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瑞香狼毒根中的一个新化合物

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摘 要:从瑞香狼毒根中分离得到了7个化合物,根据理化性质和波谱数据鉴定为:3-丁酰基-4-氨基肉桂酸乙酯(**1**)、阿魏酸(**2**)、香草酸(**3**)、姜黄素(**4**)、5′-去甲氧基-姜黄素(**5**)、3′-羟基-4′-*O*-*β*-*D*-葡萄糖苷黄酮(**6**)、3-甲氧基-4-*O*-*β*-*D*-葡萄糖苯甲酸(**7**),其中化合物**1**~**3**,**6**~**7**为首次从该植物中分离得到,化合物**1**为新化合物。

关键词:瑞香狼毒;瑞香科;酚性化合物;苯丙烯化合物

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A New Compound Isolated from Roots of *Stellera chamaejasme* L.

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Abstract: Seven compounds were isolated from the roots of *Stellera chamaejasme* L. Their structures were identified as 3-butyryl-4-amino ethylcinnamate(**1**), ferulic acid(**2**), vanillic acid(**3**), daphneticin(**4**), 5′-demethoxy daphneticin(**5**), 3′-hydroxy-4′-*O*-*β*-*D*-glucopyranoside flavone(**6**) and 3-methoxy-4-*O*-*β*-*D*-gluco-benzoic acid(**7**) by comparing physicochemical properties and NMR data with published literatures. Among them, compounds **1-3**, **6-7** were isolated from this species for the first time, compound **1** is a new compound.

Key words: *Stellera chamaejasme* L.; *Thymelaeaceae*; phenolic compounds; phenylpropanoid

Introduction

Stellera chamaejasme L. is one species of the genus *Stellera*, belonging to family *Thymelaeaceae*. In China, this plant is mainly distributed in northwest and northeast areas, including Inner Mongolia, Qinghai, Gansu, Tibet provinces[1]. The dried roots of *S. chamaejasme* L. is a well-known traditional Chinese medicine. It is often used as expectorant, anti-inflammation, detoxification, apocatastasis agent and also used for the treatment of furuncle, carbuncle and ulcers[2,3]. Zhou L *et al*[4]. and Gong XX *et al*[5]. reported the antibacterial, antivirus, anticancer activity and bactericidal effect of compounds from the roots of *S. chamaejasme* L.. Previous phytochemical investigation on *S. chamaejasme* L. had resulted in the isolation and identification of a variety of secondary metabolites, which mainly included coumarins, flavonoids, lignans and phenylpropanoid glycosides[3-6]. Our laboratory had recently reported a number of coumarins and flavonoids from the roots of *S. chamaejasme* L.[7]. As a continuation of our phytochemical investigation, the present study reported another 7 compounds of this plant. The structures of these compounds were identified as 3-butyryl-4-amino ethylcinnamate(**1**), ferulic acid(**2**), vanillic acid(**3**), daphneticin(**4**), 5′- demethoxy daphneticin(**5**), 3′-hydroxy-4′-*O*-*β*-*D*-glucopyranoside flavone(**6**) and 3-methoxy-4-*O*-*β*-*D*-gluco-benzoic acid(**7**) by comparing physicochemical properties and NMR data with published literatures. Among them, compounds **1-3**, **6-7** were reported from this species for the first time, compound **1** is a new compound.

Materials and Reagents

The roots of *S. chamaejasme* L. were collected in August 2008 from Huining county of Gansu province, China. It

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was identified by Professor CHEN Xue-lin (College of Life Science, Northwest Normal University). A voucher specimen (No. 200807) was deposited in the College of Chemistry and Chemical Engineering, Northwest Normal University.

^{1}H NMR and ^{13}C NMR spectral data were recorded on a Bruker-DRX-400 FT NMR spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) with tetramethylsilane (TMS) as internal standard; Electron ionization mass spectrometry (EI-MS) and HREI-MS spectral data were acquired on a Bruker APEX II; Silica gel (200-300, 300-400 mesh) and silica gel GF_{254} (10-40 μm) were purchased from Qingdao Hai Yang Chemical Group Company, Shandong; Sephadex LH-20 gel were used for column chromatography; Spots were detected on TLC under UV lamp or by heating after spraying with 5% H_2SO_4 in C_2H_5OH (v/v).

