Chemical Compounds from Patrinia Villosa (Thunb.) Juss

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ABSTRACT

The objective of this research is to isolate and identify the bioactive components from *Patrinia villosa* (Thunb.) Juss. 70% EtOH extract of *P. villosa* was firstly partitioned with light petroleum, dichloromethane and n-BuOH, and then subjected to normal-phase silica, ODS silica gel column chromatography and semi-preparative HPLC chromatography. NMR method was adopted in this research to elucidate the chemical structures of the compounds. Four known compounds were isolated from *P. villosa*, and identified as Patrinalloside (1), Patrinoside-aglycone-11-O-2′-deoxy-β-D-glucopyranoside (2), Patrinoside-a-glucone (3), Sweroside (4) by comparison of their spectral data with the reported data. This is the first time that the compounds mentioned above were isolated from *P. villosa*.1

INTRODUCTION

It has been reported that Patrinia as a pivotal ancient herbal medicine is widely grown in North America and East Asia. The genus of Patrinia was confirmed to include over 20 species, nearly half of which have been discovered in China [1]. One of species named Patrinia villosa (Thunb.) Juss. contains pharmacological properties in leaves, which has been employed for wound healing, abdominal pain and inflammation. A famous ancient Chinese medicinal literary, Shen Nong Ben Cao Jing, recorded its wide application for more than 2000 years. Constituents of *P. villosa* in leaves have been studied to mainly contain Pentacyclic triterpenoids,

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iridoids, and flavonoids, showing potential ability of anti-inflammatory and anti-tumor [2-5]. Until now, some of Chinese take Patrinia as tasty vegetables.

MATERIALS AND METHODS

General Experimental Procedures

Nuclear magnetic resonance (NMR) spectra were recorded with tetramethylsilane as internal standard on a Bruck AVANCE 500 FT-NMR spectrometer. Column chromatography was performed on silica gel (200-300 mesh) (Marine Chemical Factory, Qingdao, China) and octa decylsilyl silicion (ODS) (YMC C18, 40-70 µm). High performance liquid chromatography (HPLC) separation was performed with an HITACHI chromatograph apparatus using an ODS column (YMC ODS-A, 5 µm, 250×10 mm) and detected with an ultraviolet detector.

Materials and Chemicals

The P. villosa Juss., leaves were purchased from Hebei Qixin Traditional Chinese Medicine Pellets Co., Ltd., P.R. China, and identified by Dr. Wu Jian, Harbin University of Commerce. Organic solvents (analytical grade or HPLC grade) for the experiment were purchased from Kermel Chemical Co., (Tianjin, China).

Extraction and Isolation

The dried leaves of P. villosa Juss., (15 kg) were extracted three times with 70% alcohol under reflux. Evaporation of the solvent under reduced pressure gave a condensed extract (1.8 kg), which was subjected to macroporous resin and eluted with a gradient of EtOH-H2O (0%, 10%, 30%, 50%, 95%, v/v). 50% fraction was then subjected to normal phase silica gel column chromatography and eluted with a gradient of CH2Cl2-MeOH (100:0 → 0:100, v/v) to give twelve fractions. Fraction 4 (CH2Cl2-MeOH, 20:1, v/v) was subjected to further separation using ODS silica gel column chromatography eluted with MeOH in water, respectively. Subfraction 4.2 and 4.3 were purified by semi-preparative HPLC to give compound 1 (12.0 mg), 2 (15.2 mg), 3 (21.3 mg) and 4 (28.1 mg).

RESULTS AND DISCUSSION

In this research, four known compounds were isolated from P. villosa, and identified as Patrinalloside (1), Patrinoside-aglycone-11-O-2′-deoxy-β-D-glucopyranoside (2), Patrinoside-a-glucone (3), Sweroside (4) by comparison of their spectral data with references [6-8].
Patrinalloside (1): 1H-NMR (400 MHz in DMSO-d6): 6.34(1H, bra, H-3), 5.93(1H, d, J= 5.5 Hz, H-1), 4.12(1H, d, J= 7.9 Hz, H-1'), 4.11(1H, m, H-7), 4.10(1H, m, H-10c), 3.94(1H, m, H-11), 3.68(1H, m, H-10a), 3.66(1H, m, H-5'b), 3.44(1H, m, h-6'), 3.43(1H, m, H-10b), 3.12(1H, m, H-3'), 3.06(1H, m, H-5'a), 3.04(1H, m, H-4'), 2.96(1H, m, H-2'), 2.81(1H, m, H-5), 2.22(2H, d, J= 7.1 Hz, H-13), 2.07(1H, m, H-9), 1.98(1H, m, H-14), 1.86(1H, m, H-6a), 1.76(1H, m, H-8), 1.71(1H, m, H-6b), 0.91(3H, s, H-15), 0.91(3H, s, H-16); 13C-NMR (100 MHz in DMSO-d6): 171.3(C-12), 137.6(C-3), 114.9(C-4), 101.9(C-1'), 91.7(C-1), 76.9(C-3'), 76.8(C-5'a), 73.5(C-2'), 70.8(C-7), 70.2(C-4'), 67.4(C-11), 61.1(C-10), 60.6(C-5'b), 47.7(C-8), 42.6(C-13), 41.7(C-9), 39.2(C-6), 31.8(C-5), 25.8(C-14), 22.1(C-15), 22.1(C-16).

