Chemistry of Natural Compounds, Vol. 47, No. 5, November, 2011 [Russian original No. 5, September–October, 2011]

IRIDOID GLYCOSIDES AND PHENYLETHANOID GLYCOSIDES FROM *Phlomis younghusbandii* ROOTS

Mao-xing Li,[1*] Jin Huang,[2*] Chao Zhang,[3] Zheng-ping Jia,[1,3] Peng-cheng Fan,[1] Li-li Wei,[1] Quan-long Zhang,[1] and Ru-xue Zhang[1]

UDC 547.918

Phlomis younghusbandii is a perennial herb (family Labiatae) and grows wildly in the Qinghai-Tibet Plateau in northwestern China. For thousands years, *P. younghusbandii* has been widely used to treat colds, coughs, sore ulceration, rheumatoid arthritis, pneumonia, bronchitis, and other diseases [1]. Iridoid glycosides and phenylethanoids with antinociceptive and anti-inflammatory activities have been isolated from several plants of the genus *Phlomis* [2]. As to *P. younghusbandii*, only several iridoid glycosides and diterpenoid glycosyl esters have been reported [3–5]. In this paper, six iridoid glycosides, shanzhiside methyl ester (**1**), sesamoside (**2**), 7,8-dehydropenstemoside (**3**), penstemoside (**4**), 8-*O*-acetylshanzhiside methyl ester (**5**), and phlomiol (**6**), and three phenylethanoid glycosides, acteoside (**7**), alyssonoside (**8**), and isoacteoside (**9**), were isolated and identified from *P. younghusbandii* by comparing the spectral data with those in the literature. Compound **3** and three phenylethanoid glycosides, **7**, **8**, and **9**, were isolated from this plant for the first time.

Roots of *P. younghusbandii* were collect from Tibet Province of China in July 2009 and identified by Prof. Zhigang Ma, College of Pharmacy, Lanzhou University.

Air-dried roots were soaked with 50% EtOH at 50°C for 3 days, three times, and then concentrated. The combined extract was dissolved in distilled water and then subjected to D101 macroporous adsorptive resin column chromatography. Alcohol (50%) was used to elute the column after it had been eluted with distilled water till the Molisch reaction became negative. The iridoid glycoside fraction was obtained after the alcohol eluate was vacuum-dried at 60°C. This fraction was further purified by reversed-phase preparative liquid chromatography with 30% methanol as the solvent system. Finally, six iridoid glycosides and three phenylethanoid glycosides were obtained, and their chemical structures were identified by spectral analysis using MS, NMR, and other spectrometers.

Shanzhiside methyl ester (1) white powder. $C_{17}H_{26}O_{11}$, mp 110–112°C; $[\alpha]_D^{25}$ –130.4° (*c* 0.44, MeOH). UV (MeOH, λ_{max}, nm) (log ε): 235 (4.31). IR (KBr, ν_{max}, cm^{-1}): 3408, 1693 (C=O), 1640 (C=C), 1186, 1078, 995. EI-MS *m/z*: 429.2 $[M + Na]^+$, 445 $[M + K]^+$. The ^1H NMR and ^{13}C NMR data were consistent with the literature [3, 6, 7].

Sesamoside (2) white powder. $C_{17}H_{24}O_{12}$, mp 206–208°C; $[\alpha]_D^{25}$ –79.5° (*c* 0.5, MeOH). UV (MeOH, λ_{max}, nm) (log ε): 230 (4.21). IR (KBr, ν_{max}, cm^{-1}): 3423, 1693 (C =O), 1635 (C=C), 1194, 1076, 947. EI-MS *m/z*: 443 $[M + Na]^+$, 459 $[M + K]^+$. The ^1H NMR and ^{13}C NMR data were consistent with the literature [3, 7].

