FLAVONOIDS OF *Limonium aureum*

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Limonium genus was reported to possess blood invigorating and activating properties and hemostatic and anticancer activity [1]. So we investigated the chemical constituents of *Limonium aureum* collected from XinJiang Uighur Autonomous Region. Finely ground air-dried raw material was exhaustively extracted with ethanol. The total flavonoids were extracted with ethyl acetate and rechromatographed over polyamide, silica gel, and Sephadex LH-20. The following 14 flavonoids were isolated in pure form:

Homoeriodictyol, $[M]^+$ 302, mp 224–226°C.

PMR spectrum (300 MHz, CD_3OD, δ, ppm, J/Hz): 2.68 (1H, dd, J = 17.1, 2.8, H-3β), 3.10 (1H, dd, J = 17.1, 12.9, H-3α), 3.86 (3H, s, OMe), 5.32 (1H, dd, J = 12.9, 2.8, H-2), 5.94 (2H, s, H-6, 8), 6.82 (1H, d, J = 8.1, H-5′), 6.90 (1H, dd, J = 8.1, 1.4, H-6′), 7.03 (1H, d, J = 1.4, H-2′).

^{13}CNMR (75 MHz, CD_3OD, δ, ppm): 80.9 (C-2), 44.5 (C-3), 197.9 (C-4), 165.1 (C-5), 97.5 (C-6), 168.6 (C-7), 96.7 (C-8), 165.7 (C-9), 103.7 (C-10), 131.9 (C-1′), 111.5 (C-2′), 148.4 (C-3′), 149.4 (C-4′), 116.5 (C-5′), 120.8 (C-6′), 56.9 (OMe) [2].

Naringenin, $[M]^+$ 272, mp 245–247°C.

PMR spectrum (300 MHz, CD_3OD, δ, ppm, J/Hz): 2.68 (1H, dd, J = 17.2, 3.1, H-3β), 3.11 (1H, dd, J = 17.2, 12.9, H-3α), 5.33 (1H, dd, J = 12.8, 2.7, H-2), 5.89 (2H, s, H-8, 6), 6.81 (2H, d, J = 8.4, H-5′, H-3′), 7.31 (2H, d, J = 8.4, H-2′, H-6′).

^{13}C NMR (CD_3OD, 75 MHz, δ, ppm): 80.9 (C-2), 44.6 (C-3), 198.3 (C-4), 165.4 (C-5), 97.5 (C-6), 168.9 (C-7), 96.7 (C-8), 165.9 (C-9), 104.9 (C-10), 131.6 (C-1′), 129.5 (C-2′, 6′), 116.8 (C-3′, 5′), 159.5 (C-4′) [2].

Eriodictyol, $[M]^+$ 288, mp 267–268°C.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.68 (1H, dd, J = 15.0, 2.8, H-3β), 3.11 (1H, dd, J = 17.1, 15.0, H-3α), 5.34 (1H, dd, J = 15.0, 2.8, H-2), 5.94 (2H, s, H-6, 8), 6.76 (1H, d, J = 8.1 Hz, H-5′), 6.82 (1H, dd, J = 8.1, 1.2, H-6′), 6.83 (1H, d, J = 1.2, H-2′), 12.10 (1H, s, 5-OH), 10.75 (1H, s, 7-OH), 9.05 (1H, s, 3′-OH), 9.00 (1H, s, 4′-OH).

^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 78.4 (C-2), 42.0 (C-3), 196.3 (C-4), 162.9 (C-5), 95.7 (C-6), 166.6 (C-7), 94.9 (C-8), 163.4 (C-9), 101.8 (C-10), 129.4 (C-1′), 114.3 (C-2′), 145.1 (C-3′), 145.6 (C-4′), 115.3 (C-5′), 117.9 (C-6′) [2].

Kaempferol, mp 271–272°C.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.18 (1H, s, H-6), 6.42 (1H, s, H-8), 6.92 (2H, d, J = 8.7, H-3′, 5′), 8.04 (2H, d, J = 8.7, H-2′, 6′), 12.46 (1H, s, 5-OH), 10.77 (1H, s, 7-OH), 10.09 (1H, s, 3-OH), 9.37 (1H, s, 4′-OH).

