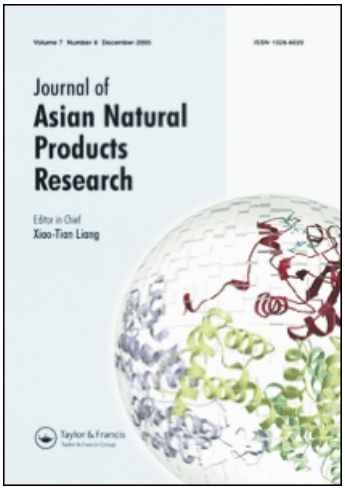

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A NEW PHENOLIC GLYCOSIDE AND A NEW *TRANS*-CLERODANE DITERPENE FROM *CONYZA BLINII*

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A new phenolic glycoside, 4-propionyl-2,6-dimethoxyphenyl β-D-glucopyranoside **(1)** and a new *trans*-clerodane diterpene named 19-deacetylconyzalactone **(2)**, were isolated from the aerial parts of *Conyza blinii*.

Keywords: *Conyza blinii*; Phenolic glycoside; 4-Propionyl-2,6-dimethoxyphenyl β-D-glucopyranoside **(1)**; Clerodane diterpene 19-deacetylconyzalactone **(2)**

INTRODUCTION

Conyza blinii Lévl. (Compositae) is distributed in southwest districts of China. Its aerial parts are used in traditional Chinese medicine for the treatment of chronic bronchitis and other inflammatory diseases [1]. Preliminary pharmacological and clinical tests showed that it possessed expectorant, antitussive, antiinflammatory, antiulcer and antibacterial effects [2]. In order to shed light on the chemical entity responsible for its medical actions, we conducted a detailed chemical investigation on the title plant. Our previous papers reported the isolation of a new diterpenoid named conyzalactone and 9 known compounds [2–4]. The present paper

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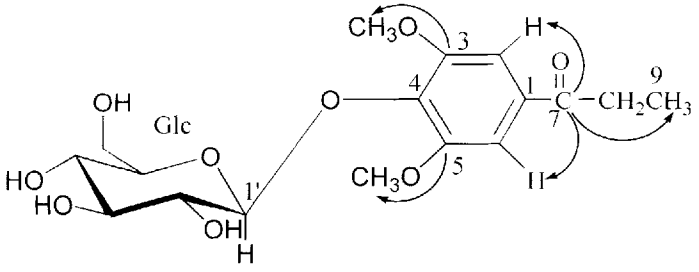
deals with the isolation and characterization of a new phenolic glycoside and a new *trans*-clerodane diterpene from the aerial parts of this plant.

RESULTS AND DISCUSSION

The ethanol–water extracts of air-dried aerial parts of *Conyza blinii* afforded a new compound **1** as colorless needles (recrystallized from methanol) with mp 173–174°C. A molecular formula $C_{17}H_{24}O_9$ was determined from its FAB-MS ($[M+Na]^+$, m/z 395) and NMR spectra. The IR spectrum of **1** showed the presence of benzene ring by its skeleton vibration at 1584 cm^{-1}, 1497 cm^{-1}, 1459 cm^{-1}. The aromatic carbon signals at δ 153.4, 132.7, 123.1 and 106.9 ppm in the ^{13}CNMR spectrum of **1** and the corresponding aromatic hydrogen signal at 7.41 ppm (*s*, 2H) in the ^{1}HNMR spectrum of **1** confirmed the presence of benzene ring and also indicated the high symmetry of the molecule. The presence of one propionyl group in **1** was proved by the signals at δ 199.2, 31.6, 8.6 in ^{13}CNMR spectrum and the signals at δ 2.9 (*q*, 2H), 1.2 (*t*, 3H) in ^{1}HNMR spectrum. Chemical shifts at δ 56.6 in ^{13}CNMR spectrum and δ 3.8 (*s*, 6H) in ^{1}HNMR spectrum were attributed to two methoxy groups. By comparing the ^{13}C, ^{1}HNMR spectral data of **1** with the literature [5], the sugar moiety was determined as β-D-glucopyranose. The correlation peaks between C-3, 5 and protons of OCH_3, C-7 and two aromatic protons, C-4 and the anomeric proton in the HMBC spectra of **1** confirmed the above elucidation. Therefore the structure of **1** was finally determined as 4-propionyl-2,6-dimethoxyphenyl β-D-glucopyranoside **(1)**.



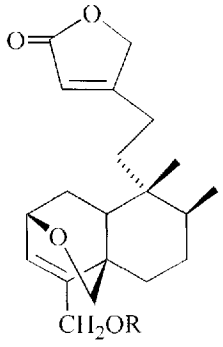
Compound **2** was obtained as colorless needles (acetone). A $[M-1]^+$ ion peak at m/z 331 ($C_{20}H_{28}O_4$, MWt: 332) in EIMS was found for compound

