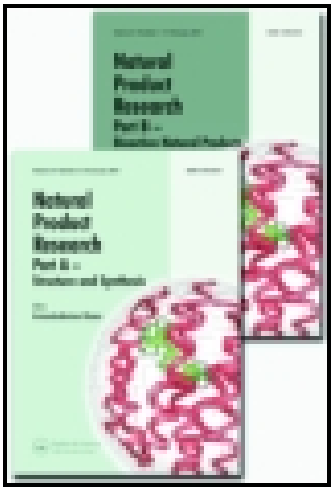

Natural Product Research: Formerly Natural Product Letters

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gnpl20

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Published online: 19 Jul 2010.

To cite this article: Xing-Qi Tan, Liang-Jun Guo, Yi-Hua Qiu, Hai-Sheng Chen & Chang-Heng Tan (2010) Chemical constituents of Trachelospermum jasminoides, Natural Product Research: Formerly Natural Product Letters, 24:13, 1248-1252, DOI: 10.1080/14786410903244962

To link to this article: http://dx.doi.org/10.1080/14786410903244962

Natural Product Research
Vol. 24, No. 13, 15 August 2010, 1248–1252

Chemical constituents of *Trachelospermum jasminoides*

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(*Received 18 April 2009; final version received 11 August 2009*)

Ten compounds, comprising a new C_8 normonoterpenoid glycoside, trachelinoside (**1**), structurally as 4-(2-*O*-*β*-D-glucopyranosyl)-hydroxyethyl-5,5-dimethyldihydrofuran-2(3H)-one, together with nine known compounds, were isolated from the 85% ethanol extract of the vines and leaves of *Trachelospermum jasminoides* (Lindl.) Lem.

Keywords: *Trachelospermum jasminoides*; Apocynaceae; trachelinoside

1. Introduction

The vines of *Trachelospermum jasminoides* (Lindl.) Lem. (Apocynaceae) are a common traditional Chinese medicine for the treatment of rheumatic arthralgia, aching of the waist and knee and traumatic injuries (Tu, Fang, & Yuan, 1992). Previous phytochemical investigations have disclosed that triterpenoids (Tan, Chen, Zhou, & Zhang, 2006), lignans (Tan et al., 2005), alkaloids (Fatima, Crank, & Wasti, 1988; Fatima, Ijaz, Crank, & Wasti, 1987) and flavanoids (Fu, Zhao, Wang, & Yu, 2008) can be isolated from the title plant. As a continuation of our investigation of phytochemicals from *T. jasminoides* (Tan et al., 2005, 2006), we re-examined the chemical constituents of the 85% EtOH extract and obtained a new C_8 normonoterpenoid glycoside named trachelinoside (**1**), structurally as 4-(2-*O*-*β*-D-glucopyranosyl)-hydroxyethyl-5,5-dimethyldihydrofuran-2(3H)-one, together with four megastigmane glycosides: (6*R*,9*R*)-3-oxo-*α*-ionol-*β*-D-apiofuranosyl-(1 → 6)-*β*-D-glucopyranoside (**2**), roseoside (**3**), icariside B5 (**4**) and actinidioionoside (**5**); four aromatic compounds: sodium ferulate (**6**), salicylic acid (**7**), vanillic acid (**8**) and benzenyl methanol *β*-D-glucopyranoside (**9**), as well as dambonitol (**10**). Compounds **2**–**9** were isolated from this genus for the first time.

2. Results and discussion

Compound **1**, obtained as a white amorphous powder, had the molecular formula $C_{14}H_{24}O_8$, as deduced from the HRESIMS quasi-molecular ion peak at *m*/*z* 343.1368

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ISSN 1478–6419 print/ISSN 1029–2349 online

DOI: 10.1080/14786410903244962
http://www.informaworld.com

([M + Na]$^+$, $C_{14}H_{24}O_8Na$ requires 343.1369). The IR adsorption at 1784 cm^{-1}, proton signals of a methylene (δ_H 2.61 and 2.49, each dd, $J_{geminal} = 16.8$ Hz) and carbon signal at δ_C 175.4, suggested the presence of a five-member lactone ring. The carbon resonances at δ_C 102.6, 78.0, 76.9, 75.2, 71.6 and 61.1, as well as an anomeric proton signal at δ_H 4.12 (d, $J = 8.0$ Hz) combined with the hydrolysis experiment indicated a β-D-glucopyranosyl as the sugar moiety (Agrawal, 1992).