Quercetin, mp>300°C.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.18 (1H, s, H-6), 6.41 (1H, s, H-8), 6.87 (1H, d, J = 8.5, H-5′), 7.54 (1H, d, J = 8.5, H-6′), 7.70 (1H, s, H-2′), 12.47 (1H, s, 5-OH), 10.76 (1H, s, 7-OH), 9.57 (1H, s, 3-OH), 9.35 (1H, s, 3′-OH), 9.29 (1H, s, 4′-OH).

Myricetin, mp>300°C.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.14 (1H, s, H-6), 6.35 (1H, s, H-8), 7.24 (2H, s, H-2′, 6′), 12.66 (1H, s, 5-OH), 10.85 (1H, s, 7-OH), 9.37 (1H, s, 3-OH), 9.16 (2H, s, 3′, 5′-OH), 9.09 (1H, s, 4′-OH).

^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 146.7 (C-2), 135.7 (C-3), 175.7 (C-4), 160.7 (C-5), 98.3 (C-6), 163.6 (C-7), 93.4 (C-8), 156.4 (C-9), 102.7 (C-10), 120.6 (C-1′), 107.6 (C-2′, 6′), 145.6 (C-3′, 5′), 135.6 (C-4′).

Quercetin-3-*O*-α-L-rhamnopyranoside, $[M]^+$ 448, mp 172–174°C.

UV spectrum (MeOH, λ_{max}, nm): 206, 255, 351.

IR spectrum (KBr, ν_{max}, cm^{-1}): 3289, 1658, 1605, 1574, 1501, 1455, 1381, 1360.

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PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.25 (1H, s, H-1″), 6.18 (1H, s, H-6), 6.38 (1H, s, H-8), 6.88 (1H, d, J = 8.4, H-5′), 7.25 (1H, d, J = 8.4, H-6′), 7.30 (1H, s, H-2′), 12.66 (1H, s, 5-OH), 10.85 (1H, s, 7-OH), 9.64 (1H, s, 3′-OH), 9.35 (1H, s, 4′-OH).

^{13}C NMR (DMSO-d_6, 75 MHz, δ, ppm): 157.3 (C-2), 134.2 (C-3), 177.7 (C-4), 161.3 (C-5), 98.6 (C-6), 164.1 (C-7), 93.6 (C-8), 156.4 (C-9), 104.1 (C-10), 120.7 (C-1′), 115.4 (C-2′), 145.1 (C-3′), 148.4 (C-4′), 115.6 (C-5′), 121.1 (C-6′), 101.8 (C-1″), 70.6 (C-2″), 70.3 (C-3″), 71.2 (C-4″), 70.0 (C-5″), 17.5 (C-6″). Acid hydrolysis produced quercetin and rhamnose [3].

Quercetin-3-*O*-*β*-D-galactopyranoside, $[M]^+$ 464, mp 231–233°C.

UV spectrum (MeOH, λ_{max}, nm): 256, 297, 361.

IR spectrum (KBr, ν_{max}, cm^{-1}): 3318, 1658, 1565, 1503, 1453, 1367.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.38 (1H, d, J = 7.7, H-1″), 6.21 (1H, d, J = 1.8, H-6), 6.41 (1H, d, J = 1.8, H-8), 6.83 (1H, d, J = 8.4, H-5′), 7.54 (1H, d, J = 2.0, H-2′), 7.67 (1H, dd, J = 8.4, 2.0, H-6′), 12.63 (1H, s, 5-OH), 10.88 (1H, s, 7-OH), 9.73 (1H, s, 3′-OH), 9.16 (1H, s, 4′-OH).

^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 157.5 (C-2), 133.5 (C-3), 177.5 (C-4), 161.2 (C-5), 98.6 (C-6), 164.1 (C-7), 93.4 (C-8), 156.2 (C-9), 103.9 (C-10), 121.1 (C-1′), 115.2 (C-2′), 144.7 (C-3′), 148.3 (C-4′), 115.9 (C-5′), 122.0 (C-6′), 101.8 (C-1″), 71.2 (C-2″), 73.2 (C-3″), 67.9 (C-4″), 75.8 (C-5″), 60.1 (C-6″). Acid hydrolysis produced quercetin and galactose [3].

Myricetin-3-*O*-*α*-L-rhamnopyranoside, $[M]^+$ 464, mp 233–234°C.

UV spectrum (MeOH, λ_{max}, nm): 210, 261, 357.

