

Studies on the Chemical Constituents of *Sarcandra glabra*

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Abstract. From the total water extracted from *Sarcandra glabra* extraction part chloroform extract, nine compounds were isolated and identified as isofraxidin(1), 8-methoxy-6,7-methylenedioxy-coumarin(2), 7-methylnaringenin(3), kaemferol(4), kaemferol-3-O- rhamno-pyranosyl (1→6) glucopyranoside(5), eleutheroside B₁(6), isofraxidin-7-O- β -D-xylopyranosyl(1-3)- α -D-glucopyranoside(7), rosmarinic acid (8), 3, 4-dihydroxyphenethyl caffeate(9). Their structures were determined by spectral data.

Introduction

Sarcandra glabra (Thunb) Nakai is distributed in the southern part of China. The whole plant has been used as an antibacterial and antitumour agent in China[1~3]. In our previous chemical investigations of this plant, sesquiterpene lactones and flavonoids have been identified as constituents of the plant[4]. In the course of our continuing search for this plant, nine compounds were isolated and identified as isofraxidin(1), 8-methoxy- 6,7-methylenedioxy-coumarin(2), 7-methylnaringenin(3), kaemferol(4), kaemferol-3-O- rhamno- pyranosyl(1→6)glucopyranoside(5), eleutheroside B₁(6), isofraxidin-7-O- β -D-xylopyranosyl(1- 3)- α -D-glucopyranoside(7), rosmarinic acid (8), 3, 4-dihydroxyphenethyl caffeate(9). Here we report the isolation and structure elucidation of these compounds.

Experimental

General experimental procedures All melting points were determined on a X-4A micro-melting point apparatus and are uncorrected. IR spectra were recorded with an American Nicolet IMPACT-400 Fourier Transform Infrared Spectrometer. ¹H-NMR, ¹³C-NMR, HSQC and HMBC were recorded on an American Varian company INOVA-400 and SYSTEM-600 FT NMR spectrometer. Silica gel (200–300 mesh; Qingdao Marine Chemical Plant) was used for column chromatography.

Plant material *Sarcandra glabra* were collected at Chongyi County, Jiangxi Province, China in July of 2013 and authenticated by Professor Q. Lui, Jiangxi University of Traditional Chinese Medicine. A voucher specimen (2013-07-08) of the plant is deposited at the Herbarium of Jiangxi University of Traditional Chinese Medicine.

Extraction and isolation The whole air-dried plant of *Sarcandra glabra* was reduced to a coarse powder and refluxed with 95% ethanol three times, After evaporation of ethanol in vacuo, the aqueous residue was diluted with water and was extracted with chloroform, ethyl acetate and butanol saturated with water to give the respective extracts after solvent removal. The chloroform-solution portion was subjected to column chromatography on silica gel using a gradient mixture of light petroleum/ethyl acetate (from 5:1 to 1:1) as eluting solvent to afford compound 1, 2.

The ethyl acetate-solution portion was evaporated, and the part extract was fractionated by silica gel column chromatography, eluted with chloroform- ethyl acetate to give compound 3, 4, 6. The butanol-solution portion was subjected to a silica-gel column eluted with $\text{CHCl}_3\text{--MeOH--H}_2\text{O}$ (6:4:1) to give compound 5, 7, 8, 9.

Results and Discussion

Compound 1 was obtained as a yellow needles, mp: 156-157°C(dec). UV λ_{max} (MeOH): 244nm, 344nm. IR (KBr) cm^{-1} : 3298, 2981, 2941, 1705, 1606, 1574, 1496, 1456, 1415, 1302, 1161, 1122, 1036, 976, 914, 850, 596. EI-MS $m/z(\%)$: 222(M^+ , 100), 207(34), 194(20), 179(23), 161(8), 151(16), 133(9), 123(21), 108(13), 95(17), 79(17), 63(6), 51(16). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, 400MHz) δ : 6.25(1H, d, $J=9.6\text{Hz}$, H-3), 7.29(1H, d, $J=9.6\text{Hz}$, H-4), 7.05(1H, s, H-5), 4.08 (3H, s, OCH_3), 3.95(3H, s, OCH_3). $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$, 100MHz) δ : 160.6 (C-2), 110.7(C-3), 146.0 (C-4), 104.9 (C-4a), 112.5 (C-5), 145.3 (C-6), 143.4 (C-7), 144.6 (C-8), 135.1 (C-8a), 56.6 (OCH_3), 61.2(OCH_3). On the basis of relevant reference[5] and its spectral data, its structure was elucidated to be isofraxidin.