In addition to those protons and carbons due to the glucose, its ^{1}H and ^{13}C NMR spectra showed signals for two tertiary methyls (δ_H 1.37 and 1.19), three methylenes (δ_C 67.1, 34.2 and 28.9), one methine (δ_C 42.1 and δ_H 2.33), one oxygen-bearing quaternary carbon (δ_C 86.1) and one carbonyl group (δ_C 175.4). The HMQC and ^{1}H–^{1}H COSY spectra exhibited a proton spin system of –CH_2–CH_2–CH–CH_2– (Figure 1). The terminal methylenes were determined to be connected with the glucosyloxyl and the carbonyl, respectively, by HMBC correlations (Figure 1). The quaternary carbon was assigned to be linked with the methine of the fragment and the O-atom of the lactone to form the five-member lactone ring. Therefore, the structure of trachelinoside (**1**) was strictly proven to be 4-(2-*O*-β-D-glucopyranosyl)-hydroxyethyl-5,5-dimethyldihydrofuran-2(3H)-one. This is the first report of a monoterpene glycoside from this genus.

Subramanian and Krishna Rao (1967) reported a similar structure, ethyl (−)-terpenylate (ethyl tetrahydro-2,2-dimethyl-5-oxo-3-furanacetic acid, Vb therein), which was synthesised starting from α-pinene via pinonic acid. It suggested that **1** might be biogenetically transformed from a monoterpenoid. Furthermore, the aglycone of **1** had been also synthesised through a photochemical alkylation of 5,6-dihydro-2-pyrone with Me_2CHOH by Guzman and Mendoza (1981).

The known compounds were identified to be (6*R*,9*R*)-3-oxo-α-ionol-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside (**2**) (De Tommasi, Aquino, De Simone, & Pizza, 1992), roseoside (**3**) (De Tommasi et al., 1992), icariside B5 (**4**) (Miyase, Ueno, Takizawa, Kobayashi, & Oguchi, 1988), actinidioionoside (**5**) (Otsuka, Hirata, Shinazato, & Takeda, 2003), sodium ferulate (**6**), salicylic acid (**7**), vanillic acid (**8**) (Chen, Wu, & Ryan, 2002), benzenyl methanol β-D-glucopyranoside (**9**) (Seiglera, Pauli, Nahrstedt, & Leen, 2002), and dambonitol (**10**) (Shima, Hisada, & Inagaki, 1972) by optical rotation, ^{1}H, ^{13}C NMR and MS analysis, and comparisons with literature data and/or authentic samples.

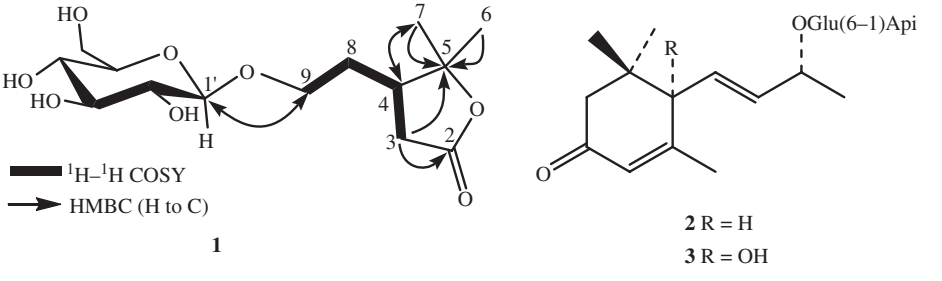

Figure 1. The structures of **1–3** and significant 2D NMR correlations of **1**.

3. Experimental

3.1. *General experimental procedures*

Optical rotations were measured on a Perkin–Elmer 343 polarimeter. IR spectra were recorded on a Bruker Vector 22 (KBr). All mass data were obtained with a Q-Tof micro mass spectrometer. NMR spectra were recorded on a Bruker DRX-500 instrument. The chemical shift values are reported in units (δ) and coupling constants (J) are given in Hertz. Silica gel (200–300 mesh), macroporous resin (AB-8, Tianjin Zheng-Tian-Cheng Clarify Technology Co. Ltd, Tianjin, China), Sephadex LH-20 (Pharmacia Biotech AB, Uppsala, Sweden) and ODS-A gel (Greenberbs Science & Technology Development Co. Ltd, Beijing, China) were used for column chromatography (CC) and precoated plates of silica gel ($HSGF_{254}$) were used for for TLC.

3.2. *Plant material*

The fresh stems with leaves of *Trachelospermum jasminoides* (Lindl.) Lem. were collected in Daochang Mountain, Zhejiang Province, China, in November 2001 and identified by Prof. Han-Cheng Zheng of the Second Military Medical University. A voucher specimen (20010511027) was deposited in the Herbarium of the Department of Pharmcognosy, Second Military Medical University.