IR spectrum (KBr, ν_{max}, cm^{-1}): 3391, 1657, 1609, 1503, 1452, 1353.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.20 (1H, br.s, H-1″), 6.19 (1H, d, J = 1.8, H-6), 6.38 (1H, d, J = 1.8, H-8), 6.89 (2H, s, H-2′, H-6′), 12.69 (1H, s, 5-OH), 10.86 (1H, s, 7-OH), 9.27 (2H, s, 3′, 5′-OH), 8.87 (1H, s, 4′-OH).

^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 157.5 (C-2), 134.3 (C-3), 177.7 (C-4), 161.3 (C-5), 98.6 (C-6), 164.0 (C-7), 93.5 (C-8), 156.4 (C-9), 104.0 (C-10), 119.6 (C-1′), 107.9 (C-2′, 6′), 145.6 (C-3′, 5′), 136.3 (C-4′), 101.9 (C-1″), 70.3 (C-2″), 70.5 (C-3″), 71.2 (C-4″), 70.0 (C-5″), 17.5 (C-6″). Acid hydrolysis produced myricetin and rhamnose [4].

Myricetin-3-*O*-*α*-L-arabinopyranoside, $[M]^+$ 450, mp 194–197°C.

UV spectrum (MeOH, λ_{max}, nm): 210, 252, 301, 361.

IR spectrum (KBr, ν_{max}, cm^{-1}): 3423, 1657, 1604, 1564, 1497, 1457, 1383.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.20 (1H, br.s, H-1″), 6.19 (1H, d, J = 1.8, H-6), 6.38 (1H, d, J = 1.8, H-8), 7.15 (2H, s, H-2′, H-6′), 12.65 (1H, s, 5-OH), 10.86 (1H, s, 7-OH), 9.14 (2H, s, 3′, 5′-OH), 8.93 (1H, s, 4′-OH).

^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 156.4 (C-2), 134.0 (C-3), 177.5 (C-4), 161.2 (C-5), 98.6 (C-6), 164.1 (C-7), 93.3 (C-8), 156.2 (C-9), 103.9 (C-10), 119.8 (C-1′), 108.4 (C-2′, 6′), 145.5 (C-3′, 5′), 136.7 (C-4′), 101.6 (C-1″), 71.7 (C-2″), 70.6 (C-3″), 66.1 (C-4″), 64.3 (C-5″). Acid hydrolysis produced myricetin and arabinose [4].

Myricetin-3-*O*-*β*-D-glucopyranoside, $[M]^+$ 480, mp 275–277°C.

UV spectrum (MeOH, λ_{max}, nm): 256, 308, 364.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.26 (1H, d, J = 7.5, H-1″), 6.20 (1H, d, J = 1.8, H-6), 6.39 (1H, d, J = 1.8, H-8), 7.25 (2H, s, H-2′, H-6′), 12.65 (1H, s, 5-OH), 10.86 (1H, s, 7-OH), 9.16 (2H, s, 3′, 5′-OH), 8.99 (1H, s, 4′-OH).

^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 156.4 (C-2), 134.0 (C-3), 177.5 (C-4), 161.4 (C-5), 98.7 (C-6), 164.2 (C-7), 93.3 (C-8), 156.3 (C-9), 104.1 (C-10), 120.4 (C-1′), 108.7 (C-2′, 6′), 145.3 (C-3′, 5′), 137.9 (C-4′), 100.1 (C-1″), 73.2 (C-2″), 76.5 (C-3″), 69.0 (C-4″), 78.2 (C-5″), 60.7 (C-6″). Acid hydrolysis produced myricetin and glucose [4].

Myricetin-3-*O*-*β*-D-galactopyranoside, $[M]^+$ 480, mp 196–198°C.

UV spectrum (MeOH, λ_{max}, nm): 256, 308, 362.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.25 (1H, d, J = 7.5, H-1″), 6.18 (1H, d, J = 1.8, H-6), 6.40 (1H, d, J = 1.8, H-8), 7.21 (2H, s, H-2′, H-6′), 12.66 (1H, s, 5-OH), 10.86 (1H, s, 7-OH), 9.17 (2H, s, 3′, 5′-OH), 8.95 (1H, s, 4′-OH).

