Chemistry of Natural Compounds, Vol. 45, No. 5, 2009

PHENOLIC COMPOUNDS FROM *Populus davidiana* Wood

Chuan-Ling Si,[1,2,3*] Qian Xu,[1] Shu-Ming Li,[3] and Zhong Liu[1]

UDC 547.586

*Five phenolic compounds, including a new phenolic glycoside, 2-hydroxycyclohexyl-6′-*O*-p-coumaroyl-β-D-glucopyranoside, as well as the known flavonoids, naringenin, kaempferol, quercetin and luteolin, were isolated from the wood of* Populus davidiana *by repeated column chromatography over Sephadex LH-20. The structures of the compounds were elucidated by spectral evidence.*

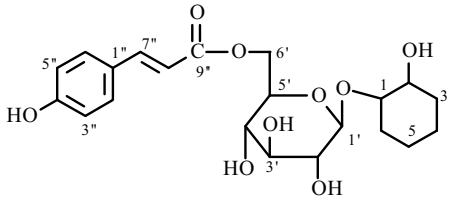
Key words: *Populus davidiana*, phenolic compound, phenolic glycoside, 2-hydroxycyclohexyl-6′-*O*-*p*-coumaroyl-*β*-D-glucopyranoside, flavonoid.

Populus davidiana Dode (Salicaceae), a fast-growing hardwood species, is distributed throughout Northern China, Korea, and Siberia [1]. The tree has been used in folk medicine to cure diarrhea, paralysis, pulmonary disease, pox, and variola [1, 2]. Previous phytochemical studies of *P. davidiana* bark resulted in the isolation of coumarins, phenolic glycosides, and flavonoids [2–4].

Herein we report the results of an investigation of the chemical constituents of *P. davidiana* wood, which was collected in April of 2007 in Tianjin, China.

Repeated column chromatography of the EtOAc soluble fraction of the 70% acetone extract led to the isolation of a new phenolic glycoside, 2-hydroxycyclohexyl-6′-*O*-*p*-coumaroyl-*β*-D-glucopyranoside (**1**) of composition $C_{21}H_{28}O_9$, as well as the known flavonoids, including naringenin, kaempferol, quercetin, and luteolin.

Compound **1** was obtained as a yellow amorphous powder. The MALDI-TOF MS spectrum revealed an $[M+Na]^+$ ion at *m/z* 447, indicating the molecular weight 424 and molecular formula $C_{21}H_{28}O_9$. The melting point was measured at 260–262°C and $[\alpha]_D^{20}$ +36.8° (*c* 0.12, MeOH). The presence of the phenolic hydroxyl group in molecular of **1** was recognized from the grey-green color with 1% ethanolic $FeCl_3$ solution on TLC [5]. The IR spectrum of **1** showed absorption bands for hydroxyls at 3400 cm^{-1}, ketone C=O at 1690 cm^{-1}, and aromatic C=C bonds at 1510 and 1480 cm^{-1} [2].



1

1) Tianjin Key Laboratory of Pulp & Paper, College of Material Science and Chemical Engineering, Tianjin University of Science and Technology, Tianjin 300457, China, fax: +86 22 60271982, e-mail: sichli@tust.edu.cn; 2) Key Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China; 3) Institut fur Pharmazeutische Biologie und Biotechnologie, Heinrich-Heine-Universitat Dusseldorf, 40225 Dusseldorf, Germany. Published in Khimiya Prirodnykh Soedinenii, No. 5, pp. 535–536, September–October, 2009. Original article submitted March 14, 2008.

