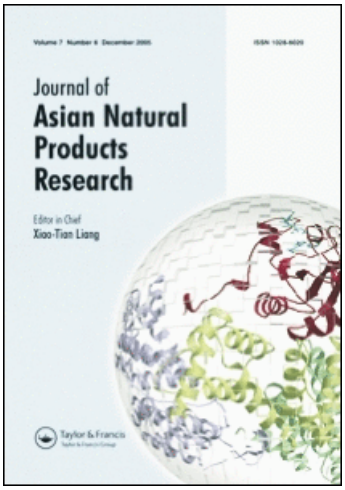

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TWO NEW COMPOUNDS FROM *PEUCEDANUM DECURSIVUM*

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Two new compounds, decuroside VI (**1**) and decursidate (**2**), were isolated from the roots of *Peucedanum decursivum*. Their structures were elucidated as 6′-O-crotonyl-nodakenin and 2-[4′-hydroxyphenyl]-glycol mono *trans*-ferulate on the basis of spectral analyses and chemical methods.

Keywords: *Peucedanum decursivum*; 6′-O-crotonyl-nodakenin; 2-[4′-hydroxyphenyl]-glycol mono *trans*-ferulate

INTRODUCTION

The roots of *Peucedanum decursivum* (Miq.) Maxim and *P. praeruptorum* Dunn are traditional Chinese medicines widely used for the treatment of diseases such as cough due to "pathogenic wind-heat, accumulation of phlegm and heat in the lung". The former contains xanthyletin-type coumarins [1] and coumarin-glycosides [2], and the latter contains seselin-type coumarins [3]. This paper describes the isolation and structural elucidation of two new compounds, named decuroside VI (**1**) and decursidate (**2**), from the roots of *Peucedanum decursivum*.

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RESULTS AND DISCUSSION

Compound **1** was isolated as light, yellow powder. The molecular formula was assigned as $C_{24}H_{28}O_{10}$ on the basis of its HRFAB-MS at $(M-H)^-$ *m/z* 475.1594 (calcd. 475.1604 for $C_{24}H_{27}O_{10}$). The UV spectrum showed absorptions at 203 and 334 nm. The IR absorption bands at 3388, 1712, 1626 and 1566 cm^{-1} were attributed to hydroxy, carbonyl and aromatic moiety of coumarin skeleton, respectively. The ^1H NMR spectrum in the aromatic proton region of **1** contained a pair of doublets at δ 6.14 (1H, *d*, $J = 9.5$ Hz), 7.84 (1H, *d*, $J = 9.5$ Hz) and two singlets at δ 7.40 (1H, *s*), 6.65 (1H, *s*), which were attributed to C_3—H, C_4—H of the α-pyrone ring moiety and C_5—H, C_8—H of the benzene part. The above spectral evidence indicated **1** to be a coumarin substituted at C-6 and C-7 positions. Two methyl singlets at δ 1.20 and 1.37 demonstrated the presence of a hydroxy isopropyl. A characteristic signal at δ 4.91 (1H, *t*, $J = 8.0$ Hz) was assigned to the methine proton at C-2′, attached to a hydroxy isopropyl group. Therefore, **1** must be a linear furocoumarin. The ^{13}C NMR signal pattern (see Tab. I) and the anomeric proton of the sugar at δ 4.60 (1H, *d*, $J = 7.7$ Hz) showed that **1** contained a β-D-glucose, attached to the isopropyl hydroxy group of **1**. On acid hydrolysis, **1** afforded nodakenetin as an aglycone and D-glucose, which confirmed its composition and linkage. The ^1H NMR spectrum showed the signals of one methyl proton at δ 1.72 (3H, *dd*, $J = 7.0$, 2.0 Hz), two olefinic protons at δ 5.77 (1H, *dd*, $J =$ 15.5, 2.0 Hz) and 6.88 (1H, *dd*, $J = 15.5$, 7.0 Hz), which suggested the presence of 2-*trans* butenoyl moiety. By comparison with the ^{13}C NMR data of nodakenin [2] (see Tab. I), the downfield shift of 3.3 ppm at C-6 of D-glucose suggested that crotonyl was linked to C-6 of D-glucose. Thus, the structure of decuroside VI was established as 6′-crotonyl-nodakenin.

