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Two new alkaloid galactosides from the kernel of *Prinsepia uniflora*

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Two new alkaloid galactosides have been isolated from the kernel of *Prinsepia uniflora*. Their structures were elucidated as 5-[(\textalpha-D-galactopyranosyloxy) methyl]-1\textit{H}-pyrrole-2-carbaldehyde (1) and 6-[(\textalpha-D-galactopyranosyloxy) methyl]-3-pyridinol (2) by various spectroscopic means including HR-ESI-MS, IR, 1D and 2D NMR. The determined structures were characterized with a unit of galactose which is rarely seen in the previously isolated pyrrole and pyridinol compounds.

**Keywords:** *Prinsepia uniflora*; alkaloid galactoside; 5-[(\textalpha-D-galactopyra-nosyloxy) methyl]-1\textit{H}-pyrrole-2-carbaldehyde; 6-[(\textalpha-D-galactopyranosyl-oxy) methyl]-3-pyridinol

1. Introduction

*Prinsepia uniflora* Batal, belonging to the genus *Prinsepia* (Rosaceae), is a shrub plant mainly growing in the northwest of China (H.X. Li, X. Li, & Wang, 2006). The kernel of this plant, which is called ‘ruiren’ in traditional Chinese medicine, has long been used for the treatment of eye diseases (N. Li, H.X. Li, Meng, & X. Li, 2009). Two flavonoids, one lignan, three sterols, two triterpenoids, six phenolic acids and N-acetyl-glutamic acid have been reported in previous phytochemical studies on *Prinsepia uniflora* (Li et al., 2006, 2009). In this article, two new alkaloid galactosides were found in the chemical constituents of the kernel of *Prinsepia uniflora*. The structures were determined by spectral methods including HR-ESI-MS, IR, 1D and 2D NMR and characterised with a unit of galactose, which is rarely seen in the previously isolated pyrrole and pyridinol compounds.

2. Results and discussion

Compound 1 was obtained as a yellow gum, [\(\alpha\)]\textsubscript{D}\textsuperscript{25} + 45° (CH\textsubscript{3}OH, \(c = 0.1\)). Its molecular formula was determined to be C\textsubscript{12}H\textsubscript{17}NO\textsubscript{7} based on the result of HR-ESI-MS with a quasi molecular ion peak of [M – H]\textsuperscript{+} at \(m/z\) 286.0929 (Calcd 286.0927). The IR spectrum of 1 displayed the strong absorption bands of hydroxyl groups at 3390 cm\textsuperscript{–1} and a carbonyl group at 1645 cm\textsuperscript{–1}. NMR spectra indicated one sugar unit, which was confirmed to be \(\alpha\)-D-galactose by the chemical shifts of its anomic proton at \(\delta\textsubscript{H} 4.77 (1H, d, J = 3.6\text{ Hz})\) and the \(\delta\textsubscript{C}\) NMR spectral data at 98.5, 71.5, 69.7, 68.9, 68.5, 60.6, these data

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were coincident with reported spectral of 5-[(\(\alpha\)-D-galactopyranosyloxy)methyl]-2-
furancarboxaldehyde (Martin & Lichtenthaler, 2006). Acidic hydrolysis of 1 afforded
galactose which was detected by TLC (Xu et al., 2009). A nitrogen containing heterocyclic
ring was characterised as 2,5-disubstituted pyrrole ring by NMR spectra, two doublet
protons at \(\delta_H 6.95\) and 6.25, which appeared as an AB system (d, \(J = 3.6\) Hz) and the
\(^{13}\)C NMR spectral data at \(\delta_C 137.9, 132.7, 121.2, 109.8\) (Chin et al., 2003). An aldehyde

group was identified by chemical shift at 9.43 (1H, s). The remaining resonances were an
AB system of two protons at \(\delta_H 4.46\) (1H, d, \(J = 12.6\) Hz) and 4.45 (1H, d, \(J = 12.6\) Hz),
which belong to a methylene group and were oxygenated (\(\delta_C 61.3\)). In the HMBC
experiment, the correlations between the signals of the aldehyde at \(\delta_H 9.43\) and C-2 at \(\delta_C
137.9\) suggested that the aldehyde group was attached to the pyrrole ring. Connections
between the methylene at \(\delta_H 4.66, 4.45\) and C-5 (\(\delta_C 137.9\)), C-4 (\(\delta_C 109.8\)) indicated that
the methylene was linked to the pyrrole ring directly. The sugar moiety was attached to the
methylene of C-7 (\(\delta_C 69.1\)) showed that the galactose moiety was attached to the
methylene of C-7. Thus, compound 2 was established to be a new pyrrole alkaloid galactoside
and was assigned to be 6-[(\(\alpha\)-D-galactopyranosyloxy) methyl]-3-pyridinol (Figure 1).

Figure 1. The structures of 1 and 2.
3. Experimental

3.1. General experimental procedures

General NMR spectra were obtained with a Bruker AV 600 NMR spectrometer (chemical shift values are presented as δ values with TMS as the internal standard). UV spectra were recorded on UV-2550 visible spectrophotometer. IR spectra were recorded on an FTIR-8400S spectrometer. The optical rotations were obtained in MeOH at 25°C on a Perkin-Elmer 341 digital polarimeter. HR-ESI-MS spectra were performed on a LTQ-Orbitrap XL spectrometer. Sephadex LH-20 (Pharmacia, Uppsala, Sweden), MCI gel (CHP 20 P, 75–150 μm, Mitsubishi Chemical Corporation, Tokyo, Japan) and silica gel (100–200 mesh, Qingdao Marine Chemical plant, Qingdao, People’s Republic of China) were used for column chromatography. Semipreparative HPLC was performed on a Knauer Smartline 1000 with a Knauer Smartline 2600 photodiode array detector. All solvents were analytical grade (Beijing Chemical Plant).