 0009-3130/09/4505-0634

In the ^{1}H NMR spectrum, compound **1** showed an anomeric proton of *β*-D-glucose at δ 4.31 (1H, d, J = 8.1 Hz, H-1′). The other protons of the sugar residue revealed multiplets between δ 3.15 and 4.39 (6H, H-2′, 3′, 4′, 5′, 6′a, 6′b) [6]. Two peaks at δ 3.60 (m, H-1) and 3.69 (m, H-2), along with broad multiple signals ranging from δ 1.14 to 1.65 (8H, H-3a, 3b, 4a, 4b, 5a, 5b, 6a, 6b), were assigned to the cyclohexyl moiety [7]. The ^{1}H NMR spectrum of **1** also exhibited a *p*-coumaroyl unit. A set of AA′BB′ spin system protons at δ 6.81 (2H, d, J = 8.0 Hz, H-3″, 5″) and 7.55 (2H, d, J = 8.0 Hz, H-2″, 6″), was ascribed to a 1,4-disubstituted aromatic ring. In the downfield, the doublet at δ 7.59 (1H, J = 16.0 Hz) was attributed to the olefinic proton of H-7″, which showed trans coupling with the olefinic proton of H-8″ resonating as a doublet at δ 6.39 (1H, J = 16.0 Hz). These ^{1}H NMR spectral data were almost identical to those for grandidentatin (2-hydroxycyclohexyl-2′-*O*-*p*-coumaroyl-*β*-D-glucopyranoside) [7], except for slight upfield H-2′ (about –1.5 ppm) and downfield H-6′a and H-6′b (about +1.2 ppm) signal shifts in the glucose unit; hence the structure of **1** was assigned as 2-hydroxycyclohexyl-6′-*O*-*p*-coumaroyl-*β*-D-glucopyranoside [6, 8, 9].

In the ^{13}C NMR spectrum of compound **1,** all the carbon signals were similar to those for grandidentatin, except for the downfield shifts for C-6′ (about +3 ppm) and upfield shifts for C-2′ (about –3 ppm). This further indicated that the *p*-coumaroyl unit is attached to the C-6′ site of the glucose moiety [6, 8, 9].

In support of these assignments, long-range H-C couplings (HMBC) were observed between H-6′a (δ 4.16, 1H, dd, J = 7.0, 11.0 Hz) and H-6′b (δ 4.39, 1H, br d, J = 11.0 Hz) in glucose and the carbonyl C-9″ (δ 166.42) in the *p*-coumaroyl unit. In addition, the HMBC spectrum revealed cross-peaks between H-1′ (δ 4.31, 1H, d, J = 8.1 Hz) and C-1 (δ 77.74), confirming the binding site assignments above. The DEPT spectrum of compound **1** showed 21 carbons, including 3 quaternary, 13 methine, and 5 methylene carbons.

Thus, compound **1** was characterized as 2-hydroxycyclohexyl-6′-*O*-*p*-coumaroyl-*β*-D-glucopyranoside, which was an isomer of grandidentatin, isolated and elucidated here for the first time in *P. davidiana* wood.

Compound **1** is a new natural compound, while quercetin and luteolin were isolated from *P. davidiana* for the first time.

EXPERIMENTAL

Instrument. Melting points (uncorrected) were determined with an Electro Thermal 9100 apparatus. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter in MeOH. IR spectra were obtained on a Perkin-Elmer BX FT-IR spectrometer in a KBr disk. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded in DMSO-d_6 with TMS as an internal standard using a Bruker 600 spectrometer. FAB MS spectroscopy was carried out with a Micromass Autospec M363 spectrometer and MALDI-TOF MS spectroscopy was carried out on a Model Voyager-DE STR spectrometer.

TLC analysis was carried out on DC-Plastikfolien Cellulose F (Merck Co.) plates and developed with *t*-BuOH–HOAc–H_2O (3:1:1, v/v/v, solvent A) and HOAc–H_2O (3:47, v/v, solvent B). TLC spots were detected by UV-light (254 and 365 nm) and by spraying with 1% $FeCl_3$ (in EtOH) solution followed by heating.

Extraction, Fractionation, and Isolation of Compounds. Air-dried ground *P. davidiana* wood (2.0 kg) was extracted three times at room temperature with 70% aqueous acetone. Then the aqueous acetone was decanted, filtered, and evaporated under reduced vacuum. The aqueous residue was successively fractionated and freeze-dried to give fractions soluble in *n*-hexane (4.1 g), CH_2Cl_2 (4.7 g), EtOAc (21.8 g) and H_2O (210.6 g).

A portion of the EtOAc fraction powder (17.0 g) was subjected to repeated Sephadex LH-20 column chromatography, eluting with MeOH–H_2O (3:1, 1:1, 1:3 and 1:5, v/v) and EtOH–hexane (3:1, 1:1 and 1:3, v/v). With the composition monitored by TLC, fractionation finally led to the isolation of compound **1** (48 mg), naringenin (134 mg) [10], kaempferol (321 mg) [11], quercetin (82 mg) [12], and luteolin (108 mg) [13].

