# FLAVONOID AGLYCONES OF *Oxytropis falcata*

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*Oxytropis falcata* is a wild growing Leguminosae plant distributed mainly in the Qinghai-Tibet Plateau in China. The herb of this plant has been known as one of the "Three Anti-inflammatory Drugs" and "King of Herbs" in Chinese Tibetan medicine, and been used to treat inflammation, nociception, pyreticosis, and bleeding for thousands of years [1, 2]. At present, there are many Chinese traditional patent prescriptions that include this medicine in the market. However, there is still only little information on the phytochemistry [3–5] and pharmacological actions of OFB [6–8].

This report describes the isolation from *Oxytropis falcata* of 2′,4′-dihydroxydihydrochalcone, 2′-methoxy-4′-hydroxychalcone, 2′-hydroxy-4′-methoxychalcone, 2′,4′-dihydroxychalcone, isoliquiritigenin, pinostrobin, pinocembrin, 7-hydroxyflavonone, liquiritigenin, kaempferol, isorhamnetin, quercetin, myricetin, chrysin, apigenin, and luteolin, and the structure elucidation of these crystalline substances by physical and chemical properties and NMR analysis.

*Oxytropis falcata* herb was collected from Qinghai Province, China. The material was identified by Professor Chen Jianwei (College of Pharmacy, Nanjing University of Chinese Medicine), dried, and (2 kg) macerated ordinally with 95% ethanol 3 times for 3 days and 50% ethanol 3 times for 3 days in each extraction at ambient temperature. The mixture was filtered under reduce pressure on a filter paper (medium speed for quantitative analysis), and a deep green solution was obtained. The solution was concentrated under reduced pressure at 50–60°C until the ethanol was removed thoroughly. The concentrated residue was suspended in water and extracted by petroleum ether, chloroform, ethyl acetate, and *n*-butanol. The chloroform and ethyl acetate solution were evaporated under reduced pressure. The chloroform extract was further separated by silica gel (200–300 mesh) column chromatography using petroleum ether–ethyl acetate (30:1–1:2) as eluent. Compounds **1** (15 mg), **2** (9 mg), **3** (6 mg), **4** (38 mg), **6** (10 mg), **7** (11 mg), **8** (21 mg), and **9** (3 mg) were obtained. In addition, the chloroform extract was further separated by silica gel (200–300 mesh) column chromatography using petroleum ether–$Me_2CO$ (100:1–1:5) as eluent. Compounds **5** (5 mg), **10** (9 mg), **11** (8 mg), **12** (6 mg), **13** (11 mg), **14** (8 mg), **15** (5 mg), and **16** (12 mg) were obtained.

Compound **1**: $C_{15}H_{14}O_3$. Colorless crystals ($CHCl_3$), mp 89–91°C. $^1$H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 12.81 (1H, s, 2′-OH), 7.59 (1H, d, J = 8.6, H-6′), 7.30~7.27 (2H, m, H-3,5), 7.24~7.18 (3H, m, H-2,4,6), 6.38~6.35 (2H, m, H-3′,5′), 3.20 (2H, t, H-2$\alpha$), 3.04 (2H, t, H-2$\beta$); $^{13}$C NMR (125 MHz, $CDCl_3$, δ, ppm): 203.9 (CO), 165.0 (C-4′), 163.1 (C-2′), 140.7 (C-1), 132.2 (C-6′), 128.6 (C-3,5), 128.3 (C-2,6), 126.3 (C-4), 113.6 (C-1′), 108.0 (C-5′), 103.5 (C-3′), 39.6 (C-$\alpha$), 30.4 (C-$\beta$).

Thus compound **1** was identified as 2′,4′-dihydroxydihydrochalcone, with NMR data in agreement with [5].

Compound **2**: $C_{16}H_{14}O_3$. Yellow needles (EtOH), mp 110–112°C. $^1$H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 7.70 (1H, d, J = 8.0, H-6′), 7.68 (1H, d, J = 15.6, H-$\beta$), 7.58 (2H, m, H-3,5), 7.52 (1H, d, J = 15.6, H-$\alpha$), 7.40~7.37 (3H, m, H-2,4,6), 6.52~6.49 (2H, d, J = 8.0, H-3′,5′), 3.85 (3H, s, $OCH_3$); $^{13}$C NMR (125 MHz, $CDCl_3$, δ, ppm): 191.2 (CO), 161.6 (C-2′), 161.0 (C-4′), 142.7 (C-$\beta$), 135.4 (C-1), 133.1 (C-6′), 130.1 (C-4), 128.9 (C-2,6), 128.4 (C-3,5), 127.1 (C-$\alpha$), 121.5 (C-1′), 108.1 (C-5′), 99.4 (C-3′), 55.7 ($OCH_3$). It was identified by NMR as 2′-methoxy-4′-hydroxychalcone, with spectral data in agreement with [9].