7,8-Dehydropenstemoside (3) white powder. $C_{17}H_{24}O_{11}$, mp 119–120°C; $[\alpha]_D^{20}$ –78.1° (*c* 0.48, MeOH). UV (MeOH, λ_{max}, nm) (log ε): 234.2 (5.82). IR (KBr, ν_{max}, cm^{-1}): 3400, 1709 (C=O), 1633 (C=C), 1294, 940. EI-MS *m/z*: 427.2 $[M + Na]^+$, 443.2 $[M + K]^+$. ^1H NMR (400 MHz, D_2O, δ, ppm, J/Hz): 5.94 (1H, d, J = 2, H-1), 7.59 (1H, s, H-3), 4.54 (1H, s, H-6), 5.61 (1H, d, J = 1.6, H-7), 3.23 (1H, s, H-9), 1.82 (3H, s, H-10), 3.78 (3H, s, OCH_3), 4.79 (1H, d, J = 8, Glc-1). ^{13}C NMR (400 MHz, D_2O, δ, ppm): 94.02 (C-1), 154.43 (C-3), 110.71 (C-4), 72.29 (C-5), 76.3 (C-6), 127.03 (C-7), 142.96 (C-8), 54.8 (C-9), 14.62 (C-10), 168.32 (C-11), 51.76 (OCH_3), 98.61 (Glc-1), 72.08 (Glc-2), 75.2 (Glc-3), 69.47 (Glc-4), 77.09 (Glc-5), 60.54 (Glc-6) [8].

Penstemoside (4) white powder. $C_{17}H_{26}O_{11}$, mp 115–116°C; $[\alpha]_D^{20}$ –140.2° (*c* 0.55, MeOH). UV (MeOH, λ_{max}, nm) (log ε): 234.4 (5.23). IR (KBr, ν_{max}, cm^{-1}): 3400, 1700 (C=O), 1670 (C=C), 1285, 990. EI-MS *m/z*: 429.2 $[M + Na]^+$, 445.2 $[M + K]^+$. The ^1H NMR and ^{13}C NMR data were consistent with the literature [3, 9].

1) Department of Pharmacy, Lanzhou General Hospital of PLA, Lanzhou, 730050, P. R. China, fax: 86931 266-1767, e-mail: limaox2005@yahoo.com.cn; 2) Department of Pharmacy, Changhai Hospital, Second Military Medical University, Shanghai, 200433, P. R. China; 3) Department of Life Sciences, Lanzhou University, Lanzhou, 730000, P. R. China. Published in Khimiya Prirodnykh Soedinenii, No. 5, pp. 740–741, September–October, 2011. Original article submitted June 15, 2010.

 0009-3130/11/4705-0848

8-*O*-Acetylshanzhiside methyl ester (5) white powder. $C_{19}H_{28}O_{12}$, mp 104–105°C; $[\alpha]_D^{25}$ –85.0° (*c* 0.99, MeOH). UV (MeOH, λ_{max}, nm) (log ε): 234.8 (7.12). IR (KBr, ν_{max}, cm^{-1}): 3420, 1710 (C=O), 1675 (C=C), 1280, 1080, 995. EI-MS *m/z*: 471 $[M + Na]^+$, 487 $[M + K]^+$; The ^1H NMR and ^{13}C NMR data were consistent with the literature [3, 6, 7].

Phlomiol (6) white powder. $C_{17}H_{26}O_{13}$, mp 145–147°C; $[\alpha]_D^{25}$ –151.1° (*c* 0.41, MeOH). UV (MeOH, λ_{max}, nm) (log ε): 234 (2.12). IR (KBr, ν_{max}, cm^{-1}): 3315, 1697 (C=O), 1635 (C=C), 1161, 1063, 1005. EI-MS *m/z*: 461 $[M + Na]^+$, 477 $[M + K]^+$. The ^1H NMR and ^{13}C NMR data were consistent with the literature [3].

Acteoside (7) white powder.$C_{29}H_{36}O_{15}$, mp 115–117°C; $[\alpha]_D^{23}$ –81.9° (*c* 1.67, MeOH). UV (MeOH, λ_{max}, nm) (log ε): 326, 289 (3.23). IR (KBr, ν_{max}, cm^{-1}): 3384, 1717 (C=O), 1635 (C=C), 1521, 1385. EI-MS *m/z*: 647 $[M + Na]^+$, 663 $[M + K]^+$, 623 $[M – H]^-$. The ^1H NMR and ^{13}C NMR data were consistent with the literature [10].