Extraction and Isolation

The powder of dried roots (5 kg) of *S. chamaejasme* L. was exhaustively extracted with 90% ethanol 3 times under reflux. The combined extract was evaporated under reduced pressure to yield a syrupy residue (670 g). The residue was suspended in water and extracted with petroleum ether (PE, 60-90 °C), $CHCl_3$, EtOAc and *n*-BuOH, successively. The PE fraction (71 g), $CHCl_3$ fraction (26 g), EtOAc fraction (125 g) and *n*-BuOH fraction (54 g) were yielded, respectively. The $CHCl_3$ fraction was chromatographed on silica gel column using gradient elution with PE/$CHCl_3$ (50∶1 to 1∶1) to yield 6 fractions (Fr. 1-Fr. 6). Fr. 5 was sequentially separated on silica gel column eluted with $CHCl_3$/CH_3COCH_3 (30∶1 to 1∶1) to yield **2** (20.9 mg) and **3** (9.0 mg). The EtOAc fraction was subjected to silica gel column, gradiently eluted with $CHCl_3$/EtOAc (50∶1 to 5∶1), 18 fractions were obtained. Fr. 1 was retreated on silica gel column and eluted with $CHCl_3$/EtOAc (20∶1 to 10∶1) to yield **4** (23.3 mg) and **5** (12 mg). The *n*-BuOH fraction was subjected to silica gel column using a gradient of EtOAc/MeOH (30∶1 to 1∶1), 4 fractions were obtained. Fr. 1 was isolated and purified in combination of silica gel and Sephadex LH-20 column to yeild **1** (15 mg). By the same method, compound **6** (14 mg) and **7** (9 mg) were obtained from Fr. 2 eluted with $CHCl_2$/MeOH (30∶1 to 1∶1).

Structural elucidation

Compound **1** was obtained as white crystal with a molecular formula of $C_{15}H_{19}O_3N$ deduced from its positive HREI-MS data ([M]$^+$ at *m/z*: 261.1357, calc. 261.1360). The IR (KBr) spectrum of **1** revealed absorption bands of amino (3480, 3325 cm^{-1}), carbonyl (1688 cm^{-1}), aromatic ring (1603, 1510, 1444 cm^{-1}) and double bond (1661 cm^{-1}). The ^{1}H NMR spectrum of **1** (Table 1) indicated the signals of a 1,3,4-trisubstituted benzene ring at δ 6.88, 7.21 (each 1H, d, J = 8.0 Hz) and 7.61 (1H, s), a *trans*-double bond at δ 7.58 and 6.27 (each 1H, d, J = 16.0 Hz), which suggested the presence of phenylpropanoid moiety [8]. Besides, conspicuous signals of an ethyoxyl group at δ 4.19 (2H, q, J = 7.6 Hz) and 1.35 (3H, t, J = 7.6 Hz), an active hydrogen at 3.89 (which can be exchanged by D_2O) were also observed. The ^{13}C NMR and DEPT data of 1 (Table 1) contained 15 signals, including 10 sp^2 carbons and 5 sp^3 carbons, which revealed two carbonyl groups at δ_C 167.9 (s) and 196.9 (s), a double bond carbon at 144.8 (d), 114.4 (d), an aromatic carbons at 124.6 (s), 127.8 (d), 126.2 (s), 145.7 (s), 115.5 (d), 132.4 (d) and an ethyoxyl carbons at 61.4 (t), 14.5 (q). The presence of a butyryl group was deduced from the signals of δ_H 0.87 (t, 3H), 1.53 (m, 2H), 2.88 (t, 2H) and δ_C 14.1, 18.7, 40.3 and 196.9. Considering the molecular formula of **1**, an ethyoxyl and an amino were presented in **1**, in addition to the phenylpropanoid moiety and an butyryl group. The configuration between C-7 and C-8 was *trans* inferred from the coupling constant (16.0 Hz). The location of butyryl group was assigned by HMBC correlations of δ_H 7.61 (H-2) with δ_C 196.9 (C-1′) and δ_H 2.88 (H-2′) with δ_C 196.9 (C-1′) (Fig. 1). Besides, the observed correlations of δ_H 7.58 (H-7) with δ_C 124.6 (C-1), δ_H 6.27