Compound 2 was obtained as a yellow needles, mp 146~149°C. The $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, 400MHz) δ : 6.32(1H, d, $J=9.6\text{Hz}$, H-3), 7.94(1H, d, $J=9.6\text{Hz}$, H-4), 7.05 (1H, s, H-6), 6.22 (2H, s, $-\text{OCH}_2\text{O}-$). $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$, 100MHz) δ : 145.2 (C-2), 110.7(C-3), 128.7 (C-4), 114.7 (C-4a), 113.9 (C-5), 143.5 (C-6), 143.4 (C-7), 142.6 (C-8), 133.7 (C-8a), 56.5 (OCH_3), 61(OCH_3). on the basis of all the above results, its structure was elucidated to be 8-methoxy-6,7-methylenedioxy-coumarin.

Compound 3 was obtained as a yellow needles, mp 243~245°C (dec). EI-MS $m/z(\%)$: 286(M^+), 271(31), 153(100), 120(61), 69(21), 43(5). $^1\text{H-NMR}$ (CD_3OD , 400MHz) δ : 7.41 (2H, d, $J=8\text{Hz}$, H-2', 6'), 6.91 (2H, d, $J=8\text{Hz}$, H-3', 5'), 6.19 (1H, d, $J=2\text{Hz}$, H-8), 6.02 (1H, d, $J=2\text{Hz}$, H-6), 5.42 (1H, dd, $J=3, 12\text{Hz}$, H-2), 3.83 (3H, s, OCH_3), 2.96 (1H, dd, $J=12, 16\text{Hz}$, H-3 trans), 2.70 (1H, dd, $J=3, 16\text{Hz}$, H-3 cis). $^{13}\text{C-NMR}$ (CD_3OD , 100MHz) δ : 80.2 (C-2), 46.4 (C-3), 191.8 (C-4), 166.6 (C-5), 97.1 (C-6), 167.0 (C-7), 94.2 (C-8), 164.2 (C-9), 105.8 (C-10), 125.0 (C-1'), 130.2 (C-2', C-6'), 117.2 (C-3', C-5'), 161.2 (C-4'), 56.4(OCH_3). On the basis of relevant reference [6] and its spectral data, its structure was elucidated to be 7-methylnaringenin.

Compound 4 was obtained as a yellow needles, mp: 275~277°C. UV λ_{max} nm (MeOH): 365, 327sh, 294sh, 265, 253sh. IR(KBr) cm^{-1} : 3747, 3321, 2463, 2364, 1654, 1607, 1503, 1378, 1180, 1101, 985, 820. EI-MS $m/z(\%)$: 286 (M^+ , 100), 270 (5), 258 (27), 229 (25), 213 (18), 153 (21), 121(60), 93 (22), 77 (18), 69 (30). $^1\text{H-NMR}$ (CD_3COCD_3 , 400MHz) δ : 6.2 (1H, d, $J=2\text{Hz}$, H-6), 6.5 (1H, d, $J=2\text{Hz}$, H-8), 7.0 (2H, d, $J=9, 3\text{Hz}$, H-3', H-5'), 8.1 (2H, d, $J=9, 3\text{Hz}$, H-2', H-6'). $^{13}\text{C-NMR}$ (CD_3OD , 100MHz) δ : 147.0 (C-2), 136.4 (C-3), 176.4 (C-4), 157.6 (C-5), 99.0 (C-6), 165.1 (C-7), 94.3 (C-8), 161.8 (C-9), 103.9 (C-10), 123.0 (C-1'), 130.3 (C-2', C-6'), 116.2 (C-3', C-5'), 160.2 (C-4'). On the basis of relevant reference [7] and its spectral data, its structure was elucidated to be kaemferol.

