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柴达木盆地唐古特白刺种子的化学成分研究

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摘 要:从唐古特白刺种子 75%乙醇提取物中分离得到 6种化合物,应用波谱方法及与文献对照的手段鉴定为:胡萝卜苷(daucosterol, **1**),4-hydroxypipecolic acid(**2**),槲皮素(quercetin, **3**),尿囊素(allantoin, **4**),1, 2, 3, 4-tetrahydro-1-methyl-β-carboline-3-carboxylic acid(**5**),L-tyrosine(**6**)。除槲皮素外的其他五种化合物均为首次从该植物中分离得到。

关键词:唐古特白刺;种子;化学成分;尿囊素;分离;结构鉴定

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Chemical Constituents of *Nitraira tangutorum* Seed from Qaidam Basin

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Abstract: Six compounds were isolated from the 75% ethanol extract of *Nitraria tangutorum* seed. On the basis of spectroscopic methods including ^{1}H NMR, ^{13}C NMR and ESI-MS and comparison with literature, their structures were elucidated as daucosterol(**1**), 4-hydroxypipecolic acid(**2**), quercetin(**3**), allantoin(**4**), 1, 2, 3, 4-tetrahydro-1-methyl-β-carboline-3-carboxylic acid(**5**) and L-tyrosine(**6**). Compounds **1**, **2**, **3**, **5** and **6** were isolated from *Nitraria tangtorum* for the first time.

Key words: *Nitraria tangutorum*; seed; 1, 2, 3, 4-tetrahydro-1-methyl-β-carboline-3-carboxylic acid; allantoin

Introduction

The genus *Nitraria* (Zygophyllaceae) is a shrub that bears edible berries and widely distributed in the Middle East, Central Asia, and the Northwest region of China. Among the *Nitraria* species, only *N. tangutorum* Bobr. grows in China, especially in the desert of Qinghai-Tibetan Plateau. A main function of a *N. tangutorum* Bobr. forest is to conserve the soil and water from the wind-blown sand [1,2]. In addition, its leaves, fruits and seeds are often used in folk medicines such as antispasmodic, antineuropathic, and anti-arrhythmicagent [3,4] to cure weaknesses in the spleen and stomach [5,6] and decrease blood lipid levels and anti-oxidation [7].

The chemical constituents of *Nitraria tangutorum* seed collected from Gansu Province and the chemical constituents of *Nitraria tangutroum* leaves from Ningxia Province had been reported [5,8]. And it revealed the presence of flavonids, phenolic acids and alkaloids. However, the chemical constituents of *Nitraria tangutorum* seeds from Qaidam basin, Qinghai Province were not reported. In this study, six compounds were isolated from the ethanol extract of the *Nitraira tangutorum* seed collected from Qaidam basin. Their structures were elucidated as daucosterol (**1**), 4-hydroxypipecolic acid (**2**), quercetin (**3**), allantoin (**4**), 1, 2, 3, 4-tetrahydro-1-methyl-β-carboline-3-carboxylic acid (**5**), L-tyrosine (**6**) on the basis of spectral data or in comparison with literature.

Materials and Methods

Apparatus and materials

All melting points were determined on a PHMK micromelting point apparatus and uncorrectd. IR spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrophotometer (KBr). NMR spectra were obtained on a

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Bruker AM400 and Varian Mercury 400B NMR spectrometer. Elements were analyzed on the Elementar Analysensysteme GmbH VarioEL. ESI-MS were carried on a Bruker Apex Ⅱ. Silica gel (Qingdao Haiyang Chemical Co., Ltd., China), RP-C18 and Sephadex LH20 (Pharmacia Co., American) were used for column chromatography. The *Nitraria tangutorum* seeds were collected in September 2003 in Dulan country, Qinghai Province and identified by Prof. Liu Shang-wu.

Extraction and isolation

The air-dired and powered seeds (15 kg) of *Nitraria tangutorum* were extracted firstly by supercritical carbon dioxide for extracting the fatty acids, and then the seeds were extracted by 75% EtOH three times under reflux. After the solvent was evaporated *in vacuo*, the residue (1200 g) was suspended in water and extracted with petroleum ether (bp. 60-90 ℃), chloroform, ethyl acetate and n-butanol respectively. The ethyl acetate fraction (45 g) was separated over silica column chromatography (CC) eluting with chloroform-methanol (70: 1→0: 1) to obtain compounds **1** (30 mg) and **3** (39 mg). The *n*-butanol (75 g) fraction was isolated on silica CC eluting with chloroform-methanol (50: 1→0: 1), and 5 fractions (Fr1-Fr5) were obtained according to detection by TLC (GF_{254}). Fr1 was separated by silica gel CC and purified Sephedex LH-20 column eluting methanol to obtain compound **4** (115 mg). Fr3 was purified by sephadex LH-20 and RP-C18 to give compound **5** (43 mg) and compound **6** (16 mg). Fr5 was isolated on silica gel CC eluting with chloroform-methanol (4: 1→0: 1) to yield compound **2** (220 mg).

Identification

Daucosterol (1) White powder (methanol), mp. 270-272 ℃, $C_{35}H_{60}O_6$. ^{1}H NMR (Pyridine-d_5, 400 MHz) δ: 5.34 (1H, m, H-6), 5.05 (1H, d, *J* = 7.6 Hz, H-1′), 4.60-3.90 (m, H-2′-6′), 2.80-1.00 (m), 0.97-0.83 (m, 5 ×-CH_3), 0.64 (s, -CH_3); ^{13}C NMR (Pyridine-d_5, 100 MHz) δ: 149.9, 121.9, 102.6, 78.6, 78.3, 78.1, 75.3, 71.7, 62.8, 56.8, 56.2, 50.3, 46.0, 42.5, 39.9, 39.3, 37.5, 36.9, 36.4, 34.2, 32.2, 32.0, 30.2, 29.4, 28.5, 26.3, 24.5, 23.4, 21.3, 20.0, 19.4, 19.2, 19.0, 12.1, 12.0. Its data were consistent with those of daucosterol[9].

