Pale yellow solid; $^1\text{H-NMR}$ (500 MHz, $\text{DMSO}-d_6$) δ : 8.11 (1H, d, $J = 8.5$ Hz, H-6), 5.90 (1H, d, $J = 6.0$ Hz, H-1'), 5.74 (1H, d, $J = 6.5$ Hz, H-5), 5.40 (1H, d, $J = 5.6$ Hz), 5.13 (1H, d, $J = 4.8$ Hz), 5.11 (1H, d, $J = 4.8$ Hz), 4.55 (1H, d, $J = 5.0$ Hz, H-2'), 4.14 (1H, t, $J = 8.5$ Hz, H-3'), 3.97 (1H, d, $J = 4.0$ Hz, H-4'), 3.67 (1H, m, H-5'a), 3.56 (1H, m, H-5'e); $^{13}\text{C-NMR}$ (125 MHz, $\text{DMSO}-d_6$) δ : 158.7 (C-4), 149.1 (C-2), 140.9 (C-6), 101.7 (C-5), 87.8 (C-1'), 85.9 (C-4'), 73.8 (C-3'), 70.4 (C-2'), 61.3 (C-5').

2-Methyl butanedioic acid-4-ethyl ester (**62**). Pale yellow oil; $^1\text{H-NMR}$ (500 MHz, CD_3OD) δ : 4.11 (2H, dd, $J = 8.5, 5.5$ Hz, H-6), 2.85 (1H, m, H-2), 2.64 (1H, dd, $J = 17.0, 8.5$ Hz, H-3b), 2.41 (1H, dd, $J = 16.5, 5.5$ Hz, H-3a), 1.23 (3H, t, $J = 7.0$ Hz, H-7), 1.20 (3H, d, $J = 7.5$ Hz, H-5); $^{13}\text{C-NMR}$ (125 MHz, CD_3OD) δ : 179.1 (C-1), 173.8 (C-4), 61.6 (C-6), 38.7 (C-3), 37.5 (C-2), 17.5 (C-5), 14.5 (C-7).

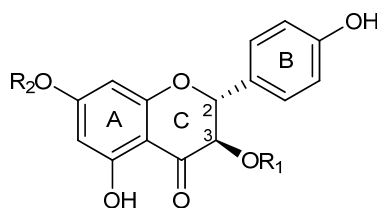
Isoselachoceric acid (**63**). Pale yellow powder; EIMS m/z (%): 368 (M^+); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 2.36 (2H, t, $J = 7.2$ Hz, H-2), 1.63 (2H, m, H-3), 1.27 ($19 \times \text{CH}_2$, 38H, br. s), 0.87 (3H, t, $J = 7.0$ Hz, H-24).

Figure S1. Structures of the investigated flavan-3-ols (**1**, **20–22**).**Table S1.** MIC values of investigated flavan-3-ols (**1**, **20–22**) against the microorganisms tested.

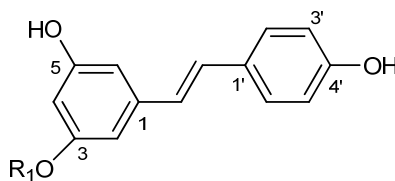
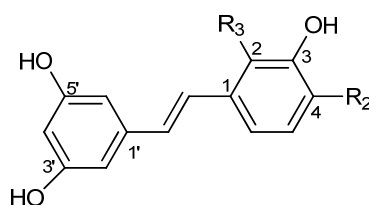
Compound	Microorganisms (MICs, mM)
1	EC, PA, KP (0.604); MRSA, SA, EF (0.302); CA (0.146)
20	MRSA, EF (1.03); SA (0.517)
21	>2.07
22	PA (0.663); MRSA, SA (0.0801); EF, CA (0.160)

Figure S2. Flavanone skeletons of compounds **7**, **11–14**.**Table S2.** MIC values of investigated flavanones (**7**, **11–14**) against the microorganisms tested.

Compound	R	Bond 1	Bond 2	Microorganisms (MICs, mM)
7	H		▶	>1.97
11	Rha			>1.33
12	Rha		▶	CA (0.666)
13	Rha	▶		MRSA(1.33)
14	Rha	▶	▶	SA (0.666); EC, PA, KP, MRSA, EF, CA (1.33)

Figure S3. Flavanone skeletons of compounds **9**, **15–17**.**Table S3.** MIC values of investigated flavanones (**9**, **15–17**) against the microorganisms tested.

Compound	R ₁	R ₂	Microorganisms (MICs, mM)
9	H	H	MRSA, SA (2.10)
15	Rha	H	>1.38
16	Glc	H	>1.33
17	H	Glc	MRSA, SA, EF (1.33)

Figure S4. Stibene skeletons of compounds **37** and **38**.**Figure S5.** Stibene skeletons of compounds **4** and **39**.**Table S4.** MIC values of investigated stibenes (**4**, **37–39**) against the microorganisms tested.

Compound	R ₁	R ₂	R ₃	Microorganisms (MICs, mM)
37	H	-	-	MRSA, EF (0.159); SA (0.0794); CA (0.657)
38	Glc	-	-	MRSA, SA (0.768); EF (1.54)
4	-	H	OH	EC, PA, KP (1.64); MRSA (0.409); SA (0.205); EF, CA (0.819)
39	-	OH	H	EC, PA, KP (1.64); MRSA (0.409); SA (0.205); CA (0.819)

EC, *Escherichia coli*; PA, *Pseudomonas aeruginosa* PA01; KP, *Klebsiella pneumonia*(clinical isolate); MRSA, methicillin-resistant *Staphylococcus aureus*(clinical isolate); SA, *Staphylococcus aureus* ATCC6538; EF, *Enterococcus faecalis*; CA, *Candida albicans* SC5314.