Compound 5 was obtained as a yellow needles, mp: 223~224°C. UV λ_{max} nm (MeOH): 351, 319sh, 265. λ_{max} nm (MeOH+NaOAc): 383, 352, 305sh, 273. IR (KBr) cm^{-1} : 3425, 2930, 2361,

1684, 1563, 1507, 1180, 887, 831, 582. FAB-MS $m/z(\%)$: 595 ($M+H$, 27), 449 (12), 287 (44), 113 (100), 87 (14), 59 (8). 1H -NMR (CD_3OD , 600MHz) δ : 8.1 (2H, d, $J=7.5$ Hz, H-2', H-6'), 6.9 (2H, d, $J=7.5$ Hz, H-3', H-5'), 6.4 (1H, s, H-8), 6.2 (1H, s, H-6), 5.2 (1H, d, $J=7$ Hz, glc-H-1), 4.5 (1H, s, rha-H-1), 3.2~3.8 (10H, m, rha and glc-H), 1.3~1.7 (3H, m, rha-CH₃). ^{13}C -NMR (CD_3OD , 150MHz) δ : 158.6 (C-2), 135.5 (C-3), 179.4 (C-4), 159.4 (C-5), 99.9 (C-6), 166.1 (C-7), 95.0 (C-8), 163.0 (C-9), 105.7 (C-10), 122.7 (C-1'), 132.4 (C-2', C-6'), 116.1 (C-3', C-5'), 161.5 (C-4'), 104.6 (C-1''), 75.8 (C-2''), 77.2 (C-3''), 71.4 (C-4''), 78.1 (C-5''), 68.6 (C-6''), 102.4 (C-1'''), 72.3 (C-2'''), 72.1 (C-3'''), 73.9 (C-4'''), 69.7 (C-5'''), 17.9 (C-6'''). On the basis of relevant reference [7] and its spectral data, its structure was elucidated to be kaemferol-3-O-rhamnopyranosyl (1 \rightarrow 6) glucopyranoside.

Compound 6 was obtained as colorless needles, mp: 218~219°C. ESI-MS m/z : 407 [$M+Na$]⁺. 1H -NMR (C_5D_5N , 400MHz) δ : 6.38 (1H, d=10Hz, H-3), 7.62 (1H, d=10Hz, H-4), 6.82 (1H, s, H-5), 6.09 (1H, d=2Hz, H-1'), 4.15 (3H, s, OCH₃), 3.73 (3H, s, OCH₃). ^{13}C -NMR (C_5D_5N , 100MHz) δ : 160.4 (C-2), 115.0 (C-3), 144.0 (C-4), 104.9 (C-4a), 115.3 (C-5), 143.6 (C-6), 143.1 (C-7), 143.1 (C-8), 135.6 (C-8a), 56.7 (OCH₃), 61.7 (OCH₃), 105.5 (C-1'), 75.9 (C-2'), 78.4 (C-3'), 71.5 (C-4'), 79.2 (C-5'), 62.5 (C-6'). On the basis of relevant reference [5] and its spectral data, its structure was elucidated to be eleutheroside B₁.