3.2. Plant material

The kernels of *Prinsepia uniflora* Batal were bought from a local market in the province of Shaanxi, China, in October 2007. The plant was identified by Prof. G.Q. Li. A voucher specimen (No. NP0710) was deposited in the Institute of Medicinal Plant Development, Peking Union Medical College and Chinese Academy of Medical Sciences, Beijing, China.

3.3. Extraction and isolation

The kernels of *Prinsepia uniflora* Batal (30 kg) were extracted with 95% EtOH (180 L) under reflux then concentrated to 3.0 L in vacuo three times. The extract was washed with petroleum ether (3.0 L) and the residue was concentrated to a gummy mass (328 g). The latter was suspended in distilled water (2.0 L) and extracted with CHCl₃ (3 L × 3.0 L), EtOAc (3 L × 3.0 L), and n-BuOH (3 L × 3.0 L), respectively. The residue of the H₂O layer (178 g) was on a macroporous absorption resin column with D101 resin as the stationary phase. The column was eluted by distilled water firstly until the fractions were colourless, and then eluted with a mixture of H₂O–CH₃OH (70:30) to yield the eluent after concentration. The eluent (20 g) was chromatographed over a Sephadex LH-20 column (100 cm × 5 cm) eluting with H₂O–CH₃OH (50:50) to give three fractions (Fr. a-c). Fr. C (2.0 g) was chromatographed over a MCI gel column (60 cm × 4 cm), and then separated by semipreparative HPLC (30% CH₃OH) to give compound 1 (12 mg). The n-BuOH extract (58 g) was chromatographed over silica gel (580 g, 100–200 mesh) and eluted with CHCl₃–CH₃OH (100:1–1:1) to obtain nine fractions (Fr.1-9). Fr.6 (3.4 g) was purified by Sephadex LH-20 column chromatography eluting with CH₃OH followed by semipreparative HPLC (28% CH₃OH) to afford compound 2 (15 mg).

3.3.1 5-[(α-D-galactopyranosyloxy)methyl]-1H-pyrrole-2-carbaldehyde (I)

Yellow gum, [α]D25 +45° (CH₃OH, c = 0.1). UV (CH₃OH): λmax (log ε) = 295 (3.93) nm. ¹H-NMR (600 MHz, DMSO-d₆) δ: 12.06 (1H, br s, NH), 9.43 (1H, s, –CHO), 6.95 (1H, d, J = 3.6 Hz, H-3), 6.25 (1H, d, J = 3.6 Hz, H-4), 4.66 (1H, d, J = 12.6 Hz, H-6a), 4.45 (1H, d, J = 12.6 Hz, H-6b), 4.76 (1H, d, J = 3.0 Hz, H-1'), 3.58 (1H, m, H-2'), 3.57 (1H, m, H-3'), 3.72 (H-4'), 3.65 (1H, m, H-5'), 3.47 (1H, m, H-6'a), 3.52 (1H, m, H-6'b). ¹³C-NMR (150 MHz, DMSO-d₆) δ: 178.9 (–CHO), 132.7 (C-2), 121.2 (C-3), 109.8 (C-4), 137.9 (C-5), 61.3 (C-6), 98.5 (C-1'), 68.5 (C-2'), 69.7 (C-3'), 68.9 (C-4'), 71.5 (C-5'), 60.6 (C-6'). HMBC correlations were shown in Figure 2. HR-ESI-MS [M–H]⁻ at m/z: 286.0929 (Calcd for C₁₂H₁₆NO₇ 286.0927).
3.3.2 6-[(α-D-galactopyranosyloxy) methyl]-3-pyridinol (2)

Yellow gum, $[\alpha]_{D}^{25} + 98.0$ (CH$_3$OH, $c = 0.1$). UV (CH$_3$OH): $\lambda_{\text{max}}$ (log $\varepsilon$) = 224(3.90) nm, 283(3.58) nm. $^1$H-NMR (600 MHz, DMSO-$d_6$) $\delta$: 8.02 (1H, d, $J = 3.0$ Hz, H-2), 7.12 (1H, dd, $J = 8.4, 3.0$ Hz, H-4), 7.34 (1H, d, $J = 8.4$ Hz, H-5), 4.38 (1H, d, $J = 12.6$ Hz, H-7 a), 4.61 (1H, d, $J = 12.6$ Hz, H-7 b), 4.77 (1H, d, $J = 3.6$ Hz, H-1'), 3.60 (1H, m, H-2'), 3.59 (1H, m, H-3'), 3.72 (H-4'), 3.66 (1H, m, H-5'), 3.45 (1H, dd, $J = 10.8, 6.6$ Hz, H-6'a), 3.50 (1H, dd, $J = 10.8, 6.0$ Hz, H-6'b). $^{13}$C-NMR (150 MHz, DMSO-$d_6$) $\delta$: 137.0 (C-2), 153.5 (C-3), 122.4 (C-4), 122.6 (C-5), 147.6 (C-6), 69.1 (C-7), 98.6 (C-1'), 68.4 (C-2'), 69.6 (C-3'), 68.9 (C-4'), 71.5 (C-5'), 60.6 (C-6'). HMBC correlations were shown in Figure 2.

HR-ESI-MS [M–H]$^-$ at m/z: 286.0922 (Calcd for C$_{12}$H$_{16}$NO$_7$ 286.0927).

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