Alyssonoside (8) white powder. $C_{35}H_{46}O_{19}$; EI-MS *m/z*: 793.4 $[M + Na]^+$, 809 $[M + K]^+$, 769.4 $[M – H]^-$. ^1H NMR (400 MHz, D_2O, δ, ppm, J/Hz): 6.85 (1H, d, J = 2, H-2), 6.86 (1H, d, J = 8.8, H-5), 6.73 (1H, d, J = 8, H-6), 2.83 (2H, m, H-*β*), 7.25 (1H, s, H-2′), 6.95 (1H, d, J = 8, H-5′), 7.20 (1H, d, J = 8.4, H-6′), 6.43 (1H, d, J = 16, H-*α*′), 7.73 (1H, d, J = 16, H-*β*′), 3.88 (3H, s, OCH_3), 4.42 (1H, d, J = 8, Glc-1), 5.12 (1H, s, Rha-1), 1.08 (3H, d, J = 6, Rha-6), 5.06 (1H, d, J = 2, Api-1). ^{13}C NMR (400 MHz, D_2O, δ, ppm): 131.3 (C-1), 114.0 (C-2), 143.8 (C-3), 142.89 (C-4), 115.9 (C-5), 121.22 (C-6), 71.19 (C-α), 34.45 (C-*β*), 126.2 (C-1′), 111.9 (C-2′), 143.8 (C-3′), 148.24 (C-4′), 116.67 (C-5′), 124.3 (C-6′), 116.15 (C-*α*′), 147.7 (C-*β*′), 167.98 (CO), 55.81 (OCH_3), 102.13 (Glc-1), 73.77 (Glc-2), 79.44 (Glc-3), 69.38 (Glc-4), 72.1 (Glc-5), 67.0 (Glc-6), 101.57 (Rha-1),70.23 (Rha-2), 69.83 (Rha-3), 71.7 (Rha-4), 68.95 (Rha-5), 17.08 (Rha-6), 108.92 (Api-1), 76.79 (Api-2), 80.65 (Api-3), 73.85 (Api-4), 63.67 (Api-5) [11].

Isoacteoside (9) buff powder. $C_{29}H_{36}O_{15}$. UV (MeOH, λ_{max}, nm) (log ε): 322, 288 (3.23). IR (KBr, ν_{max}, cm^{-1}): 3405, 1698 (C=O), 1630 (C=C), 1523, 1383. EI-MS *m/z*: 647.4 $[M + Na]^+$, 663.2 $[M + K]^+$, 623.4 $[M – H]^-$. The ^1H NMR and ^{13}C NMR data were consistent with the literature [10].

ACKNOWLEDGMENT

This work was financed by The Generalization Project of traditional Chinese medicine, PLA (No. 2006032001). The authors would also like to express their gratitude to Lanzhou University PhD English writing foreign teacher Allan Grey who thoroughly corrected the English in the paper.

REFERENCES

1. *National Committee of Chinese Herbal Medicine. Chinese Materia Medica*, 2004, pp. 124–128.
2. M. X. Li, X. F. Shang, Z. P. Jia, and R. X. Zhang, *Chem. Biodivers.*, **7**, 283 (2010).
3. R. Kasai, M. Katagiri, K. Ohtani, K. Yamasaki, C. R. Yang, and O. Tanaka, *Phytochemistry*, **36**, 967 (1994).
4. M. Katagiri, K. Ohtani, R. Kasai, K. Yamasaki, C. R. Yang, and O. Tanaka, *Phytochemistry*, **35**, 439 (1994).
5. Y. L. Gao, R. C. Ling, G. L. Wang, H. R. Zhao, Y. Gao, and C. Bianba, *J. Chin. Med. Mater.*, **30**, 1239 (2007).
6. C. Z. Zhang, C. Li, S. L. Feng, and J. G. Shi, *Phytochemistry*, **30**, 4156 (1991).
7. O. Potterat, J. D. Msonthi, and K. Hostettmann, *Phytochemistry*, **27**, 2677 (1988).
8. J. H. Yi, X. P. Huang, Y. Chen, Z. Y. Luo, and Z. C. Zhong, *Acta Pharm. Sinica*, **32**, 357 (1997).
9. S. Damtoft, S. Rosendal Jensen, and B. J. Nielsen, *Phytochemistry*, **20**, 2717 (1981).
10. H. Kobayashi, H. Oguchi, N. Takizawa, T. Miyase, A. Ueno, K. Usmanghani, and M. Ahmad, *Chem. Pharm. Bull.*, **35**, 3309 (1987).
11. I. Calis, M. Hosny, T. Khalifa, and P. Ruedi, *Phytochemistry*, **31**, 3624 (1992).