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金铁锁地上部分化学成分研究

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摘 要:运用柱色谱方法,对金铁锁地上部分的80%乙醇提取物进行系统的化学成分研究,从中共分离得到11个化合物。利用理化性质及ESI-MS,NMR光谱分析法,分别鉴定为麦芽酚(**1**),尼克酰胺(**2**),尿嘧啶核苷(**3**),2′-脱氧尿苷(**4**),胸嘧啶核苷(**5**),2′-脱氧胸苷(**6**),尿嘧啶(**7**),1-*O*-(4-羟甲基苯基) α-*L*-吡喃鼠李糖苷(**8**),苄基-β-*D*-吡喃葡萄糖苷(**9**),(6*R*,9*R*)-3-氧代-α-紫罗兰醇-9-*O*-β-*D*-吡喃葡萄糖苷(**10**)和川牛膝甾酮(**11**)。所有化合物均为首次从该植物中分离得到。

关键词:金铁锁;地上部分;化学成分

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Chemical Constituents from the Aerial Parts of *Psammosilene tunicoides*

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Abstract: Eleven compounds were isolated from the aerial parts of *Psammosilene tunicoides* by means of column chromatography. Their structures were identified as maltol (**1**), nicotinamide (**2**), uridine (**3**), deoxyuridine (**4**), thymidine (**5**), deoxythymidine (**6**), uracil (**7**), 1-*O*-(4-hydroxymethylphenyl) α-*L*-Rhamnopyranoside (**8**), benzyl-β-*D*-glucopyranoside (**9**), (6*R*,9*R*)-3-oxo-α-ionol-9-*O*-β-*D*-glucopyranoside (**10**) and capitasterone (**11**), respectively. All compounds were isolated from *P. tunicoides* for the first time.

Key words: *Psammosilene tunicoides*; aerial parts; chemical constituents

Introduction

Psammosilene tunicoides W. C. Wu et C. Y. Wu is the only species in the genus *Psammosilene* growing in Sichuan, Yunnan, Tibet and Guizhou provinces of China. As a Yunnan folk medicine, it has been long used for stopping bleeding, relieving pain and promoting blood circulation[1]. The crude saponins obtained from this plant exhibited relieving pain, anti-inflammation and regulating the immune function[2]. In searching for bioactive constituents from this plant, several kinds of compounds have been reported from the roots of this plant, including triterpenoid saponins, cyclic peptides, and carboline alkaloids[3]. To our best knowledge, however, the chemical investigation of the aerial parts of *P. tunicoides* had not yet been investigated. In this study, the isolation and structural elucidation of **11** known compounds from the ethanol extract of the aerial parts of *P. tunicoides* are presented. All compounds were isolated from *P. tunicoides* for the first time.

Experimental

General experimental procedures

NMR spectral data were recorded on Bruker Avance 500 and 600 MHz NMR spectrometers. Chemical shifts were recorded as δ values. The ESI-MS data were acquired on an Agilent-1100-LC /MSD-Trap-XCT mass spectrometer (Agilent, USA). TLC was done on precoated silica gel 254 plates (Huanghai, 0.15-0.20 mm thick for TLC analysis, 0.40-0.50 mm thick for preparative TLC). Column chromatography was performed using silica gel (200-300 mesh and 100-200 mesh)

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(Huiyou Silica Gel Development Co. Ltd, Yantai, P. R. China), RP-C_{18} (GHODS AQ 12S50, Japan) and Sephadex LH-20 (GE Healthcare Bio-Science AB, Sweden).

Plant materials

The aerial parts of *P. tunicoides* were collected in Lijiang, Yunnan province, China, in July 2006 and identified by Prof. Li-Shan Xie, Kunming Institute of Botany, the Chinese Academy of Sciences, China. The voucher specimen (No. 2006071015) was deposited with the Herbarium of the School of Pharmacy, Second Military Medical University.

Extraction and isolation

The aerial parts of *P. tunicoides* (13 kg) was macerated and repeatedly extracted with 80% ethanol. The combined extracts were subjected to silica gel column chromatography eluted with petroleum ether, CH_2Cl_2, EtOAc, and MeOH, and resulting in four fractions, respectively. The MeOH extract (813.5 g) was separated by silica gel column chromatography eluted with EtOAc-MeOH (20∶1-1∶1) and re-crystallizated to afford compound **1** (115.3 mg). The EtOAc extract (88 g) was separated into seven fractions (A-E) by CC (ODS, MeOH∶H_2O 1∶9-1∶0). Fr. B (22.5 g) was separated over silica gel column chromatography (petroleum ether∶EtOAc∶MeOH 3∶3∶0-3∶3∶2; then Sephadex LH-20 column chromatography (MeOH) to yield compounds **2** (8.1 mg), **3** (3.4 mg), **4** (4.7 mg), **5** (7.2 mg), **6** (10.5 mg), **7** (7.3 mg), **8** (13.9 mg), **9** (15.2 mg), **10** (17.3 mg), **11** (740.8 mg). Fr. C (9.5 g) was purified onto a silica gel column chromatography eluted with $CHCl_3$∶MeOH (100∶1-5∶1) and followed Sephadex LH-20 column chromatography (MeOH) to yield **12** (22.8 mg), **13** (6.9 mg).