2. IR spectrum of **2** showed the presence of hydroxyl and ester carbonyl functional groups (ν_{max}3432 and 1728 cm^{-1}). The two tertiary methyl carbon signals at δ 15.2 and 16.2, four oxygenated carbon signals at δ 60.5, 66.6, 67.5, 73.0, two olefinic carbon signals at δ 124.8, 151.5 and two olefinic carbon accounting for the butenolide coupled with the ^{1}H information (one methyl proton doublet at δ 0.86, one methyl proton singlet at δ 1.02, five oxygenated carbon bonded proton signals at δ 2.83, 4.09, 4.24, 4.47, 4.72, and two olefinic proton signals at δ 5.81, 6.27) suggested **2** to be a clerodane type diterpenoid with β-substituted butenolide ring in the side chain. The spectral features of **2** were very similar with conyzalactone **(3)** which was isolated from the title plant by the same research group [4]. Detailed comparison of the ^{13}C, ^{1}HNMR spectra of **2** with those of conyzalactone revealed the absence of acetyl group in compound **2** by the lack of acetyl methyl proton signal at δ 2.10 in ^{1}HNMR spectrum and acetyl carbon signals at δ 20.9 and 170.4 in the ^{13}CNMR spectrum. The shift changes of H-19 and C-3, C-4, C-5, C-19 of **2** confirmed that 19-C of **2** was substituted by a hydroxyl group instead of an acetyl group (see Tab. I). On the

TABLE I ^{1}H, ^{13}CNMR spectral data of 19-deacetylconyzalactone **2** and conyzalactone **3** in $CDCl_3$

	2		**3**	
	^{13}C	^1H	^{13}C	^1H
1	29.0		28.9	
2	66.6	4.47 m	66.5	4.47 m
3	124.8	6.27d(5.5 Hz)	127.9	6.31d(5.5 Hz)
4	151.5		146.3	
5	36.5		39.1	
6	27.0		27.4	
7	26.6		26.7	
8	38.3		37.7	
9	38.9		39.0	
10	38.9		38.5	
11	36.2		36.4	
12	22.2		22.3	
13	170.8		170.5	
14	114.9	5.81 brs	115.2	5.82 brs
15	174.0		173.8	
16	73.0	4.72 brs	72.9	4.72 brs
17	15.5	0.86d(5.0 Hz, 3H)	15.6	0.87d(5.5 Hz, 3H)
18	67.5	2.83 βd(8.0 Hz), 4.10 αd(8.0 Hz)	67.6	2.87 βd(8.0 Hz), 4.11 αd(8.0 Hz)
19	60.5	4.24 brs(2H)	61.8	4.68 brs(2H)
20	16.2	1.02 s(3H)	16.3	1.02 s(3H)
CH_3CO			170.4	
CH_3CO			20.9	2.10 s(3H)

basis of the above mentioned evidence, Compound **2** was determined as 19-deacetylconyzalactone.



2 R=H
3 R=CH_3CO

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were determined on a XT4A micro-melting point apparatus and are uncorrected. The IR spectra were recorded on a Perkin-Elmer IR spectrometer. NMR spectra were measured on Varian INOVA 500(500 MHz for ^{1}H and 125 MHz for ^{13}C) spectrometer using TMS as internal standard.

Plant Material

The aerial parts of *Conyza blinii* were collected from Sichuan province in 1996 and the voucher specimen No. 960818 was deposited at the Herbarium of the school of Pharmaceutical Sciences, Beijing Medical University.

Extraction and Isolation

The air dried powdered *C. blinii* (20 kg) was refluxed with 95% ethanol twice and then with 60% ethanol once. The 95% ethanol extract was subjected to silica gel column chromatography and eluted in turn with petroleum ether, chloroform, ethyl acetate and methanol. The methanol eluate and the 60%

ethanol extract was treated with acetone supersonically, then the insoluble parts were combined and exposed to D101 resin column eluting gradiently with ethanol–water. The 30% ethanol eluate (98 g) was chromatographed on silica gel, eluting with EtOAc-EtOH-H_2O. The fractions 28–30 were pooled and rechromatographed over silica gel eluting with $CHCl_3$-MeOH-H_2O(8.5 : 1.5 : 0.2) and fraction 8 was recrystallized in acetone to give compound **1** (10 mg). The 50% ethanol eluate (220 g) was chromatographed on silica gel, eluting with $CHCl_3$-MeOH-H_2O and the fraction 5 was rechromatographed over silica gel eluting with petroleum ether–acetone twice to get compound **2** (30 mg).

Compound **1**, colorless needles, m.p. 173–174°C, IR(KBr) ν_{max} 3394 (OH), 2919, 1672(C=O), 1584, 1497, 1459(C=C), 1410, 1130, 802(=CH); ^{1}HNMR(500 MHz, C_5D_5N)δ ppm: 7.41(2H, *s*, 2,6-H), 6.10(1H, *d*, J = 7.5 Hz, glu 1-H), 4.00–4.03, 4.31–4.45 (other protons of glucose), 3.76(6H, *s*, 2 × OCH_3), 2.88(2H, *q*, J = 7.5 Hz, —CH_2—), 1.17(3H, *t*, J = 7.5 Hz, —CH_3); ^{13}CNMR(125 MHz, C_5D_5N)δ ppm: 123.1(C-2), 106.9(C-2, 6), 153.4(C-3, 5), 123.1(C-4), 199.2(C-7), 31.6(C-8), 8.6(C-9), 56.6(OCH_3), 104.0(C-1′), 76.0(C-2′), 79.1(C-3′), 71.6(C-4′), 78.5(C-5′), 62.6(C-6′); FABMS m/z 395(M + Na), 211(M-glu + 1).

Compound **2**, colorless needles, m.p. 103–104°C, IR (KBr) ν_{max}: 3432, 2948, 2921, 2868, 1728, 1629, 1451, 1178, 1127, 1030. ^{1}H, ^{13}CNMR, see Table I. EIMS m/z(%) 331 $[M-1]^+$(27), 314 $[M-H_2O]^+$(9), 301(32), 284(96), 99(100).

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