Compound **3**: $C_{16}H_{14}O_3$. Yellow needles (EtOH), mp 101–103°C. $^1$H NMR (300 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 13.42 (1H, s, 2′-OH), 8.30 (1H, d, J = 9.0, H-6′), 8.03 (1H, d, J = 15.5, H-$\beta$), 7.92 (2H, m, H-2,6), 7.83 (1H, d, J = 15.5, H-$\alpha$), 7.50–7.45 (3H, m, H-3,4,5), 6.58 (1H, dd, J = 9.0, 2.5, H-3′), 6.53 (1H, d, J = 2.5, H-5′), 3.86 ($OCH_3$); $^{13}$C NMR (125 MHz, DMSO-$d_6$, δ, ppm): 191.8 (CO), 165.9 (C-2′), 165.4 (C-4′), 143.9 (C-$\beta$), 134.4 (C-1), 132.5 (C-6′), 130.5 (C-4), 128.8 (C-2,6), 128.7 (C-3,5), 121.3 (C-$\alpha$), 115.0 (C-1′), 107.2 (C-5′), 100.9 (C-3′), 55.6 ($OCH_3$).

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Compound **3** was identified by NMR as 2′-hydroxy-4′-methoxychalcone, with spectral data in agreement with [10].

Compound **4**: $C_{15}H_{12}O_3$. Yellow needles (petroleum ether–EtOAc), mp 149–150°C. $^1$H NMR (500 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 13.41 (1H, s, 2′-OH), 10.75 (1H, s, 4′-OH), 8.22 (1H, d, J = 8.9, H-6′), 8.00 (1H, d, J = 15.2, H-$\beta$), 7.90 (2H, m, H-3,5), 7.82 (1H, d, J = 15.2, H-$\alpha$), 7.47 (3H, m, H-2,4,6), 6.46 (1H, dd, J = 8.9, 2.4, H-3′), 6.35 (1H, d, J = 2.4, H-5′); $^{13}$C NMR (125 MHz, DMSO-$d_6$, δ, ppm): 191.4 (CO), 165.8 (C-2′), 165.2 (C-4′), 143.6 (C-$\beta$), 134.6 (C-1), 133.1 (C-6′), 130.6 (C-4), 129.0 (C-2,6), 128.8 (C-3,5), 121.3 (C-$\alpha$), 113.0 (C-1′), 108.3 (C-5′), 102.6 (C-3′). It was identified by NMR as 2′,4′-dihydroxychalcone, with spectral data in agreement with [5].

Compound **5**: $C_{15}H_{12}O_4$. Yellow needles (EtOAc), mp 190–191°C. $^1$H NMR (300 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 13.57 (1H, s, 2′-OH), 10.60 (1H, s, 4′-OH), 10.11 (1H, s, 4-OH), 8.15 (1H, d, J = 8.9, H-6′), 7.76~7.73 (4H, m, H-2,6,$\beta$,$\alpha$), 6.84 (2H, d, H-3,5), 6.40 (1H, dd, J = 8.9, 2.2, H-5′), 6.28 (1H, d, J = 2.2, H-3′); $^{13}$C NMR (75 MHz, DMSO-$d_6$, δ, ppm): 191.4 (CO), 165.6 (C-4′), 164.8 (C-2′), 160.1 (C-4), 144.0 (C-$\beta$), 132.6 (C-6′), 130.9 (C-2,6), 125.7 (C-1), 117.4 (C-$\alpha$), 115.7 (C-3,5), 113.0 (C-1′), 107.9 (C-5′), 102.5 (C-3′).

The compound was identified by NMR as isoliquiritigenin, with spectral data in agreement with [11].

Compound **6**: $C_{16}H_{14}O_4$. Colorless crystals ($CHCl_3$), mp 106–108°C. $^1$H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 12.03 (1H, s, 5-OH), 7.46~7.38 (5H, m, H-2′~6′), 6.07~6.05 (2H, m, H-6,8), 5.40 (1H, dd, J = 3.1, 13.0, H-2), 3.79 (3H, s, $OCH_3$), 3.07 (1H, dd, J = 13.0, 17.2, H-3$\alpha$), 2.81 (1H, dd, J = 3.1, 17.2, H-3$\beta$); $^{13}$C NMR (125 MHz, $CDCl_3$, δ, ppm): 195.6 (CO), 167.9 (C-7), 164.0 (C-5), 162.7 (C-9), 138.3 (C-1′), 128.7 (C-3′,4′,5′), 126.0 (C-2′,6′), 103.0 (C-10), 95.0 (C-6), 94.1 (C-8), 79.1(C-2), 55.5 ($OCH_3$), 43.2(C-3).