Structural identification

Compound 1 $C_6H_6O_3$; White solid; ESI-MS *m/z* 149 $[M + Na]^+$; ^1H NMR (CD_3OD, 500 MHz) δ_H: 7.95 (1H, d, J = 5.5 Hz, H-5), 6.41 (1H, d, J = 5.5 Hz, H-6), 2.36 (3H, s); ^{13}C NMR (CD_3OD, 125 MHz) δ_C: 152.2 (C-2), 144.6 (C-3), 175.3 (C-4), 114.4 (C-5), 156.3 (C-6), 14.4 (C-7). The NMR data was consistent with the data reported in literature[4]. Hence, compound **1** was identified as maltol.

Compound 2 $C_6H_6N_2O$; white solid; ESI-MS *m/z* 145 $[M + Na]^+$; ^1H NMR (CD_3OD, 600 MHz) δ_H: 9.03 (1H, br, H-2), 8.70 (1H, br, H-6), 8.27 (1H, m, H-4), 7.54 (1H, dd, J = 8.0, 4.9 Hz, H-5); ^{13}C NMR (CD_3OD, 150 MHz) δ_C: 152.8 (C-2), 131.5 (C-3), 137.3 (C-4), 125.1 (C-5), 149.5 (C-6), 169.8 (3-$CONH_2$). The NMR data was identical with the data reported in literature[5]. Therefore, compound **2** was identified as nicotinamide.

Compound 3 $C_9H_{12}N_2O_6$; yellow oil; ESI-MS *m/z* 267 $[M + Na]^+$, 511 $[2M + Na]^+$, 487 $[2M-H]^-$; ^1H NMR (CD_3OD, 600 MHz) δ_H: 7.88 (1H, d, J = 8.1 Hz, H-6), 5.87 (1H, d, J = 4.6 Hz, H-1′), 5.85 (1H, d, J = 8.1 Hz, H-5), 4.27 (1H, t, J = 5.0 Hz, H-2′), 4.18 (1H, t, J = 5.3 Hz, H-3′), 4.08 (1H, m, H-4′), 3.87 (1H, dd, J = 12.7, 2.9 Hz, H-5 (a)), 3.77 (1H, dd, J = 12.7, 4.1 Hz, H-5 (b)); ^{13}C NMR (CD_3OD, 150 MHz) δ_C: 152.5 (C-2), 166.9 (C-4), 103.1 (C-5), 142.7 (C-6), 90.4 (C-1′), 70.5 (C-2′), 74.8 (C-3′), 85.4 (C-4′), 61.8 (C-5′). The NMR data was in agreement with the data reported in literature[6] and determined compound **3** as uridine.

Compound 4 $C_9H_{12}N_2O_5$; colorless solid; ESI-MS *m/z* 251 $[M + Na]^+$; ^1H NMR (CD_3OD, 500 MHz) δ_H: 7.97 (1H, d, J = 8.1 Hz, H-6), 6.26 (1H, t, J = 6.6 Hz, H-1′), 5.68 (1H, d, J = 8.1 Hz, H-5). 4.37 (1H, m, H-4′), 3.93 (1H, m, H-3′), 3.77 (1H, d, J = 12.0 Hz, H-5 (a)), 3.71 (1H, d, J = 12.0Hz, H-5 (b)), 2.28 (1H, m, H-2 (a)), 2.18 (1H, m, H-2 (b)); ^{13}C NMR (CD_3OD, 125 MHz) δ_C: 152.2 (C-2), 166.3 (C-4), 102.6 (C-5), 142.5 (C-6), 88.9 (C-1′), 41.4 (C-2′), 72.3 (C-3′), 86.6 (C-4′), 62.8 (C-5′). Compound **4** was identified as deoxyuridine by comparison with the spectra data reported in literature[7].

