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美脉藁本的化学成分*

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The Chemical Constituents of *Ligusticum calophlebicum*

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Ligusticum calophlebicum (Umbelliferae) is a perennial medicinal plant growing in Yunnan Province. The roots and rhizomes of this plant has been used as the Chinese drug "Han Qian-Hu" in the northwest region of Yunnan Province. As there was no reported the chemical constituents of this plant, in our continuous course of chemical study about "Qian-Hu", we undertook the investigation of this plant. Our present studies led to yield 11 compounds, and their structures were identified as umbelliferone (**1**), (+) cis-khellactone (**2**), Pd-Ib (**3**), pteryxin (**4**), (±) pareruptorin B (**5**), (+) pareruptorin B (**6**), 3′ (R)-senecionyloxy-4′ (R)-angeloyloxy-3′, 4′-dihydroseselin (**7**), angelic acid (**8**), stearic acid (**9**), β-sitosterol (**10**), daucosterol (**11**) on the spectral evidences.

The result showed that the mainly chemical constituents of *Ligusticum calophlebicum* were coumarins, mostly as angular-type dihydropyranocoumarins. The structural categories of coumarins from this plant were consistent compared with the Bai-Hua Qian-Hu of Chinese Pharmacopeia. Therefore, it suggested that this plant could be used as the substitute of "Qian-Hu".

Experimental

Melting points were uncorrected. Optical rotations were taken on a JASCO-20C digital polarimeter. IR were recorded on a Bio-Rad FTS-135 infrared spectrophotometer with KBr pellets. ^{1}H, ^{13}C NMR and 2D-NMR were obtained on a Bruker AM-400 spectrometer with TMS as an internal standard. ESI Mass were recorded on a VG Autospec-3000 spectrometer.

The roots and rhizomes of *L. calophlebicum* were collected in the Eryuan county of Yunnan Province, P. R. China, in 1996. It was identified by Prof. Liu Qixin, Jiangsu Institute of Botany. A voucher specimen is deposited in the herbarium of Jiangsu Institute of Botany.

The dried and powdered roots and rhizomes (970 g) of *L. calophlebicum* was extracted with 95% EtOH under reflux

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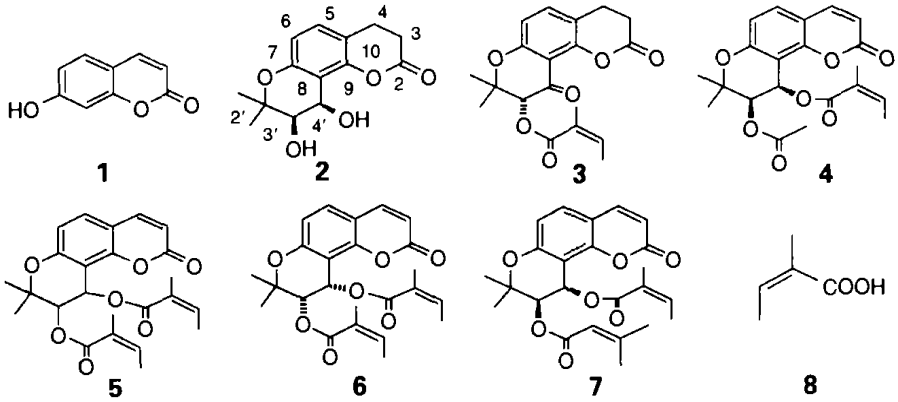
for 3 times. The extract was concentrated under vacuum to afford a brown-red residue (285 g). The residue was dissolved in water and partitioned with EtOAc. The EtOAc fraction was evaporated in vacuo to give 140 g of a brown residue, which was subjected to silica gel CC, eluted with cyclohexane-EtOAc and $CHCl_3$-MeOH to affor compounds **1** (18 mg), **2** (34 mg), **3** (25 mg), **4** (90 mg), **5** (4.6 g), **6** (50 mg), **7** (1.1 g), **8** (1.3 g), stearic acid (**9**, 260 mg), β-sitosterol (**10**, 305 mg) and daucosterol (**11**, 125 mg).



Umbelliferone (**1**): colorless needles (MeOH), mp 221 - 223℃; IR ν_{max}^{KBr} cm^{-1}: 3440, 1730, 1680, 1620, 1600, 1560, 1410, 1230, 1130. MS m/z: 162 [$C_9H_6O_3$, M]$^+$, 134 (100), 106, 78. The TLC and spectral data were identical to authentic sample (Rao *et al*, 1997).

