Study on the Chemical Constituents of a Plant in the Soil of Taibai Mountain

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Abstract

To study the chemical constituents of Fallopia cillinerve. 95% ethanol extract of the roots of Fallopia cillinerve was purified by silica gel column and Sephadex LH-20. The compounds were identified according to their physicochemical properties and spectral data as well as relevant literature data. 5 compounds were isolated and identified as β-sitosterol (1), daucosterol (2), gallic acid (3), Annulatin 3'-O-β-D-xyloside (4), kaempferitrin (5), compounds3-5 were first obtained fromthis plant.

Keywords

Fallopia Cillinerve; Chemical Constituents; Isolation and Identification.

1. Introduction

In the modern era, traditional Chinese medicine is recognised to contain an enormous reserve of knowledge, as they link ancestral oral traditions and therapeutic uses to biological activities. Reynoutria ciliinervis (Nakai) Moldenke (R. most valued traditional Chinese medicines, is a member of 'Taibai Qiyao', commonly found in hillside, forest, bosk in many north-western provinces of China [1]. It has been used traditionally in China for the treatment of quinsy, enteritis, gastritis diarrhoea, nephritis dropsy and allantois infection [2]. In addition, it has the function of nourishing the kidney and liver and the anti-ageing, anticancer, antivirus anti-micro-organism activities. Previous phytochemical studies on R. ciliinervis (Nakai) Moldenke led to the isolation of anthraquinones[3], polyphenols [4], polysaccharides [5] and glycosides [6]. In our study, a new analogue of pyrrolezanthine was discovered from the roots of R. ciliinervis (Nakai) Moldenke. Herein, the isolation, structure elucidation and the antimicrobial activities are reported. The compounds were identified according to their physicochemical properties and spectral data as well as relevant literature data. 5 compounds were isolated and identified as β-sitosterol (1), daucosterol (2), gallic acid (3), Annulatin 3'-O-β-D-xyloside (4), kaempferitrin (5), compounds3-5 were first obtained fromthis plant.

2. Results and discussion

2.1 Structure elucidation

Compound 1: White needle-like crystals (methanol), ESI-HR-MS: 413.3807 $[M-H]^-$, The molecular formula is $C_{29}H_{50}O$,m.p. 138~140 °C.^{1}H-NMR (400MHz, DMSO-d_6): δ_H 5.37 (1H, d, J = 5.04 Hz, H-6), 3.54 (1H, m, H-3), 1.03 (3H, s, H-19), 0.94 (3H, d, J = 6.52 Hz, H-21), 0.70 (3H, s, H-18);^{13}C-NMR (100 MHz, DMSO-d_6): δ_C 140.25 (C-5), 121.22 (C-6), 71.31 (C-3), 56.26 (C-14), 55.55 (C-17), 49.63 (C-9), 45.33 (C-24), 41.80 (C-13), 39.27 (C-4), 36.76 (C-12), 36.01 (C-1), 35.65 (C-10), 33.44 (C-20), 31.42 (C-22), 31.16 (C-8), 31.16 (C-7), 28.64 (C-2), 23.81 (C-23), 27.76 (C-25), 25.55 (C-16), 22.56 (C-15), 20.59 (C-28), 19.34 (C-11), 18.91 (C-27), 18.91 (C-26), 18.54 (C-19), 18.29

(C-21), 11.49 (C-18), 11.37 (C-29). The above data is basically consistent with the literature [7], so compound 1 is identified as β-sitosterol.

Compound 2: White powder, ESI-HR-MS: 575.4335 $[M-H]^-$, The molecular formula is $C_{35}H_{60}O_6$,m.p. 296~298 °C.^{1}H-NMR (400MHz, DMSO-d_6): δ_H 5.33 (1H, m, H-6), 4.90 (1H, H-1'), 4.45 (2H, t, J = 11.48 Hz, H-6'), 4.22 (1H, d, J = 7.72 Hz, H-4'), 3.64 (1H, m, H-3), 0.99 (3H, H-21), 0.96 (3H, H-19), 0.91 (3H, d, J = 6.32 Hz, H-4'), 0.84 (3H, H-29), 0.80 (3H, H-27), 0.66 (3H, s, H-18); ^{13}C-NMR (100 MHz, DMSO-d_6): δ_C 140.39 (C-5), 121.18 (C-6), 100.73 (C-1'), 76.84 (C-3), 76.84 (C-3'), 76.72 (C-5'), 73.41 (C-2'), 70.03 (C-4'), 61.04 (C-6'), 56.14 (C-14), 55.38 (C-17), 49.56 (C-9), 45.09 (C-24), 41.82 (C-13), 40.23 (C-12), 38.27 (C-4), 36.79 (C-20), 36.18 (C-1), 35.46 (C-10), 33.30 (C-22), 31.38 (C-7), 31.34 (C-8), 29.23 (C-2), 28.64 (C-25), 27.77 (C-16), 25.35 (C-23), 23.84 (C-15), 22.56 (C-28), 20.56 (C-11), 19.69 (C-26), 19.07 (C-19), 18.89 (C-21), 18.58 (C-27), 11.75 (C-18), 11.64 (C-29). The above data is basically consistent with the literature [8], so compound 1 is identified as daucosterol.