Compound 5 $C_{10}H_{14}N_2O_6$; colorless solid; ESI-MS *m/z* 281 $[M + Na]^+$, 257 $[M-H]^-$, 515 $[2M-H]^-$; ^1H NMR (CD_3OD, 500 MHz) δ_H: 7.85 (1H, s, H-6), 5.90 (1H, d, J = 4.5 Hz, H-1′), 4.16 (1H, m, H-2′), 3.99 (2H, m, H-3 (, H-4′), 3.84 (1H, dd, J = 12.3, 2.7 Hz, H-5 (a), 3.77 (1H, dd, J =

12.3, 3.0 Hz, H-5 (b), 1.98 (3H, s). ^{13}C NMR (CD_3OD, 125 MHz) δ_C: 152.5 (C-2), 166.5 (C-4), 111.5 (C-5), 138.4 (C-6), 90.4 (C-1′), 71.3 (C-2′), 75.5 (C-3′), 86.3 (C-4′), 62.3 (C-5′), 12.4 (5-CH_3). The above data was identical with the data reported in literature[8]. Consequently, compound **5** was identified as thymidine.

Compound 6 $C_{10}H_{14}N_2O_5$; white crystal (MeOH); ESI-MS *m/z* 265 $[M + Na]^+$, 507 $[2M + Na]^+$, 241 $[M-H]^-$, 483 $[2M-H]^-$; ^{1}H NMR (CD_3OD, 500 MHz) δ_H: 7.67 (1H, s, H-6), 6.28 (1H, t, *J* = 6.8 Hz, H-1′), 4.46 (1H, m, H-4′), 4.00 (1H, m, H-3′), 3.83 (1H, dd, *J* = 12.4, 3.5 Hz, H-5(a), 3.76 (1H, dd, *J* = 12.5, 4.8 Hz, H-5(b), 2.36 (2H, m, H-2′), 1.89 (3H, s, CH_3); ^{13}C NMR (CD_3OD, 125 MHz) δ_C: 152.6 (C-2), 167.4 (C-4), 112.3 (C-5), 138.4 (C-6), 87.6 (C-1′), 39.7 (C-2′), 71.5 (C-3′), 86.0 (C-4′), 62.2 (C-5′), 12.5 (5-CH_3). The NMR data was in accordance with the data reported in literature[9], and identified as deoxythymidine.

Compound 7 $C_4H_4N_2O_2$; colorless solid; ESI-MS *m/z* 135 $[M + Na]^+$; ^{1}H NMR (CD_3OD, 500 MHz) δ_H: 7.40 (1H, d, *J* = 7.7 Hz, H-6), 5.42 (1H, d, *J* = 7.7 Hz, H-5); ^{13}C NMR (CD_3OD, 125 MHz) δ_C: 152.0 (C-2), 142.7 (C-4), 100.7 (C-5), 164.8 (C-6). By comparison the NMR data with the data reported in literature[8], compound **7** was identified as uracil.

Compound 8 $C_{13}H_{18}O_6$; colorless oil; ESI-MS *m/z* 293 $[M + Na]^+$, 563 $[2M + Na]^+$, 539 $[2M-H]^-$; ^{1}H NMR(CD_3OD, 500 MHz) δ_H: 7.27 (2H, d, *J* = 8.4 Hz, H-2, H-6), 7.02 (2H, d, *J* = 8.4 Hz, H-3, H-5), 5.40 (1H, d, *J* = 2.0 Hz, H-1′), 4.52 (2H, s, H-7), 3.96 (1H, m, H-2′), 3.82 (1H, m, H-3′), 3.62 (1H, dq, *J* = 12.4, 6.2 Hz, H-5′), 3.44 (1H, t, *J* = 9.5 Hz, H-4′), 1.20 (3H, d, *J* = 6.2 Hz, H-6′). ^{13}C NMR (CD_3OD, 125 MHz) δ_C: 157.1 (C-1), 129.5 (C-2, C-6), 117.4 (C-3, C-5), 136.4 (C-4), 64.8 (C-7), 99.8 (C-1′), 72.1 (C-2′), 72.2 (C-3′), 73.8 (C-4′), 70.6 (C-5′), 18.0 (C-6′). Comparing NMR data with the data reported in literature[9], compound **8** was identified as 1-*O*-(4-hydroxymethylphenyl) α-*L*-rhamnopyranoside.

Compound 9 $C_{13}H_{18}O_6$; colorless oil; ESI-MS *m/z* 293 $[M + Na]^+$, 563 $[2M + Na]^+$, 269 $[M-H]^-$, 539 $[2M-H]^-$; ^{1}H NMR (CD_3OD, 500 MHz) δ_H: 7.40 (2H, m, H-3, H-5), 7.30 (3H, m, H-2, H-4, H-6), 4.92 (1H, d, *J* = 11.8 Hz, H-7a), 4.65 (1H, d, *J* = 11.8 Hz, H-7b), 4.34 (1H, d, *J* = 7.7 Hz, H-1′), 3.88 (1H, dd, *J* = 11.9, 2.0 Hz, H-6(a), 3.67 (1H, dd, *J* = 11.7, 5.3 Hz, H-6(b). 3.20-3.31 (4H, m, H-2(, H-3(, H-4(, H-5′); ^{13}C NMR (CD_3OD, 125 MHz) δ_C: 138.9 (C-1), 129.0 (C-2, C-6), 129.1 (C-3, C-5), 128.5 (C-4), 103.1 (C-1′), 74.9 (C-2′), 77.9 (C-3′), 71.5 (C-4′), 77.9 (C-5′), 62.6 (C-6′). The above data was consistent with the data reported in literature[10]. Hence, compound **9** was identified as benzyl-β-*D*-glucopyranoside.