(+) **Cis-Khellactone** (**2**): white needles (MeOH), mp 170 - 172℃, $[\alpha]_D^{28}$ + 130° (*c* 0.31, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3450, 1733, 1680, 1600, 1488, 1250, 1140. MS m/z: 262 [$C_{14}H_{14}O_5$, M]$^+$, 191 (100), 190, 162, 134. ^{1}H NMR ($CDCl_3$): 7.62 (1H, d, J = 9.5 Hz, H - 4), 7.55 (1H, d, J = 8.6 Hz, H - 5), 7.23 (1H, d, J = 8.6 Hz, H - 6), 6.69 (1H, d, J = 9.5 Hz, H - 3), 5.01 (1H, d, J = 5.2 Hz, H - 4′), 3.72 (1H, J = 5.2 Hz, H - 3′), 1.34 and 1.32 [each 3H, s, 2′-gem $(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): 162.1 (s, C - 2), 156.5 (s, C - 7), 154.1 (s, C - 9), 144.7 (d, C - 4), 128.4 (d, C - 5), 114.9 (d, C - 6), 112.0 (s, C - 10), 112.0 (d, C - 3), 111.4 (s, C - 8), 78.9 (s, C - 2′), 71.0 (d, C - 3′), 60.1 (d, C - 4′), 25.3 and 20.8 [q, 2′-gem $(CH_3)_2$]. The spectral data were identical to the literature (Kong *et al*, 1993).

Pd-Ib (**3**): white needles (MeOH), mp 210 - 215℃, $[\alpha]_D^{17}$ + 19° (*c* 0.25, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 2920, 2850, 1733 - 1705, 1645, 1620, 1598, 1484, 1145. MS m/z: 342 [$C_{19}H_{18}O_6$, M]$^+$, 242, 189, 160, 83 (100). ^{1}H NMR ($CDCl_3$): 7.60 (1H, d, J = 9.6 Hz, H - 4), 7.55 (1H, d, J = 8.7 Hz, H - 5), 6.72 (1H, d, J = 8.7 Hz, H - 6), 6.27 (1H, d, J = 9.6 Hz, H - 3), 5.61 (1H, s, H - 3′), 1.52 and 1.42 [each 3H, s, 2′-gem $(CH_3)_2$]; angeloyloxy: 6.16 (1H, q, J = 7.2 Hz), 2.00 (3H, d, J = 7.2 Hz), 1.93 (3H, br. s). ^{13}C NMR ($CDCl_3$): 184.1 (s, C - 4′), 161.9 (s, C - 2), 159.5 (s, C - 7), 153.6 (s, C - 9), 142.9 (d, C - 4), 134.6 (d, C - 5), 114.8 (d, C - 6), 114.0 (d, C - 3), 112.8 (s, C - 10), 108.1 (s, C - 8), 82.4 (s, C - 2′), 76.3 (d, C - 3′), 26.2 and 20.4 [q, 2′-gem $(CH_3)_2$]; angeloyloxy: 166.0 (s), 19.6 (q), 126.8 (s), 15.9 (q), 140.0 (q). The spectral data were identical to the literature (Kong *et al*, 1994).

Pteryxin (**4**): yellow glassy mass, $[\alpha]_D^{28}$ + 13° (*c* 0.52, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1740, 1610, 1490, 1230, 1150, 1100. MS m/z: 386 [$C_{21}H_{22}O_7$, M]$^+$, 326, 287, 245, 229, 175, 83 (100), 55. The TLC and spectral data were identical to authentic sample (Rao *et al*, 1990).

(±) **Pareruptorin B** (**5**): white needles (MeOH), mp 122 - 123℃, $[\alpha]_D^{17}$ ± 0° (*c* 1.12, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1730, 1606, 1470, 1230, 1150, 1090. MS m/z: 426 [$C_{24}H_{26}O_7$, M]$^+$, 229, 189, 83 (100). ^{1}H NMR ($CDCl_3$): 7.61 (1H, d, J = 9.5 Hz, H - 4), 7.36 (1H, d, J = 8.6 Hz, H - 5), 6.82 (1H, d, J = 8.6 Hz, H