Compound 3: White crystal, ESI-HR-MS: 169.0143 $[M-H]^-$, The molecular formula is $C_7H_6O_5$,m.p. 233~235°C.^{1}H-NMR (400MHz, DMSO-d_6): δ_H 12.27 (1H, brs, H-7), 9.21 (2H, s, H-3, H-5), 8.86 (1H, s, H-4), 6.92 (2H, s, H-2, H-6);^{13}C-NMR (100 MHz, DMSO-d_6): δ_C 167.41 (C-7), 145.34 (C-3 & C-5), 137.91 (C-4), 120.33 (C-1), 108.62 (C-2 & C-6). The above data is basically consistent with the literature [9], so compound 1 is identified as gallic acid..

Compound 4: Light yellow powder (methanol), ESI-HR-MS: 463.0888 $[M-H]^-$, The molecular formula is $C_{21}H_{20}O_{12}$.^{1}H-NMR (400MHz, DMSO-d_6): δ_H 12.66 (1H, s, 5-OH), 10.95 (1H, s, 7-OH), 9.51 (1H, s, 5'), 9.06 (1H, s, 4'), 7.42 (1H, d, J = 2.0 Hz, H-6'), 7.32 (1H, d, J = 2.0 Hz, H-2'), 6.43 (1H, d, J = 2.0 Hz, H-8), 6.20 (1H, d, J = 2.0 Hz, H-6), 4.75 (1H, d, J = 7.5 Hz, H-1"), 3.84 (1H, m, H-5" a), 3.80 (3H, s, OCH_3), 3.33 (1H, m, H-3"), 3.32 (1H, m, H-4"), 3.30 (1H, m, H-5"b), 3.25 (1H, m, H-2"); ^{13}C-NMR (100 MHz, DMSO-d_6): δ_C 177.84 (C-4), 164.11 (C-7), 161.18 (C-5), 156.19 (C-9), 154.95 (C-2), 145.86(C-5'), 145.54 (C-3'), 138.43 (C-4'), 137.88 (C-3), 119.71 (C-l'), 110.43 (C-6'), 108.33 (C-2'), 104.13 (C-10), 103.05 (C-1″), 98.53 (C-6), 93.53 (C-8), 75.64 (C-2″), 73.06 (C-3″), 69.35 (C-4″), 65.74 (C-5″), 59.59 (OCH_3). The above data is basically consistent with the literature [10], so compound 1 is identified as Annulatin 3'-O-β-*D*-xyloside.

Compound 5: White crystal, m.p. 208~210°C.^{1}H-NMR (400MHz, DMSO-d_6): δ_H12.6 (1H, br, 5-OH), 10.2 (1H, br, 4′-OH), 7.78 (2H, d, J =9.6 Hz, H-2′, H-6′), 6.90 (2H, d, J = 9.6 Hz, H-3′, H-5′), 6.78(1H, d, J =1.8 Hz, H-8), 6.45(1H, d, J =1.8 Hz, H-6), 5.54 (1H, d, J =1.2 Hz, C7-O-rha-H-1), 5.29 (1H, d, J =1.2 Hz, C3-Orha-H-1), 3.10~3.98(8H, rha-H ×8), 1.12(3H, d, J =6.0 Hz, C7-O-rha-CH3), 0.79 (3H, d, J =6.0 Hz, C3-O-rha-CH3); ^{13}C-NMR (100 MHz, DMSO-d_6): δ_C 177.90 (C-4),161.67(C-7), 160.9(C-5),160.11 (C-4′), 157.74 (C-9), 156.06 (C-2), 134.51 (C-3), 130.66 (C-2′, 6′), 120.32 (C-1′), 115.39 (C-3′, 5′), 105.76 (C-10), 101.85 (3-Orha-C-1), 99.43 (C-6),98.42 (7-O-rha-C-1), 94.56 (C-8), 71.57 (3-O-rha-C-4), 71.10 (7-O-rha-C-4), 70.64 (3-O-rha-C-3),70.31 (3-O-rha-C-5),70.22 (7-O-rha-C-3), 70.06 (3-O-rha-C-2), 70.06 (7-O-rha-C-2),69.78(7-Orha-C-5), 17.88 (7-O-rha-C-6), 17.44 (3-Orha-C-6). The above data is basically consistent with the literature [11], so compound 1 is identified as kaempferitrin.