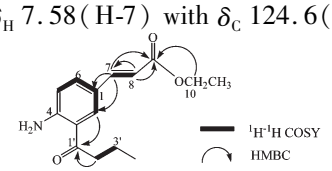

Fig. 1 Key ^{1}H-^{1}H COSY and HMBC correlations of compound 1

(H-8) with δ_C 167.9 (C-9) and δ_H 4.19 (H-10) with δ_C 167.9 (C-9) indicated that **1** had an acryloyl group located at C-1. Analysis and comparison of the ^{1}H-^{1}H COSY and HMBC spectra supported the ^{1}H NMR and ^{13}C NMR assignments (Table 1) and further suggested that compound **1** was a derivative of phenylpropanoid containing a nitrogen atom. All spectra data of **1** were in agreement with the structure as shown in Fig. 1. Therefore, the structure of **1** was established as 3-butyryl-4-amino ethylcinnamate.

Table 1 ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) data of 1 (in CD_3OD-d_4, δ ppm, J in Hz)

Position	^{1}H	^{13}C	Position	^{1}H	^{13}C
1		124.6 (s)	9		167.9 (s)
2	7.61 (s, 1H)	127.8 (d)	10	4.19 (q, 2H, J = 7.6)	61.4 (t)
3		126.2 (s)	11	1.35 (t, 3H, J = 7.6)	14.5 (q)
4		145.7 (s)	1′		196.9 (s)
5	145.7 (s)	115.5 (d)	2′	2.88 (t, 2H)	40.3 (t)
6	7.21 (d, 1H, J = 8.0)	132.4 (d)	3′	1.53 (m, 2H)	18.7 (t)
7	7.58 (d, 1H, J = 16.0)	144.8 (d)	4′	0.87 (t, 3H)	14.1 (q)
8	6.27 (d, 1H, J = 16.0)	114.4 (d)	NH_2	3.89 (s)	

Compound 2 white crystal, $C_{10}H_{10}O_4$, EI-MS *m/z*: 194 [M]$^+$; ^{1}H NMR (400 MHz, CD_3OD) δ: 7.19 (1H, d, J = 2.0 Hz, H-2), 7.08 (1H, dd, J = 2.0, 8.0 Hz, H-5), 6.83 (1H, d, J = 8.0 Hz, H-6), 7.63 (1H, d, J = 16.0 Hz, H-7), 6.34 (1H, d, J = 16.0 Hz, H-8), 3.91 (3H, s, 3-OCH_3); ^{13}C NMR (100 MHz, CD_3OD) δ: 171.2 (COOH), 127.8 (C-1), 111.7 (C-2), 150.6 (C-3), 149.3 (C-4), 116.7 (C-5), 124.2 (C-6), 146.8 (C-7), 116.2 (C-8), 55.9 (3-OCH_3). These spectral data were identical with those of ferulic acid[9].

Compound 3 white powder, $C_8H_8O_4$, EI-MS *m/z*: 168 [M]$^+$; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.43 (1H, d, J = 1.6 Hz, H-2), 6.84 (1H, d, J = 8.0 Hz, H-5), 7.44 (1H, dd, J = 1.6, 8.0 Hz, H-6), 12.47 (1H, brs, -COOH), 9.80 (1H, brs, 4-OH), 3.81 (3H, s, 3-OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 167.2 (-COOH), 121.7 (C-1), 115.1 (C-2), 147.4 (C-3), 149.8 (C-4), 112.7 (C-5), 123.6 (C-6), 56.3 (3-OCH_3). The above spectral data were identical with those of vanillic acid[10].

Compound 4 colorless needles, $C_{19}H_{12}O_7$, EI-ME *m/z*: 352 [M]$^+$; ^{1}H NMR (400 MHz, DMSO-d_6): 6.34 (1H, d, J = 9.6 Hz, H-3), 8.00 (1H, d, J = 9.6 Hz, H-4), 7.20 (1H, d, J = 8.6 Hz, H-5), 6.96 (1H, d, J = 8.6 Hz, H-6), 6.76 (2H, s, H-2′, 6′), 4.43 (1H, d, J = 7.8 Hz, H-7′), 4.34 (1H, m, H-8′), 3.40, 3.68 (each 1H, m, H-9′), 3.81 (6H, s, 2 × OCH_3), 8.54 (1H, s, 4′-OH), 4.36 (1H, s, 9′-OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 160.3 (C-2), 113.5 (C-3), 143.5 (C-4), 112.0 (C-5), 113.2 (C-6), 147.7 (C-7), 138.4 (C-8), 149.2 (C-9), 113.6 (C-10), 126.5 (C-1′), 106.1 (C-2′), 149.3 (C-3′), 132.2 (C-4′), 149.3 (C-5′), 106.1 (C-6′), 77.2 (C-7′), 78.5 (C-8′), 60.5 (C-9′), 56.7 (OCH_3). The above spectral data were identical with those of daphneticin[11].