2-Hydroxycyclohexyl-6′-*O*-*p*-coumaroyl-*β*-D-glucopyranoside (1), $C_{21}H_{28}O_9$, mp 260–262°C (dec.), $[\alpha]_D^{20}$ +36.8° (*c* 0.12, MeOH), TLC: R_f 0.80 (solvent A) and 0.52 (solvent B). IR ($\nu_{max,}$ cm^{-1}): 3400 (OH), 1690 (ketone C=O), 1510, 1480 (aromatic C=C). MALDI-TOF MS: *m/z* $[M+Na]^+$ at 447. ^{1}H NMR (600 MHz, DMSO-d_6, δ, J/Hz): 1.14~1.65 (8H, m, H-3a,3b,4a,4b,5a,5b,6a,6b), 3.15 (1H, m, H-4′), 3.21 (1H, m, H-3′), 3.31 (1H, m, H-5′), 3.41 (1H, m, H-2′), 3.60 (1H, m, H-1), 3.69 (1H, m, H-2), 4.16 (1H, dd, J = 7.0, 11.0, H-6′a), 4.31 (1H, d, J = 8.1, H-1′), 4.39 (1H, br d, J = 11.0, H-6′b), 6.39 (1H, d, J = 16.0, H-8″), 6.81 (2H, d, J = 8.0, H-3″, 5″), 7.55 (2H, d, J = 8.0, H-2″, 6″), 7.59 (1H, d, J = 16.0, H-7″). ^{13}C NMR (150 MHz, DMSO-d_6, δ): 20.57 (C-4), 22.00 (C-5), 28.89 (C-6), 30.34 (C-3), 63.45 (C-6′), 68.11 (C-2), 70.17 (C-4′), 73.06 (C-2′), 73.61 (C-5′), 76.19 (C-3′), 77.74 (C-1), 100.73 (C-1′), 113.78 (C-8″), 115.75 (C-3″, 5″), 125.18 (C-1″), 130.15 (C-2″, 6″), 144.78 (C-7″), 160.02 (C-4″), 166.42 (C-9″).

ACKNOWLEDGMENT

This project was financially supported by China Postdoctoral Science Foundation, the Natural Science Foundation of Tianjin City (09JCYBJC15800), and the Scientific Research Foundation for Returning Overseas Chinese Scholars, State Education Ministry, China (No. 2008-101).

REFERENCES

1. K. Bae, *Medicinal Plants of Korea*, Kyo-Hak Publishing Co., Seoul, 1999.
2. X. F. Zhang, P. T. Thuong, B. S. Min, T. M. Ngoc, Y. H. Seong, K. S. Song, and K. H. Bae, *J. Nat. Prod*., **69**, 1370 (2006)
3. I. A. Pearl and S. F. Darling, *Phytochemistry*, **9**, 1277 (1970).
4. P. D. Chen and J. Y. Liang, *Chin. Trad. Herb. Drugs*, **37**, 816 (2006).
5. Y. Imakura, S. Kobayashi, and A. Mima, *Phytochemistry*, **24**, 139 (1985).
6. C. L. Si, Z. Liu, J. K. Kim, and Y. S. Bae, *Holzforschung*, **62**, 197 (2008).
7. R. A. Dommisse, L. V. Hoof, and A. J. Vlietinck, *Phytochemistry*, **25**, 1201 (1986).
8. Y. Imakura, S. Kobayashi, and A. Mima, *Phytochemistry*, **24**, 139 (1985).
9. J. K. Kim, C. L. Si, and Y. S. Bae, *Holzforschung*, **61**, 161 (2007).
10. J. M. J. Vasconcelos, A. M. S. Silva, and J. A. S. Cavaleiro, *Phytochemistry*, **49**, 1421 (1998).
11. K. R. Markham, B. Ternal, R. Stanly, H. Geiger, and T. J. Mabry, *Tetrahedron*, **34**, 1389 (1978).
12. M. P. Yuldashev, E. Kh. Batirov, A. V. Butayarov, A. M. Nigmatullaev, and M. M. Tadzhibaev, *Rast. Resur*., **36**, No. 4, 53 (2000).
13. Z. A. Khushbaktova, S. K. Faizieva, V. N. Syrov, M. P. Yuldashev, E. K. Batirov, A. U. Mamatkhanov, *Khim.-Farm. Zh.*, **35**, No. 3, 35 (2001).