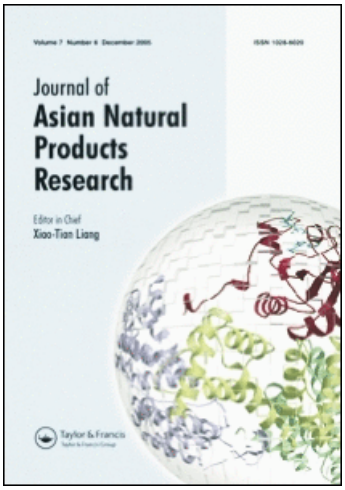

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Note

TWO COMPOUNDS FROM *PEUCEDANUM DISSOLUTUM*

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A new compound, 3′(*R*)-*O*-β-D-glucopyranosyl-3′,4′-dihydroxanthyletin (**1**), and a known compound, prim-O-glucosylcimifugin (**2**), were isolated from the roots of *Peucedanum dissolutum*. The structure of **1** was elucidated by spectral evidence and chemical reaction. The NMR signals of carbons and protons of **2** were assigned for the first time by analysis of $^{1}H-^{1}H$ COSY, HMQC and HMBC spectra.

Keywords: *Peucedanum dissolutum*; 3′(*R*)-*O*-β-D-Glucopyranosyl-3′,4′-dihydroxanthyletin; Prim-O-glucosyl-cimifugin

INTRODUCTION

Peucedanum dissolutum is a plant of Umbelliferae. In some areas of China the root of some plants of the *Peucedanum* genus, including *Peucedanum dissolutum*, have been used as Qianhu, a traditional Chinese medicine to cure diseases such as cough due to "pathogenic wind-heat, accumulation of phlegm and heat in the lung". So far there are no reports about the chemistry of the title plant. We have studied the chemical constituents of *Peucedanum dissolutum*. A new coumarin, along with a known chromone, was isolated and the structure of the new coumarin was elucidated as 3′(*R*)-*O*-β-D-glucopyranosyl-3′,4′-dihydroxanthyletin by spectral analysis. The absolute configuration was deduced by chemical correlation with a known compound. This paper describes the isolation and structural elucidation of the two compounds.

RESULTS AND DISCUSSION

Compound **1** was obtained as colorless needles. The quasi-molecular ion peak $[M + 1]^+$ at *m/z* 409.1518 in the high-resolution FAB mass spectrum indicated the molecular formula to

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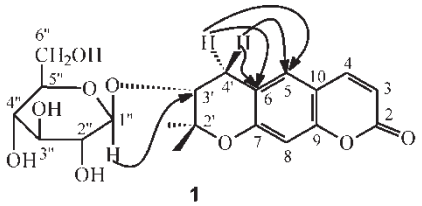
be $C_{20}H_{24}O_9$. The signals at 1705, 1622 cm^{-1} in the IR spectrum were assigned to carbonyl and the aromatic system of a coumarin skeleton respectively. The ^1H NMR spectrum in the aromatic proton region of **1** revealed a pair of doublets at δ 6.45 (1H, d, $J = 9.5$ Hz), 8.05 (1H, d, $J = 9.5$ Hz) and a pair of singlets at δ 7.64 (1H, s), 7.34 (1H, s), which were attributed to the C_3-H, C_4-H signals of the α-pyrone ring system and the signals of C_5-H, C_8-H of the benzene ring, indicating **1** to be a coumarin substituted at C-6 and C-7. In the ^1H NMR spectrum, the proton signals at δ 3.75 (1H, dd, $J = 9.9$, 3.2 Hz, H-3′) and at δ 2.52 (1H, dd, $J = 13.6$, 9.9 Hz, H-4′), 3.61 (1H, dd, $J = 13.6$, 3.2 Hz, H-4′) indicated that the substituted moiety between C-6 and C-7 formed a dihydropyran ring, and comparison with chemical shifts and the coupling pattern of the skeleton of smyrinol showed an attached group at C-3′ [1]. In the HMQC spectrum (Fig. 1), the two proton signals at δ 2.52, 3.61 were correlated with the carbon signal at δ 33.54, showing no substituted group at C-4′; the same signals at δ 2.52, 3.61 were also correlated with the carbon signals at δ 131.51 (C-5) and 129.11 (C-6) in HMBC spectrum, confirming the above conclusion. The Molish reaction of **1** was positive and paper chromatography showed the existence of glucose. The signals at δ 102.84, 75.07, 78.63, 71.58, 77.93 and 62.71 in the ^{13}C NMR spectrum were due to a glucose group. In the HMBC spectrum, the proton signal at δ 5.16 (glc-H-1) was correlated with the carbon signal at δ 79.33 (C-3′). This evidence indicates that the glucose is attached to C-3′.

To determine the absolute configuration of C-3′, a chemical correlation with a known compound was carried out. On acid hydrolysis, **1** gave a product that was identified as 3′(*R*)-hydroxy-3′,4′-dihydroxanthyletin (**3**) by comparison of its spectral data and optical rotation with those reported in the literature [2]; accordingly, the absolute configuration of C-3′ in **1** was also established as *R* (Fig. 2). The chemical structure of **1** was finally elucidated as 3′(*R*)-*O*-β-D-glucopyranosyl-3′,4′-dihydroxanthyletin. The signals in the ^1H and ^{13}C NMR spectra were assigned by HMQC and HMBC spectra and are listed in the experimental section.