Compound 10 $C_{19}H_{30}O_7$; colorless oil; ESI-MS *m/z* 393 $[M + Na]^+$, 763 $[2M + Na]^+$, 369 $[M-H]^-$, 739 $[2M-H]^-$; ^{1}H NMR (CD_3OD, 500 MHz) δ_H: 5.87 (1H, s, H-4), 5.76 (1H, dd, *J* = 14.9, 3.5 Hz, H-8), 5.58 (1H, m, H-7), 4.39 (2H, m, H-9, H-1′), 3.81 (1H, d, *J* = 11.8 Hz, H-6(a), 3.64 (1H, m, H-6(b), 3.29 (2H, m, H-4(, H-5′), 3.18 (2H, m, H-2(, H-3′), 2.66 (1H, d, *J* = 8.6 Hz, H-6), 2.42 (1H, d, *J* = 16.7 Hz, H-2a), 2.03 (1H, d, *J* = 16.9 Hz, H-2b), 1.93 (3H, s, H-13), 1.28 (3H, d, *J* = 6.3 Hz, H-10), 1.00 (6H, m, H-11, H-12). ^{13}C NMR (CD_3OD, 125 MHz) δ_C: 37.1 (C-1), 48.2 (C-2), 201.9 (C-3), 126.1 (C-4), 165.8 (C-5), 56.7 (C-6), 128.8 (C-7), 138.2 (C-8), 76.9 (C-9), 21.0 (C-10), 27.6 (C-11), 28.0 (C-12), 23.8 (C-13), 102.4 (C-1′), 75.2 (C-2′), 78.0 (C-3′), 71.4 (C-4′), 77.9 (C-5′), 62.6 (C-6′). The above data was in accordance with the data reported in literature[11]. Consequently, compound **10** was identified as (6*R*, 9*R*)-3-oxo-α-ionol-9-*O*-β-*D*-glucopyranoside.

Compound 11 $C_{29}H_{44}O_7$; white solid; ESI-MS *m/z* 527 $[M + Na]^+$, 503 $[M-H]^-$; ^{1}H NMR (C_5D_5N, 500 MHz) δ_H: 6.27 (1H, d, *J* = 2.3 Hz, H-7), 4.49 (1H, dd, *J* = 11.3, 2.6 Hz, H-22), 4.25 (1H, s, H-3), 4.18 (1H, d, *J* = 10.2 Hz, H-2), 3.60 (1H, m, H-9), 3.01 (2H, m, H-5, H-17), 2.66 (1H, td, *J* = 12.9, 4.7 Hz, H-15a), 2.45 (1H, dd, *J* = 20.8, 10.2 Hz, H-16a), 2.26-2.13 (3H, m, H-1a, H-15b, H-

25), 2.06 (3H, ddd, J = 13.8, 11.3, 8.3 Hz, H-4a, H-16b, H-23a), 1.94 (4H, m, H-1b, H-11a, H-12, H-23b), 1.75 (2H, ddd, J = 18.1, 17.2, 9.9 Hz, H-4b, H-11b), 1.50 (3H, s, H-21), 1.40 (2H, m, H-24, H-241a), 1.31 (3H, m, H-27), 1.16 (3H, s, H-18), 1.09 (3H, s, H-19), 1.05 (1H, m, H-24[1]b), 0.71 (3H, t, J = 7.4 Hz, H-242); ^{13}C NMR (C_5D_5N, 125 MHz) δ_C: 38.4 (C-1), 68.5 (C-2), 68.4 (C-3), 32.2 (C-4), 51.3 (C-5), 203.2 (C-6), 121.6 (C-7), 165.6 (C-8), 34.1 (C-9), 38.4 (C-10), 20.8 (C-11), 31.7 (C-12), 47.7 (C-13), 83.9 (C-14), 31.5 (C-15), 21.2 (C-16), 49.7 (C-17), 17.8 (C-18), 24.2 (C-19), 75.5 (C-20), 21.2 (C-21), 85.7 (C-22), 29.4 (C-23), 39.9 (C-24), 41.2 (C-25), 174.4 (C-26), 15.5 (C-27), 26.4 (C-241), 10.0 (C-242). The NMR data was consistent with the data reported in literature[12]. Hence, compound **11** was identified as capitasterone.

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