^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 156.6 (C-2), 133.9 (C-3), 177.7 (C-4), 161.4 (C-5), 98.7 (C-6), 164.5 (C-7), 93.7 (C-8), 156.5 (C-9), 104.1 (C-10), 120.2 (C-1′), 108.8 (C-2′, 6′), 145.6 (C-3′, 5′), 136.9 (C-4′), 102.2 (C-1″), 71.5 (C-2″), 73.5 (C-3″), 68.3 (C-4″), 76.1 (C-5″), 60.3 (C-6″). Acid hydrolysis produced myricetin and galactose [4].

Homoeriodictyol-7-*O*-*β*-D-glucopyranoside, $[M]^+$ 464, mp 158–160°C.

UV spectrum (MeOH, λ_{max}, nm): 242, 322, 360.

IR spectrum (KBr, ν_{max}, cm^{-1}): 3406, 1644, 1451, 1433, 1272, 1032.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.76 (1H, dd, J = 2.9, 17.1, H-3*α*), 3.14 (1H, dd, J = 17.1, 13.0, H-3*β*), 3.78 (3H, s, -OCH_3), 4.94 (1H, d, J = 7.4, H-1″), 5.48 (1H, dd, J = 2.6, 13.0, H-2), 6.15 (1H, d, J = 1.8, H-6), 6.18 (1H,

d, J = 1.8, H-8), 6.80 (1H, d, J = 8.1, H-5′), 7.11 (1H, d, J = 1.8, H-2′), 6.92 (1H, dd, J = 8.1, 1.8, H-6′), 12.09 (1H, s, 5-OH), 9.17 (1H, s, 4′-OH).

^{13}CNMR (75 MHz, DMSO-d_6, δ, ppm): 78.9 (C-2), 42.2 (C-3), 197.2 (C-4), 162.8 (C-5), 96.5 (C-6), 165.2 (C-7), 95.4 (C-8), 162.7 (C-9), 103.2 (C-10), 129.2 (C-1′), 111.2 (C-2′), 147.5 (C-3′), 147.0 (C-4′), 115.2 (C-5′), 119.8 (C-6′), 99.7 (C-1″), 73.0 (C-2″), 77.0 (C-3″), 69.5 (C-4″), 76.3 (C-5″), 60.6 (C-6″). Acid hydrolysis produced homoeriodictyol and glucose [5].

6″-Galloylmyricetin-3-*O*-β-D-galactopyranoside, $[M]^+$ 632, mp 238–239°C.

UV spectrum (MeOH, λ_{max}, nm): 266, 296, 366.

IR spectrum (KBr, ν_{max}, cm^{-1}): 3329, 1689, 1659, 1615, 1569, 1533, 1451, 1356, 1325, 1197.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.36 (1H, d, J = 7.7, H-1″), 6.18 (1H, d, J = 1.8, H-6), 6.40 (1H, d, J = 1.8, H-8), 6.89 (2H, s, H-2‴, H-6‴), 7.21 (2H, s, H-2′, H-6′), 8.90 (4H, br.s, 4′OH), 9.16 (2H, br.s, 2′OH), 10.82 (1H, s, 7-OH), 12.59 (1H, s, 5-OH).

^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 156.2 (C-2), 133.8 (C-3), 177.3 (C-4), 161.2 (C-5), 98.6 (C-6), 164.1 (C-7), 93.4 (C-8), 156.2 (C-9), 103.9 (C-10), 120.0 (C-1′), 108.6 (C-2′, 6′), 145.5 (C-3′, 5′), 136.7 (C-4′), 102.1 (C-1″), 71.1 (C-2″), 72.9 (C-3″), 67.8 (C-4″), 72.4 (C-5″), 61.9 (C-6″), 119.1 (C-1‴), 108.6 (C-2‴, 6‴), 145.4 (C-3‴, 5‴), 138.5 (C-4‴), 165.4 (C-7‴). Acid hydrolysis produced myricetin, gallic acid, and galactose [6].

Thus, kaempferol, quercetin, myricetin, quercetin-3-*O*-α-L-rhamnopyranoside, quercetin-3-*O*-β-D-galactopyranoside, myricetin-3-*O*-α-*L*-rhamnopyranoside, myricetin-3-*O*-α-L-arabinopyranoside, homoeriodictyol-7-*O*-β-D-glucopyranoside, and 6″-galloylmyricetin-3-*O*-β-D-galactopyranoside are isolated for the first time from *Limonium aureum*.

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