Compound 7 was obtained as colorless needles, mp: 206~207°C. ESI-MS m/z : 539 [$M+Na$]⁺. 1H -NMR ($DMSO-d_6$, 600MHz) δ : 6.38 (1H, d, $J=10$ Hz, H-3), 7.94 (1H, d, $J=10$ Hz, H-4), 7.12 (1H, s, H-5), 5.23 (1H, d, $J=3$ Hz, H-1'), 5.17 (1H, d, $J=7$ Hz, H-1''), 3.82 (3H, s, OCH₃), 3.31 (3H, s, OCH₃). ^{13}C -NMR ($DMSO-d_6$, 150MHz) δ : 159.7 (C-2), 114.6 (C-3), 144.3 (C-4), 105.4 (C-4a), 114.8 (C-5), 142.3 (C-6), 149.3 (C-7), 141.5 (C-8), 140.3 (C-8a), 56.5 (OCH₃), 61.3 (OCH₃), 109.1 (C-1'), 75.9 (C-2'), 81.8 (C-3'), 73.5 (C-4'), 79.0 (C-5'), 60.5 (C-6'), 101.9 (C-1''), 73.8 (C-2''), 77.1 (C-3''), 68.1 (C-4''), 63.6 (C-5''). On the basis of spectral data, its structure was elucidated to be isofraxidin-7-O- β -D-xylopyranosyl(1-3)- α -D-glucopyranoside [5].

Compound 8 was obtained as a white crystal. EI-MS $m/z(\%)$: 360 (M^+). 1H -NMR (CD_3OD , 400MHz) δ : 7.49 (1H, d, $J=16$ Hz, H-7), 7.02 (1H, s, H-2), 7.00 (1H, d, $J=8.0$ Hz, H-6), 6.76 (1H, d, $J=8$ Hz, H-5), 6.67 (1H, s, H-2'), 6.64 (1H, d, $J=8$ Hz, H-5'), 6.59 (1H, d, $J=8$ Hz, H-6'), 6.27 (1H, d, $J=16$ Hz, H-8), 5.07 (1H, dd, $J=4, 6.5$ Hz, H-8'), 3.06 (1H, dd, $J=4, 14$ Hz, H-7'a), 2.93 (1H, dd, $J=6.5, 14$ Hz, H-7'b). ^{13}C -NMR (CD_3OD , 100MHz) δ : 125.8 (C-1), 115.1 (C-2), 145.9 (C-3), 149.6 (C-4), 115.7 (C-5), 121.6 (C-6), 146.5 (C-7), 113.4 (C-8), 166.2 (C-9), 127.7 (C-1'), 116.4 (C-2'), 144.9 (C-3'), 144.0 (C-4'), 115.4 (C-5'), 120.2 (C-6'), 36.3 (C-7'), 73.3 (C-8'), 171.1 (C-9'). On the basis of relevant reference [8] and its spectral data, its structure was elucidated to be rosmarinic acid.

Compound 9 was obtained as a white crystal. EI-MS m/z : 316 (M^+). 1H -NMR (CD_3OD , 400MHz) δ : 7.49 (1H, d, $J=15.9$ Hz, H-7), 7.01 (1H, s), 6.90 (1H, d, $J=6$ Hz, H-6), 6.88 (1H, s), 6.73 (1H, d, $J=6$ Hz, H-5), 6.62 (1H, d, $J=8$ Hz, H-5'), 6.59 (1H, d, $J=8$ Hz, H-6'), 6.25 (1H, d, $J=15.9$ Hz, H-8), 5.06 (1H, d, $J=9$ Hz, H-8'), 3.10 (1H, d, $J=13$ Hz, H-7'), 2.92 (1H, d, $J=13, 9$ Hz,

H-7'). ^{13}C -NMR (CD_3OD , 100MHz) δ : 127.8 (C-1), 116.1 (C-2), 146.7 (C-3), 149.5 (C-4), 117.5 (C-5), 122.9 (C-6), 145.9 (C-7), 115.0 (C-8), 169.1 (C-9), 131.0 (C-1'), 116.4 (C-2'), 146.8 (C-3'), 144.8 (C-4'), 115.4 (C-5'), 121.7 (C-6'), 38.6 (C-7'), 77.5 (C-8'). On the basis of relevant reference [9] and its spectral data, its structure was elucidated to be 3, 4-dihydroxyphenethyl caffeate.

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