3.3. *Extraction and isolation*

Fifteen kilograms of dried vines and leaves of *T. jasminoides* were powdered, and extracted thrice with 85% EtOH, the combined extraction was concentrated under reduced pressure, then diluted with distilled water to 2 L, finally subjected to a chromatography of macroporous resin column ($\varnothing 8 \times 100$ cm), eluting with H_2O, 20, 40, 60 and 95% EtOH, to yield frs 1–5. Fr. 2 (150 g) was separated into five subfractions: frs 2a–e by silica gel CC (the lower layer of $CHCl_3$: MeOH : H_2O 65 : 10 : 10 as eluent). Frs 2b and 2c yielded **1** (19 mg), **3** (8 mg), **4** (12 mg), **5** (19 mg) and **7** (42 mg), as well as **2** (22 mg) and **6** (31 mg), respectively, after repeated purification through silica gel (eluent ditto), Sephadex LH-20 (MeOH–H_2O, 50–100%) and Rp-18 (MeOH–H_2O, 30–50%) columns. Fr. 4 (70 g) gave **9** (14 mg) and **10** (290 mg), and fr. 5 (30 g) yielded **8** (110 mg) after repeated CCs of silica gel, Sephadex LH-20 and Rp-18.

3.4. *Trachelinoside (1)*

White powder, $[\alpha]_D^{21} - 13.5$ (c 0.347, MeOH); IR (KBr) ν_{max}: 3372, 1784, 1380, 1278, 1261, 1167, 1030 cm^{-1}; ^1H NMR data: (DMSO-d_6, 500 MHz): δ 4.94 (1H, br s, 2′-OH), 4.91(1H, br s, 4′-OH), 4.88 (1H, br s, 3′-OH), 4.44 (1H, br t, $J = 6.0$ Hz, 6′-OH), 4.12 (1H, d, $J = 8.0$ Hz, H-1′), 3.75 (1H, dt, $J = 10.0$, 7.0 Hz, H-9a), 3.67 (1H, br dd, $J = 12.0$, 2.8 Hz, H-6′a), 3.50 (1H, dt, $J = 10.0$, 7.0 Hz, H-9b), 3.43 (1H, dt, $J = 12.0$, 5.8 Hz, H-6′b), 3.13 (1H, t, $J = 8.0$ Hz, H-3′), 3.09 (1H, ddd, $J = 8.8$, 5.5, 2.3 Hz, H-5′), 3.03 (1H, br t, $J = 8.8$ Hz, H-4′), 2.94 (1H, br t, $J = 8.0$ Hz, H-2′), 2.61 (1H, dd, $J = 16.8$, 7.8 Hz, H-3a), 2.49 (1H, dd, $J = 16.8$, 11.9 Hz, H-3b), 2.33 (1H, dtd, $J = 12.0$, 7.2, 3.7 Hz, H-4), 1.73 (1H, dtd, $J = 12.1$, 7.3, 4.1 Hz, H-8a), 1.50

(1H, dq, $J = 12.2$, 7.5 Hz, H-8b), 1.37 (3H, s, Me-6), 1.19 (3H, s, Me-7); ^{13}C NMR data: (DMSO-d_6, 125 MHz): δ 175.4 (C-2), 102.6 (C-1′), 86.1 (C-5), 76.8 (C-5′), 76.7 (C-3′), 73.3 (C-2′), 70.1 (C-4′), 67.1 (C-9), 61.1 (C-62), 42.1 (C-4), 34.2 (C-3), 26.9 (C-6), 28.9 (C-8), 21.6 (C-7),. ESI-MS: m/z 343 ($[M + Na]^+$), 359 ($[M + K]^+$) and 663 ($[2M + Na]^+$). HR-ESI-MS: m/z 343.1368 ($[M + Na]^+$), Calcd. for $C_{14}H_{24}O_8Na$, 343.1369.

3.5. *Acid hydrolysis of 1*

A solution of **1** (2 mg) in 2 M HCl : dioxane (1 : 1, v/v, 2 mL) was heated under reflux for 2 h. After cooling, the reaction mixture was neutralised with $NaHCO_3$, then filtrated to remove the solid. The solution was subjected to CC (Sephadex LH-20, MeOH : H_2O 1 : 1) to afford a sugar fraction. The sugar fraction and standard D-glucose (Sigma, USA) were respectively treated with L-cysteine methyl ester hydrochloride (2 mg) in pyridine (1 mL) at 60°C for 1 h; then the solution was treated with *N*,*O-bis*(trimethylsilyl)-trifluoroacetamide (0.02 mL) at 60°C for 1 h, after subjecting the supernatant to GLC analysis (Supelco, 230°C, flow rate: 15 mL min^{-1}). D-Glucose (standard: $t_R = 23.9$ min, **1**: $t_R = 24.0$ min) was detected.

Acknowledgement

This project was supported by grants from the Natural Science Fund of Huzhou (2004–20).

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