Thus **6** was identified by NMR as pinostrobin, with spectral data in agreement with [12].

Compound **7**: $C_{15}H_{12}O_4$. White needles (petroleum ether–EtOAc), mp 198–200°C, was identified as pinocembrin [13].

Compound **8**: $C_{15}H_{12}O_3$. Colorless needles (EtOH), mp 188–190°C. $^1$H NMR (300 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 10.57 (1H, s, 7-OH), 7.66 (1H, d, J = 8.5, H-5), 7.52~7.38 (5H, H-2′~6′), 6.53 (1H, dd, J = 8.5, 2.2, H-6), 6.38 (1H, d, J = 2.2, H-8), 5.58 (1H, dd, J = 12.7, 3.0, H-2), 3.12 (1H, dd, J = 16.8, 12.7, H-3$\alpha$), 2.72 (1H, dd, J = 16.8, 3.0, H-3$\beta$); $^{13}$C NMR (75 MHz, DMSO-$d_6$, δ, ppm): 190.0 (CO), 164.6 (C-7), 162.9 (C-9), 139.0 (C-1′), 128.4 (C-3′), 128.3 (C-4′,5′,5), 126.5 (C-2′,6′), 113.5 (C-10), 110.6 (C-6), 102.6 (C-8), 78.9 (C-2), 43.2 (C-3). Compound **8** was identified by NMR as 7-hydroxyflavonone, with spectral data in agreement with [14].

Compound **9**: $C_{15}H_{12}O_4$. White needles (EtOAc), mp 205–206°C. $^1$H NMR (300 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 10.54 (1H, s, 7-OH), 9.56 (1H, s, 4′-OH), 7.66 (1H, d, J = 8.6, H-5), 7.33 (2H, d, H-2′,6′), 6.80 (2H, d, H-3′,5′), 6.51 (1H, dd, J = 8.6, 2.2, H-6), 6.34 (1H, d, J = 2.2, H-8), 5.44 (1H, dd, J = 12.8, 2.8, H-2), 3.11 (1H, dd, J = 16.8, 12.8, H-3α), 2.62 (1H, dd, J = 16.8, 2.8, H-3$\beta$); $^{13}$C NMR (75 MHz, DMSO-$d_6$, δ, ppm): 189.9 (CO), 164.5 (C-7), 163.1 (C-9), 157.6 (C-4′), 129.3 (C-1′), 128.3 (C-5), 128.1 (C-2′,6′), 115.1 (C-3′,5′), 113.6 (C-10), 110.4 (C-6), 102.5 (C-8), 78.9 (C-2), 43.2 (C-3).

Thus **9** was identified by NMR as liquiritigenin, with spectral data in agreement with [15].

Compound **10**: $C_{15}H_{10}O_6$. Yellow needles (EtOH), mp 268–270°C. A positive HCl-Mg test was obtained. It was identified as kaempferol [16].

Compound **11**: $C_{16}H_{12}O_7$. Yellow needles (EtOH), mp 309–310°C. A positive HCl-Mg test was obtained. The compound was identified as isorhamnetin [16].

Compound **12**: $C_{15}H_{10}O_7$. Yellow needles (EtOH), mp 316–318°. A positive HCl-Mg test was obtained. Thus **12** was identified as quercetin [17].

Compound **13**: $C_{15}H_{10}O_8$. Yellow needles (MeOH), mp 328–330°C. $^1$H NMR (300 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 12.48 (1H, s, 5-OH), 7.24 (2H, s, H-2′,6′), 6.37 (1H, d, J = 2.0, H-6), 6.18 (1H, d, J = 2.0, H-8); $^{13}$C NMR (75 MHz, DMSO-$d_6$, δ, ppm): 175.6 (CO), 163.8 (C-7), 160.6 (C-5), 156.0 (C-9), 146.8 (C-2), 145.6 (C-3′,5′), 135.8 (C-3), 135.7 (C-4′), 120.7 (C-1′), 107.2 (C-2′,6′), 102.9 (C-10), 98.0 (C-6), 93.1 (C-8). It was identified by NMR as myricetin, with spectral data in agreement with [18].

Compound **14**: $C_{15}H_{10}O_4$. Yellow needles (EtOH), mp 275–276°C. A positive HCl-Mg test was obtained. Thus **14** was identified as chrysin [19].

Compound **15**: $C_{15}H_{10}O_5$. Yellow needles (EtOH), mp 338–339°C. A positive HCl-Mg test was obtained. Thus **15** was identified as apigenin [20].

Compound **16**: $C_{15}H_{10}O_6$. Yellow needles (EtOH), mp 320–321°C. A positive HCl-Mg test was obtained. Thus **16** was identified as luteolin [17].

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