4-Hydroxypipecolic acid (2) White powder (EtOH), mp. 261-263 ℃, $C_6H_{11}NO_3$. Elements analysis (%): C 46.42, H 7.05, N 7.75; IRν_{max}^{KBr} cm^{-1}: 3266, 3121, 2938, 1610. ^{1}H NMR (D_2O, 400 MHz) δ: 4.05 (1H, m, H-4), 3.73 (1H, dd, *J* = 11.6, 3.6 Hz, H-2), 3.12 (2H, m, H-6), 2.04, 1.79 (1H, m, H-4), 1.72 (2H, m, H-5); ^{13}C NMR (D_2O, 100 MHz) δ: 177.04 (COOH), 64.64 (C-4), 56.74 (C-2), 41.35 (C-6), 35.61 (C-3), 30.74 (C-5). The IR, NMR data were identical to those reported[10].

Quercetin (3) Yellow powder (methanol), mp. 310-312 ℃, $C_{15}H_{10}O_7$. ^{1}H NMR (CD_3OD, 400 MHz) δ: 7.72 (1H, d, *J* = 2.0 Hz, H-2′), 7.62 (1H, dd, *J* = 8.4, 2.0 Hz, H-6′), 6.87 (1H, d, *J* = 8.4 Hz, H-5′), 6.38 (1H, d, *J* = 2.0 Hz, H-8), 6.17 (1H, d, *J* = 2.0 Hz, H-6); ^{13}C NMR (CD_3OD, 100 MHz) δ: 177.3 (C-4), 165.6 (C-7), 162.5 (C-9), 158.2 (C-5), 148.8 (C-4′), 148.0 (C-2), 146.2 (C-3′), 136.6 (C-3), 124.1 (C-1′), 121.6 (C-6′), 116.2 (C-5′), 116.0 (C-2s), 104.5 (C-10), 99.2 (C-6), 94.4 (C-8). Its NMR data were consistent with those of quercetin[11].

Allantoin (4) White powder (methanol), mp. 237-239 ℃, $C_4H_6N_4O_3$, HR-ESI-MS: $[M+H]^+$ 159.0513. IRν_{max}^{KBr} cm^{-1}: 3438, 3345, 1782, 1709, 1658, 1603, 1530, 1184. ^{1}H NMR (DMSO, 400 MHz) δ: 10.53 (1H, s), 8.05 (1H, s), 6.88 (1H, d, *J* = 8.0 Hz), 5.78 (2H, s), 5.24 (1H, d, *J* = 6.8 Hz), 5.23 (1H, s); ^{13}C NMR (DMSO, 100 MHz) δ: 173.6 (-NH-CO-NH_2), 157.4 (-NH-CO-), 156.8 (-NH-CO-), 62.4 (CH). Its melting point and R_f were same to an authentic allantoin sample (National Institute for the Control of Pharmaceutical and Biological Products, No. 1501-200001). It was identified as allantoin[12,13].

1, 2, 3, 4-Tetrahydro-1-methyl-β-carboline-3-carboxylic acid (5) White powder (methanol), mp. 286-288 ℃, $C_{13}H_{14}N_2O_2$, HR-ESI-MS: $[M+H]^+$ 231.1140. IRν_{max}^{KBr} cm^{-1}: 3294, 2981, 2922, 1644, 1577, 1384, 742; ^{1}H NMR (DMSO, 400 MHz) δ: 11.12 (1H, s), 7.43 (1H, d, *J* = 8.0 Hz, H-9), 7.33 (1H, d, *J* = 8.0 Hz, H-12), 7.08 (1H, t, *J* = 7.2, 7.6 Hz, H-11), 7.00 (1H, t, *J* = 7.6, 7.2 Hz, H-10), 4.56 (1H, m, H-3), 3.69 (1H, dd, *J* = 12.0, 4.8 Hz, H-5), 3.22, 2.80

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(2H, m, H-6), 1.61 (3H, d, J = 6.8 Hz, -CH3); ^{13}C NMR (DMSO, 100 MHz) δ: 170.45 (-COOH), 136.87 (C-13), 131.73 (C-2), 126.33 (C-8), 122.08 (C-11), 119.52 (C-10), 118.52 (C-9), 111.77 (C-12), 106.93 (C-7), 58.05 (C-5), 49.63 (C-3), 23.23 (C-6), 17.03 (-CH_3). The IR, MS, NMR spectral data were identical with those of 1, 2, 3, 4-tetrahydro-1-methyl-β-carboline-3-carboxylic acid.

L-Tyrosine (6) White powder (methanol), mp. 244-246 ℃. IRυ_{max}^{KBr} cm^{-1}: 3206, 2928, 1611, 1588, 1513, 1454, 1329, 1245; ^{1}H NMR (DMSO + D_2O, 400 MHz) δ: 7.02 (2H, d, J = 8.0 Hz, H-6, 8), 6.66 (2H, d, J = 8.0 Hz, H-5, 9), 3.46 (1H, m, H-2), 2.98, 2.73 (2H, m, H-3); ^{13}C NMR (DMSO + D_2O, 100 MHz) δ: 171.96 (CO), 156.45 (C-7), 130.70 (C-6, 8), 116.32 (C-5, 9), 56.45 (C-2), 36.35 (C-3). Its IR, NMR data were consistent with those of L-tyrosine [14].

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