-6), 6.70 (1H, d, J=4.9 Hz, H-4'), 6.21 (1H, d, J=9.5 Hz, H-3), 5.45 (1H, d, J=4.9 Hz, H-3'), 1.49 and 1.46 [each 3H, s, 2'-gem $(CH_3)_2$]; angeloyloxy: 6.12 (1H, q, J=7.2 Hz), 6.02 (1H, q, J=7.2 Hz), 1.96 (6H, br. d, J=7.2 Hz), 1.85 (6H, br. s). ^{13}C NMR ($CDCl_3$): 159.7 (s, C-2), 156.6 (s, C-7), 154.0 (s, C-9), 143.2 (d, C-4), 129.2 (d, C-5), 114.3 (d, C-6), 113.2 (d, C-3), 112.4 (s, C-10), 107.5 (s, C-8), 77.4 (s, C-2'), 70.2 (d, C-3'), 60.1 (d, C-4'), 25.4 and 22.4 [q, 2'-gem $(CH_3)_2$]; angeloyloxy: 166.4 and 166.2 (s), 139.7 and 138.3 (d), 127.3 and 127.0 (s), 20.3 and 20.2 (q), 15.7 and 15.5 (q). The [α] and ^{1}H NMR data were identical to the literature (Chen *et al*, 1979).

(+) **Pareruptorin B** (**6**): white needles (MeOH), mp 175-176℃, $[\alpha]_D^{17}$ +46° (*c* 0.83, $CHCl_3$). The spectral data were identical to compound **5**, but it was dextrorotatory. The [α] was similar to (+)-pareruptorin B (Dai *et al*, 1995).

3'(R)-Senecionyloxy-4'(R)-angeloyloxy-3', 4'-dihydroseselin (**7**): yellow glassy mass, $[\alpha]_D^{28}$ +10° (*c* 0.19, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1730, 1608, 1490, 1457, 1230, 1150, 1070. MS m/z: 426 [$C_{24}H_{26}O_7$, M]$^+$, 229, 245, 189, 83 (100). ^{1}H NMR ($CDCl_3$): 7.62 (1H, d, J=9.4 Hz, H-4), 7.37 (1H, d, J=8.6 Hz, H-5), 6.75 (1H, d, J=8.6 Hz, H-6), 6.56 (1H, d, J=4.0 Hz, H-4'), 6.11 (1H, d, J=9.4 Hz, H-3), 5.27 (1H, d, J=4.0 Hz, H-3'), 1.38 and 1.35 [each 3H, s, 2'-gem $(CH_3)_2$]; angeloyloxy: 5.89 (1H, q, J=7.0 Hz), 1.87 (3H, d, J=7.0 Hz), 1.75 (3H, s); senecionyloxy: 5.59 (1H, s), 2.08 and 1.81 (each 3H, s). ^{13}C NMR ($CDCl_3$): 164.5 (s, C-2), 158.1 (s, C-7), 153.5 (s, C-9), 143.2 (d, C-4), 129.1 (d, C-5), 114.6 (d, C-6), 114.0 (d, C-3), 112.1 (s, C-10), 106.8 (s, C-8), 76.7 (s, C-2'), 69.0 (d, C-3'), 59.4 (d, C-4'), 24.8 and 21.9 [q, 2'-gem $(CH_3)_2$]; angeloyloxy: 166.1 (s), 137.6 (d), 127.2 (s), 19.8 and 14.9 (q); senecionyloxy: 165.9 (s), 159.3 (s), 112.4 (d), 26.9 and 19.7 (q). The locations of the angeloyloxy and senecionyloxy were designated by HMQC and HMBC. The [α] was similar to the literature (Murray *et al*, 1982).

Angelic acid (**8**): colorless ctystal (MeOH), mp 50-51℃. IR ν_{max}^{KBr} cm^{-1}: 3630-2500, 2920, 1700, 1460, 1030, 720. MS m/z: 100 [$C_5H_8O_2$, M]$^+$, 85, 57 (100). ^{1}H NMR ($CDCl_3$): 6.25 (1H, q, J=7.3 Hz, H-3), 2.06 (3H, q, J=7.3 Hz, H-4), 1.93 (3H, s, 2-CH_3). ^{13}C NMR ($CDCl_3$): 174.0 (s, C-1), 141.1 (d, C-3), 127.2 (s, C-2), 20.3 (q, 2-CH_3), 16.0 (q, C-4).

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