Compound 5 yellow powder, $C_{19}H_{16}O_7$, EI-MS *m/z*: 356 [M]$^+$; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.32 (1H, d, J = 10.0 Hz, H-3), 7.98 (1H, d, J = 10.0 Hz, H-4), 7.19 (1H, d, J = 8.0 Hz, H-5), 6.95 (1H, d, J = 8.0 Hz, H-6), 7.03 (1H, d, J = 2.0 Hz, H-2′), 6.81 (1H, d, J = 8.0 Hz, H-5′), 6.88 (1H, dd, J = 8.0, 2.0 Hz, H-6′), 3.38, 3.70 (1H, m, H-9′), 3.80 (3H, s, -OCH_3), 4.31 (1H, m, H-8′), 9.19 (1H, s, 4′-OH), 4.45 (1H, s, 9′-OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 160.2 (C-2), 112.5 (C-3), 144.6 (C-4), 119.8 (C-5), 113.2 (C-6), 146.8 (C-7), 131.0 (C-8), 143.1 (C-9), 112.9 (C-10), 126.5 (C-1′), 112.0 (C-2′), 146.9 (C-3′), 147.5 (C-4′), 115.3 (C-5′), 120.5 (C-6′), 76.5 (C-7′), 78.1 (C-8′), 59.9 (C-9′), 55.9 (-OCH_3). The above spectral data were identical with those of 5′- demethoxy daphneticin[11].

Compound 6 colorless needles, $C_{21}H_{20}O_9$, EI-MS *m/z* (neg.): 415 [M-H]$^-$; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.89 (1H, s, H-3), 8.02 (1H, d, J = 8.0 Hz, H-5), 7.48 (1H, t, J = 7.0 Hz, H-6), 7.80 (1H, m, H-7), 7.79 (1H, m, H-8), 7.55 (1H, d, J = 2.0 Hz, H-2′), 7.24 (1H, t, J = 8.5 Hz, H-5′), 7.55 (1H, t, J = 8.5 Hz, H-6′), 9.10 (1H, brs, 3′-OH), 4.85 (1H, d, J = 7.2 Hz, H-1″), 3.15-3.73 (6H, protons of glycoside); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.5 (C-2), 105.7 (C-3), 177.2 (C-4), 125.6 (C-5), 134.4 (C-6), 118.7 (C-7), 124.6 (C-8), 156.9 (C-9), 124.9 (C-10), 123.5 (C-1′), 113.5 (C-2′), 146.9 (C-3′), 148.5 (C-4′), 115.8 (C-5′), 118.7 (C-6′), 101.3 (C-1″), 73.3 (C-2″), 77.4 (C-3″), 69.7 (C-4″), 75.8 (C-5″), 60.8 (C-6″). These spectral data were identical with those of 3′-hydroxy -4′-*O*-*β*-*D*-glucopyranoside flavone[12].

Compound 7 white powder, $C_{14}H_{18}O_9$, EI-MS *m/z*: 330 [M]$^+$; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.74 (1H, brs, H-2), 7.48 (1H, d, J = 8.4 Hz, H-6), 7.14 (1H, d, J = 8.4 Hz, H-5), 5.01 (1H, d, J = 6.0 Hz, H-1′), 3.66 (1H, d, J = 12.0 Hz H-6′a), 3.45 (1H, dd, J = 5.6, 12.0 Hz, H-6′b), 3.35 (1H, m, H-2′), 3.18 (1H, m, H-4′), 3.35 (1H, m, H-5′), 3.80 (3H, s, 3-OCH_3). These spectral data were identical with those of 3-methoxy-4-*O*-*β*-*D*-gluco-benzoic acid[13].

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