Compound **2** was isolated as a yellow oil, and gave a positive Molish reaction. ESI-MS gave a quasi-molecular ion peak at *m/z* 469. Combining the data of ^1H, ^{13}C NMR and



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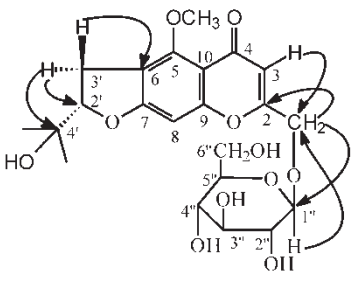

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FIGURE 1 Structures and key HMBC correlations of **1** and **2**.

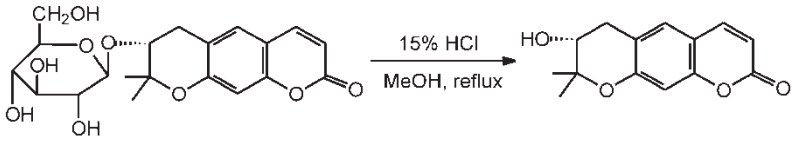

FIGURE 2 Acid hydrolysis of **1**.

DEPT spectra, the molecular formula *M/Z* **2** was elucidated as $C_{22}H_{28}O_{11}$. The ^{1}H and ^{13}C NMR spectra showed the characteristics of chromone. The DEPT spectrum showed three methyls, three methylenes, eight methines and eight quaternary carbons. The correlations in $^{1}H—^{1}H$ COSY, HMQC and HMBC spectra indicated that the C-6 and C-7 positions of chromone formed part of a dihydrofuran ring whose C-2′ was attached to an isopropanol group, C-5 linked with a methyloxy group, and C-2 linked with a hydroxymethyl group that was attached to a glucose. The structure of **2** was identical with prim-O-glucosylcimifugin reported in the literature [3]. However, there are some wrong assignments of proton and carbon signals in the literature, and we have reassigned the proton and carbon signals of **2** by $^{1}H–^{1}H$ COSY, HMQC and HMBC spectra as listed in the Experimental section.

EXPERIMENTAL

General Experimental Procedures

Mps were determined on an X-4 micro melting-point apparatus, and uncorrected. UV spectra were recorded on a Shimadzu UV-2501 PC spectrophotometer in MeOH solution. IR spectra were obtained on a Nicolet Impact-410 spectrometer. 1D and 2D NMR spectra were recorded on a Bruker-DRX-400 spectrometer using TMS as internal standard. FABMS were measured on a MAT 212 mass spectrometer. ESIMS were taken on a PE-Mariner AFI-TOF mass spectrometer. Optical rotations were determined on a Perkin-Elmer 241 automatic polarimeter at 20°C. Silica gel H (10–40 μm) was used for column chromatography.

Plant Material

Roots of *Peucedanum dissolutum* were collected in Chongqing city, China, in November 1998, and identified by Professor Xianqi Liu, Nanchuan Institute of Materia Medica in Chongqing, China. A voucher specimen (No 981103) has been deposited in the Department of Natural Medicinal Chemistry, China Pharmaceutical University.

Extraction and Isolation

The dried root (1.31 kg) was extracted 3 × with 95% ethanol (3 L) at 80°C. After filtration and evaporation, the residue (156 g) was dissolved in water (1.5 L) and the solution was extracted 3 × with light petroleum (60–90°C, 1.5 L), EtOAc (1.5 L) and n-BuOH (1.5 L), respectively. The EtOAc extract (67 g) was subjected to column chromatography on silica gel (350 g) eluted with a mixture of $CHCl_3$ and MeOH of increasing polarity (each Fr. 300 ml). After evaporation of Frs. 15–28, eluted with $CHCl_3$–MeOH (90:10), the residue (2.6 g) was further separated by silica gel CC (100 g) eluted with $CHCl_3$–MeOH, and compound **1**

(23 mg) was obtained from the elution of $CHCl_3$–MeOH (92:8) and **2** (39 mg) was obtained from the elution of $CHCl_3$–MeOH (88:12).