3. Experimental

UV spectra were recorded with a Varian Cary 60; IR spectra were recorded with a Bruker VECTOR-22FT-IR; MS spectra were obtained in the Bruker ImpactHD Q-TOF; single-crystal X-ray diffraction analyses spectra were recorded with a Bruker-D8 QUEST PHOTON 100; 1D and 2D nuclear magnetic resonance (NMR) spectra were recorded on Bruker AVANCEIII-400 MHz spectrometer with tetramethylsilane (TMS) as internal standard; melting points were determined by using an X-6 micro-melting point apparatus were uncorrected. Deuterated dimethylsulfoxide was purchased from Beijing Boya Dabei Technological Development (China), the other solvents were purchased from Tianjin Hongyan Chemical Reagents Factory (Tianjin, China). The silica gel for column chromatography (200–300 mesh). was purchased from Tsingtao Marine Chemical Factory (Tsingtao,

Shandong Province, China). The bacteria (Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus, Streptococcus lactis) and the fungi (Cytospora mandshurica, Gibberella saubinerii, Setosphearia turcica, Alternaria alternata, S. sclerotiorum, Botrytis cinerea, Peony anthracnose) were provided from the School of Food and Biological Engineering, Shaanxi University of Science & Technology (Xi'an, China).

1.75 Kg of dried Polygonum pilosa tuber was soaked in 95% alcohol, refluxed for 3 times, combined the extracts, distilled under reduced pressure and concentrated to obtain 330g of crude extract. Add distilled water to the crude extract and suspend it evenly in water by repeated stirring, Were extracted with petroleum ether, ethyl acetate, n-butanol, and the water-soluble substances were left in the water and discarded. Three parts are obtained after recovering the extraction solvent: petroleum ether extract 7.7 g, ethyl acetate extract 33.2 g, and n-butanol extract 169.5 g. After dissolving the petroleum ether extract with methanol, take 8 g of silica gel, mix the sample, and dry it in an oven. The sample was chromatographed on a silica gel column and eluted with petroleum ether-ethyl acetate (100:2, 100:5, 100:10, 100:20, 100:50, 0:100) to obtain 6 components: Fr.1-Fr.6, Fr.2 and Fr.6 were recrystallized from methanol to obtain compounds 1 (15.2 mg) and 2 (20.5 mg), respectively. After the ethyl acetate extract was dissolved in methanol, 35 g of silica gel was taken, mixed with a sample, and dried in an oven. The sample was chromatographed on a silica gel column with petroleum ether-ethyl acetate (100:100, 100:200, 0:100) and ethyl acetate-methanol (100:5, 100:10, 100:20, 100:50, 100:100) to obtain 8 components: Fr.1-Fr.8. The Fr.1 component was purified by silica gel column chromatography and recrystallization to obtain compounds 3 (5.2 mg). The Fr.3 component was purified by repeated silica gel column chromatography, Sephadex LH-20 and recrystallization to obtain compounds 4 (50.9 mg), 5 (3.4 mg).

4. Conclusion

This study showed that by extracting and separating the crude extracts of Polygonum pilosa dry tuber with 95% ethanol, 5 compounds were isolated from it. Among them, compounds 3-5 were obtained from Polygonum multiflorum for the first time. Isolated from this plant. This experiment found that the plant not only contains the currently reported anthraquinones, triterpenes, polyphenols, polysaccharides and other compounds, but also contains flavonoids. Flavonoids are widely present in Polygonaceae, and the antioxidant effects of these compounds are more significant. This topic makes up for the insufficiency of the research on the chemical composition of Polygonum pilosa in the Qinling Mountains, and lays a certain theoretical foundation for the further development and utilization of the medicinal plant resources of Polygonum pilosa

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