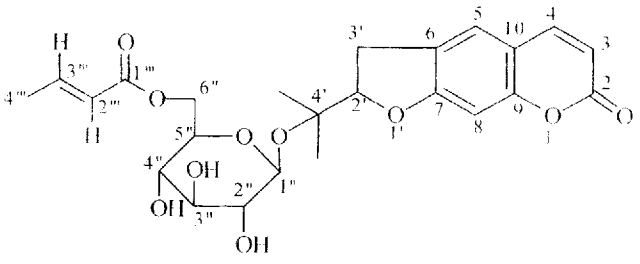
Compound **2** was isolated as light, yellow powder. The molecular formula was assigned as $C_{18}H_{18}O_6$ on the basis of its HREI-MS at *m/z* 330.1106 (calcd. 330.1108 for $C_{18}H_{18}O_6$). The UV spectrum showed absorption maximum at 325 nm. The IR absorption bands at 3378, and 1688 cm^{-1} were attributed to hydroxy and carbonyl groups, respectively. The ^1H NMR and ^1H-^1H COSY spectra of **2** revealed an aromatic ABX and an AA′BB′ system. The former was located at δ 6.87 (1H, *d*, $J = 8.3$ Hz), 7.13 (1H, *dd*, $J = 8.3$, 2.0 Hz) and 7.30 (1H, *d*, $J = 2.0$ Hz), which indicated the presence of 1,2,4-trisubstituded aromatic ring. The latter was located at δ 7.25 (2H, *d*, $J = 8.0$ Hz) and 6.81 (2H, *d*, $J = 8.0$ Hz), which indicated the presence of para-disubstituded aromatic ring. A pair of doublets at δ 7.63 (1H, *d*, $J = 16$ Hz) and 6.40 (1H, *d*, $J = 16$ Hz) were assigned to two olefinic protons

TABLE I ^{1}H and ^{13}C NMR spectral data comparison between compound **1** and nodakenin

	1		*Nodakenin*	
Position	H^a	C^a	H^b	C^b
Aglycone				
2		161.5		160.3
3	6.14 (1H, *d*, $J=9.5$ Hz)	112.4	6.24 (1H, *d*, $J=9.5$ Hz)	111.2
4	7.84 (1H, *d*, $J=9.5$ Hz)	145.7	7.92 (1H, *d*, $J=9.5$ Hz)	144.4
5	7.40 (1H, *s*)	124.8	7.52 (1H, *s*)	123.8
6		126.4		125.4
7		164.3		162.9
8	6.65 (1H, *s*)	97.7	6.80 (1H, *s*)	96.7
9		156.4		154.9
10		113.5		112.2
2′	4.91 (1H, *t*, $J=8.0$ Hz)	90.9	4.97 (1H, *t*, $J=8.0$ Hz)	89.7
3′	Overlap	29.7	Overlap	29.0
4′		78.5		77.0
Gem$(CH_3)_2$	1.20 (3H, *s*)	21.3	1.17 (3H, *s*)	20.6
	1.37 (3H, *s*)	23.7	1.35 (3H, *s*)	23.2
Glucose				
1″	4.60 (1H, *d*, $J=7.7$ Hz)	98.2	4.50 (1H, *d*, $J=7.5$ Hz)	97.1
2″	Overlap	74.5	Overlap	73.4
3″	Overlap	77.7	Overlap	76.6
4″	Overlap	71.6	Overlap	70.3
5″	Overlap	74.6	Overlap	76.6
6″	Overlap	64.5	Overlap	61.2
1‴		166.6		
2‴	5.77 (1H, *dd*, $J=15.5$, 2.0 Hz)	123.1		
3‴	6.88 (1H, *dd*, $J=15.5$, 7.0 Hz)	145.7		
4‴	1.72 (3H, *dd*, $J=7.0$, 2.0 Hz)	17.9		

[a] In $(CD_3)_2CO$.
[b] In DMSO-d_6.

of *trans* double bond. Aliphatic signals at δ 4.91 (1H, *dd*, $J=7.0$, 5.0 Hz) and 4.21 (2H, *m*) were ascribable to an ABX system, whose chemical shifts and coupling pattern indicated the presence of a —CH(OH)CH_2O— subunit. The HMBC spectrum showed that the olefinic proton at δ H 7.63 correlated with δ C 111.4, 123.9 (aromatic carbon) and 167.7 (carbonyl) (Fig. 2). In NOESY spectrum, the aromatic proton at δ H 7.30 (1H, *d*, $J=2.0$ Hz) correlated with methoxyl proton at δ H 3.90 (3H, *s*) (Fig. 3), which in turn correlated with δ C 148.8 (aromatic carbon) in HMBC spectrum, the above spectral evidence suggested the presence of *trans*-feruloyl. The HMBC spectrum showed that the methine proton at δ H 4.91 correlated with aromatic carbon at δ C 133.2 and 128.3, the methylene protons at δ H 4.21 correlated with carbonyl carbon at δ C 167.7 (Fig. 2), these $^{1}H-^{13}C$ long range correlations suggested the presence of 4′-hydroxyphenyl glycol esterified with *trans*-feruloyl. Therefore, the chemical