3′(R)-O-β-D-Glucopyranosyl-3′,4′-dihydroxanthyletin (1)

Colorless cubic crystals, mp 206–207°C, $[\alpha]_D$ −3.1 (*c* 0.5, $CHCl_3$). UV λ_{max} (nm): 393.0, 325.5, 293.0; IR ν_{max} (cm^{-1}): 3490, 3371, 1705, 1622, 1269, 1117, 1054, 856; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.45 (1H, d, $J = 9.5$ Hz, H-3), 8.05 (1H, d, $J = 9.5$ Hz, H-4), 7.64 (1H, s, H-5), 7.34 (1H, s, H-8), 3.75 (1H, dd, $J = 9.9$, 3.2 Hz, H-3′), 2.52 (1H, dd, $J = 13.6$, 9.9 Hz, H-4′), 3.61 (1H, dd, $J = 13.6$, 3.2 Hz, H-4′), 1.45 (3H, s, C-2′-CH_3), 1.43 (3H, s, C-2′-CH_3), 5.16 (1H, d, $J = 7.4$ Hz, H-1″), 3.93–3.69 (4H, m, H-2″-H-5″), 4.14 (1H, m, H-6″), 3.93 (1H, m, H-6″); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.79 (C-2), 114.35 (C-3), 146.10 (C-4), 131.51 (C-5), 129.11 (C-6), 160.32 (C-7), 104.07 (C-8), 155.68 (C-9), 114.98 (C-10), 74.53 (C-2′), 79.33 (C-3′), 33.54 (C-4′), 27.55 (C-2′-CH_3), 23.67 (C-2′-CH_3), 102.84 (C-1″), 75.07 (C-2″), 78.63 (C-3″), 71.58 (C-4″), 77.93 (C-5″), 62.71 (C-6″); HR-FABMS *m/z*: 409.1518 ($C_{20}H_{24}O_9$ calcd 409.1499 for $[M + H]^+$).

Acid Hydrolysis of 3′(R)-O-β-D-Glucopyranosyl-3′,4′-dihydroxanthyletin (1)

Compound **1** (10 mg) dissolved in MeOH (3.0 mL) was added to 15% HCl (1.5 mL) and the reaction mixture refluxed for 1 h. The solution was then neutralized with 10% NaOH, and extracted with $CHCl_3$. The glucose in the water layer was identified by paper chromatography. The $CHCl_3$ layer was dried with Na_2SO_4, and evaporated, and the residue was purified with preparative TLC, developed with light petroleum–EtOAc (3:1) to give 3′(*R*)-hydroxy-3′,4′-dihydroxanthyletin (**3**, 5 mg).

3′(R)-Hydroxy-3′,4′-dihydroxanthyletin (3)

White cubic crystals, mp 176.0–178.0°C, $[\alpha]_D$ −13.9 ($CHCl_3$, *c* 0.05), literature [2]: −11.0 ($CHCl_3$). IR ν_{max} (cm^{-1}): 3384, 2975, 1706, 1628, 1575, 1386, 1145, 815; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.19 (1H, d, $J = 9.4$ Hz, H-3), 7.91 (1H, d, $J = 9.4$ Hz, H-4), 7.44 (1H, s, H-5), 6.72 (1H, s, H-8), 3.48 (1H, dd, $J = 10.2$, 2.0 Hz, H-3′), 2.97 (1H, dd, $J = 13.7$, 2.0 Hz, H-4′), 2.34 (1H, dd, $J = 13.7$, 10.2 Hz, H-4′), 1.15 (3H, s, C-2′-CH_3), 1.12 (3H, s, C-2′-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.65 (C-2), 111.18 (C-3), 144.73 (C-4), 130.34 (C-5), 125.11 (C-6), 159.51 (C-7), 101.55 (C-8), 153.65 (C-9), 110.92 (C-10), 76.74 (C-2′), 71.77 (C-3′), 31.34 (C-4′), 26.28 (C-2′-CH_3), 24.71 (C-2′-CH_3).

Prim-O-glucosylcimifugin (2)

Yellow oil, $[\alpha]_D$ +6.3 (*c* 0.6, $CHCl_3$). UV λ_{max} (nm): 293.0, 214.0; IR ν_{max} (cm^{-1}): 3353, 2924, 2853, 1731, 1657, 1608, 1461, 1382, 1115; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 6.56 (1H, s, H-3), 6.79 (1H, s, H-8), 4.96 (1H, m, H-2′), 3.52 (2H, m, H-3′), 1.48 (3H, s, C-4′-CH_3), 1.43 (3H, s, C-4′-CH_3), 4.12 (3H, s, OCH_3), 4.79 (1H, d, $J = 15.0$ Hz, —CH_2—), 4.95 (1H, d, $J = 15.0$ Hz, —CH_2—), 4.62 (1H, d, $J = 7.6$ Hz, H-1″), 3.48–3.59 (4H, m, H-2″–H-5″), 4.07 (1H, m, H-6″), 3.87 (1H, m, H-6″); ^{13}C NMR (100 MHz, CD_3OD): δ (ppm): 165.31 (C-2), 111.27 (C-3), 179.91 (C-4), 157.25 (C-5), 118.70 (C-6), 167.39 (C-7), 94.88 (C-8), 161.39 (C-9), 112.64 (C-10), 92.89 (C-2′), 29.06 (C-3′), 72.57 (C-4′), 25.68 (C-4′-CH_3), 25.58 (C-4′-CH_3), 61.37 (OCH_3), 67.60 (-CH_2-), 104.30 (C-1″), 75.22 (C-2″), 78.38 (C-3″), 71.78 (C-4″), 78.20 (C-5″), 62.94 (C-6″); ESIMS *m/z*: 469 $[M + H]^+$.

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