Patinoside-aglycone-11-O-2'-deoxy-β-D-glucopyranoside (2): 1H-NMR (400 MHz in DMSO-d6): 198(1H,m, H-14), 6.34(1H, bra, H-3), 5.93(1H, d, J= 4.6 Hz, H-1), 4.11(1H, d, J= 7.9 Hz, H-1'), 4.10(1H, m, H-7), 4.10(1H, m, H-10c), 3.92(1H, d, J= 11.9 Hz, H-11), 3.68(1H, m, H-10a), 3.66(1H, m, H-5'b), 3.44(1H, m, h-6'), 3.43(1H, m, H-10b), 3.12(1H, m, H-3'), 3.10(1H, m, H-5'a), 3.08(1H, m, H-4'), 2.81(1H, m, H-5), 2.54(1H, m, H-2'), 2.22(2H, d, J= 7.1 Hz, H-13), 2.06(1H, m, H-9), 1.86(1H, m, H-6a), 1.78(1H, m, H-8), 1.71(1H, m, H-6b), 0.91(3H, s, H-15), 0.91(3H, s, H-16); 13C-NMR (100 MHz in DMSO-d6): 171.2(C-12), 137.4(C-3), 115.1(C-4), 102.4(C-1'), 91.7(C-1), 75.4(C-5'a), 72.3(C-4'), 70.9(C-3'), 70.7(C-7), 67.4(C-11), 63.9(C-10), 60.6(C-5'b), 47.7(C-8), 42.6(C-13), 41.6(C-9), 39.2(C-6), 35.9(C-2'), 31.8(C-5), 25.2(C-14), 22.1(C-15), 22.1(C-16).

Patinoside –α-glucone (3): 1H-NMR (400 MHz in DMSO-d6): 6.34(1H, bra, H-3), 5.93(1H, d, J= 3.0 Hz, H-7), 3.86(1H, d, J= 12.6 Hz, H-3), 3.76(1H, d, J= 7.6 Hz, H-11b), 3.65(1H, d, J= 10.5 Hz, H-10a), 3.48(1H, dd, J= 10.5, 6.4 Hz, H-10b), 2.79(1H, m, H-5), 2.22(2H, d, J= 7.1 Hz, H-13), 2.05(1H,m, H-9), 1.97(1H, m, H-8), 1.96(1H, m, H-14), 1.86(1H, m, H-6a), 1.63(2H, m, H-6b), 0.91(6H, s, H-15), 13C-NMR (100 MHz in DMSO-d6): 171.2(C-12), 135.5(C-3), 118.9(C-4), 91.9(C-1), 70.8(C-7), 60.6(C-10), 60.1(C-10), 47.7(C-8), 42.6(C-13), 41.6(C-9), 39.2(C-6), 31.4(C-5), 25.2(C-14), 22.1(C-15).

Sweroside (4): 1H-NMR (400 MHz in DMSO-d6): 7.48(1H, d, J= 2.5 Hz, H-3), 5.48(1H, m, H-8), 5.43(1H, d, J= 1.6 Hz, H-1), 5.31(1H, dd, J= 17.1 Hz, H-10a), 5.25(1H, dd, J= 10.1 Hz, H-10b), 4.50(1H, d, J= 7.9 Hz, H-1'), 4.26(2H, m, H-7), 4.02(1H, m, H-6a), 3.71(1H, m, H-3'), 3.65(1H, m, H-6b), 3.44(1H, m, H-5'), 3.31(1H, m, H-4'), 3.22(1H,m, H-2'), 3.14(1H,m, H-5), 2.65(1H, m, H-9), 1.75(1H, m, H-6a), 1.51(1H, m, H-6b); 13C-NMR (100 MHz in DMSO-d6): 164.7(C-11), 151.5(C-3), 132.4(C-8), 120.4(C-10), 104.9(C-4), 98.1(C-1'), 95.6(C-1), 77.4(C-5'), 76.4(C-3'), 73.2(C-2'), 70.1(C-4'), 67.7(C-7), 61.1(C-6'), 41.6(C-9), 26.8(C-5), 24.3(C-6).
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