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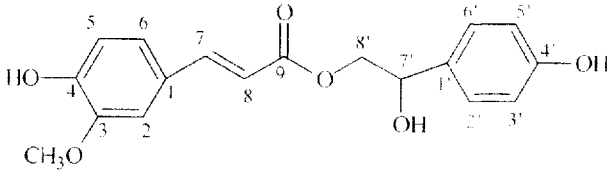

2

FIGURE 1 Structures of decuroside VI (1) and decursidate (**2**).

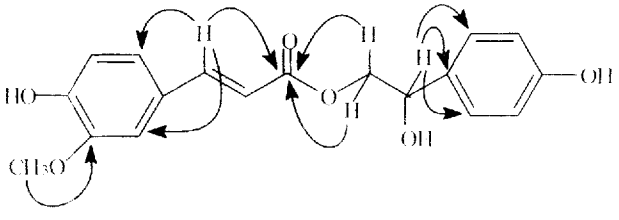

FIGURE 2 Major correlations in HMBC spectrum of **2**.

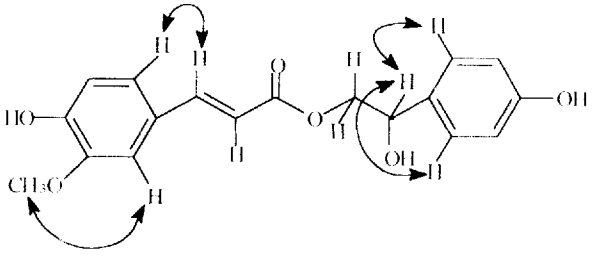

FIGURE 3 Major correlations in NOESY spectrum of **2**.

structure of decursidate (**2**) was finally elucidated as 2-[4′-hydroxyphenyl]-glycol mono *trans*-ferulate. The stereochemistry of C-7′ remains to be clarified.

Experimental Section

General Experimental Procedures

Mps were determined on a *X*4 micromelting point apparatus and are uncorrected. Optical rotations were measured on a PE-241 MC polarimeter. UV spectra were recorded on an UV-2051 spectrophotometer in MeOH. IR spectra were recorded on an Impact-410 (Nicolet) spectrograph. 1D NMR and 2D NMR spectra were recorded on Bruker DRX 400 and JEOL-600 MHz spectrometers, using TMS as internal standard. EIMS were measured on JMS-D300 mass spectrometer. FABMS were measured on JEOL JMS-HX 110/110 A. Preparative HPLC was carried out on a Shimadzu Liquid Chromatograph LC-8A equipped with a UV detector using Shim - pack PREP-ODS 20.0 mm ID × 25 cm P/N 228-00815-91 column.

Plant Material

Roots of *P. decursivum* (Miq.) Maxim were collected in the Laoshan Mountain, Jiangsu Province, China, in November, 1996, and identified by Doctor Zhu-Nan Gong. A voucher specimen has been deposited in the Department of Natural Medicinal Chemistry, China Pharmaceutical University.

Extraction and Isolation

Powdered roots (3.29 kg) were refluxed with 95% EtOH. The ethanolic extract was suspended in water and successively extracted with petroleum benzene, ethyl acetate and *n*-butanol. The solvent was removed from the ethyl acetate fraction and the gummy residue was chromatographed over silica gel (100–200 mesh) and eluted with mixtures of chloroform–methanol of gradually increasing polarity to yield three fractions (I–III). The fraction I was further purified by Sephadex LH-20 with the elution of methanol to give compound **2** (17 mg). The fraction III was further separated by HPLC (65% MeOH in H_2O, 10 ml/min, UV detector, 320 nm) to give compound **1** (30 mg).

Decuroside VI (1)

Light yellow powder, UV λ_{max}^{MeOH}: 334.8, 203.4 nm; IR ν_{max}: 3388, 1712, 1626, 1566, 1487, 1446, 1398, 1263, 1128, 1035, 994, 968, 829 cm^{-1}; ^1H NMR (400 MHz, $(CD_3)_2CO$) see Table I, and ^{13}C NMR (100 MHz, $(CD_3)_2CO$) see Table I; FABMS *m/z* 475 $[M-H]^-$ (21), 269 (18), 227 (92), 187 (34), 127 (25), 85 (100); HRFAB-MS $[M-H]^-$ *m/z* obs. 475.1594, calcd. 475.1604 for $C_{24}H_{27}O_{10}$.

Acid Hydrolysis of Decuroside VI (1)

Compound **1** (20 mg) was heated in 5 ml 1 N H_2SO_4 at 70°C for 1 h in a water bath. After cooling, the reaction mixture was extracted with $CHCl_3$. The aqueous supernatant was neutralized with $NaHCO_3$, and concentrated *in vacuo*. The residue was identified to be D-glucose by CO-PC analysis with standard D-glucose (developing solvent: *n*-BuOH : EtOAc : H_2O 7 : 3 : 3, color reagent: aniline-phthalic acid reagents). The $CHCl_3$ layer was washed subsequently with 10% $NaHCO_3$ and water, and dried with Na_2SO_4. The extract was concentrated in water bath. The residue was recrystallized from MeOH as colorless needles which was identified to be nodakenetin (**3**) by comparison with the spectral data of nodakenetin in literature [4].

Nodakenetin (3)

Colorless needles, m.p.: 183–184°C; $[\alpha]_D^{23} = -19.4°$ ($CHCl_3$); UV λ_{max}^{MeOH}: 335.0, 224.6, 207.2 nm; IR ν_{max} 3462, 1708, 1629, 1570, 1491, 1446, 1360, 1267, 1128, 960, 893, 829, 792, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 6.18 (1H, *d*, $J = 9.5$ Hz, H-3), 7.58 (1H, *d*, $J = 9.5$ Hz, H-4), 7.21 (1H, *s*, H-5), 6.69 (1H, *s*, H-8), 4.74 (1H, *t*, $J = 8.5$ Hz, H-2′), 3.21 (2H, *m*, H-3′), 1.24 (3H, *s*, C-4′ $-CH_3$), 1.37 (3H, *s*, C-4′ $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.5 (C-2), 112.1 (C-3), 143.7 (C-4), 123.4 (C-5), 125.1 (C-6), 163.2 (C-7), 97.8 (C-8), 155.5 (C-9), 112.7 (C-10), 91.1 (C-2′), 29.4 (C-3′), 71.6 (C-4′), 24.3 (C-4′ $-CH_3$), 26.0 (C-4′ $-CH_3$).

Decursidate (2)

Light yellow powder, UV λ_{max}^{MeOH}: 325.8, 220.0 nm; IR ν_{max}: 3378, 2922, 1688, 1626, 1295, 1514, 1449, 1431, 1380, 1265, 1163, 1030, 754 cm^{-1}; ^1H NMR (400 MHz, $(CD_3)_2CO$) see Table II, and ^{13}C NMR (100 MHz, $(CD_3)_2CO$) see Table II; EIMS *m/z*: 330 (M^+) (2.9), 312 (2.1), 194 (100), 177

TABLE II ^{1}H and ^{13}C NMR spectral data of compound **2***

Position	*δH*	*δC*
1		127.2
2	7.30 (1H, *d*, *J* = 2.0 Hz)	111.4
3		148.8
4		150.1
5	6.87 (1H, *d*, *J* = 8.3 Hz)	116.1
6	7.13 (1H, *dd*, *J* = 8.3, 2.0 Hz)	123.9
7	7.63 (1H, *d*, *J* = 16.0 Hz)	146.0
8	6.40 (1H, *d*, *J* = 16.0 Hz)	115.5
9		167.7
1′		133.2
2′ or 6′	7.25 (2H, *d*, *J* = 8.0 Hz)	128.3
3′ or 5′	6.81 (2H, *d*, *J* = 8.0 Hz)	115.8
4′		157.7
7′	4.91 (1H, *dd*, *J* = 7.0, 5.0 Hz)	71.8
8′	4.21 (2H, *m*)	69.9
CH_3O	3.90 (3H, *s*)	56.3

* The signals of ^{1}H and ^{13}C were assigned by ^{1}H-^{1}H COSY, HMQC and HMBC spectra.

(49.4), 167 (8.6), 161 (6.0), 153 (1.4), 137 (8.0), 136 (31.3), 133 (21.6), 123 (48.3), 107 (44.5), 77 (23.4), 72 (14.1), 55 (10.0), 51 (13.0); HREI-MS at *m/z*: 330.1106, calcd. 330.1108 for $C_{18}H_{18}O_6$.

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