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### Chemical constituents of *Selinum cryptotaenium*

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## Note

### Chemical constituents of *Selinum cryptotaenium*

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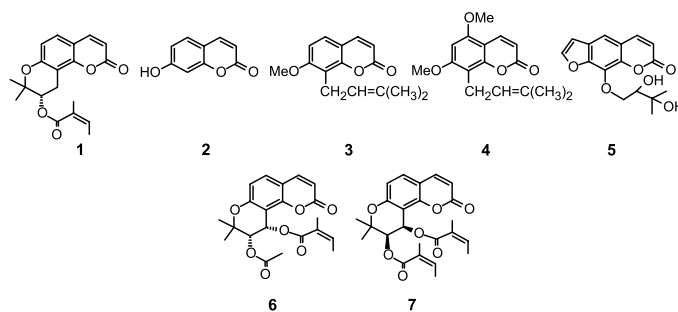
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A new pyranocoumarin, named secriptotaenin A, determined as 3'-(S)-angeloyloxy-3',4'-dihydroseselin, was isolated from the roots of *Selinum cryptotaenium*, along with thirteen known compounds, umbelliferone, osthol, coumurrayin, (+)-heraclenol, longshengensin A, anomalin, ferulic acid, galactitol, stearic acid, melissic acid, lignoceric acid,  $\beta$ -sitosterol and daucosterol. Their structures were determined on the basis of spectroscopic methods.

**Keywords:** *Selinum cryptotaenium*; Umbelliferae; Constituents; Coumarins; Secriptotaenin A

#### 1. Introduction

*Selinum cryptotaenium* de Boiss. (Umbelliferae) is a herb growing in Yunnan Province, China. Its roots have been used as the Chinese traditional drug 'Qian-Hu', which is used for the treatment of many ailments such as cough, bronchitis, asthma and so on [1,2]. However, no phytochemical study has so far been undertaken. In continuation of our studies on Qian-Hu, we investigated the chemical constituents of this plant. As a result, a new pyranocoumarin, named secriptotaenin A (**1**), along with 13 known compounds, umbelliferone (**2**) [3], osthol (**3**) [5], coumurrayin (**4**) [5], (+)-heraclenol (**5**) [4], longshengensin A (**6**) [8], anomalin (**7**) [9], ferulic acid (**8**) [5], galactitol (**9**) [10], stearic acid (**10**) [5], melissic acid (**11**) [5], lignoceric acid (**12**) [3],  $\beta$ -sitosterol (**13**) [5] and daucosterol (**14**) [5], were isolated from this plant for the first time.



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## 2. Results and discussion

Secryptotaenin A (**1**), obtained as colourless glassy mass,  $[\alpha]_{\text{D}}^{28} + 6.2$  (c 0.13,  $\text{CHCl}_3$ ) and  $[\alpha]_{\text{D}}^{17} - 9.2$  (c 0.25, 1,4-dioxane), was found to possess the molecular formula  $\text{C}_{19}\text{H}_{20}\text{O}_5$ , determined by high-resolution electron spray ionisation mass spectra (HRESIMS) and NMR data. The infrared spectrum showed the presence of aromatic ring (1606, 1490 and  $1456\text{ cm}^{-1}$ ),  $\alpha,\beta$ -unsaturated lactone and ester function groups ( $1710\text{--}1730\text{ cm}^{-1}$ ). The UV absorptions at 328, 258 and 240 nm supported the presence of a conjugated lactone and an aromatic ring. These data are characteristic of a coumarin skeleton. The  $^1\text{H}$  NMR spectrum contained two pairs of doublets at  $\delta$  7.67 and 6.17 (each 1H,  $J = 9.5\text{ Hz}$ ), 7.29 and 6.77 (each 1H,  $J = 8.6\text{ Hz}$ ), since the natural coumarins has an oxy-substituent at C-7, these two pairs of doublets are in agreement with the H-4 and H-3 signals of the  $\alpha$ -pyranone ring and *ortho* coupling signals due to H-5 and H-6 on the aromatic ring. It implied that was substituted at C-7 and C-8. Its  $^1\text{H}$  NMR spectrum also exhibited signals at  $\delta$  5.07 (1H, t,  $J = 5.2\text{ Hz}$ ), 3.24 (1H, dd,  $J = 17.8, 5.2\text{ Hz}$ ), 2.95 (1H, dd,  $J = 17.8, 5.2\text{ Hz}$ ), 1.50 and 1.46 (each 3H, s), corresponded to the H-3', H-4'a, H-4'b and 2'-gem  $(\text{CH}_3)_2$  of the dihydropyrone system. The above spectral data indicated that compound **1** was an angular-type dihydropyrano-coumarin with an ester substituent at C-3'. The signals at  $\delta$  6.07 (1H, q,  $J = 7.2\text{ Hz}$ ), 1.90 (3H, d,  $J = 7.2\text{ Hz}$ ) and 1.88 (3H, br.s) suggested that the substituent at C-3' was an angeloyloxy. Therefore, secryptotaenin A (**1**) was elucidated as 3'-angeloyloxy-3',4'-dihydro-seselin. The absolute configuration of C-3' was determined according to the optical rotation which was opposite to that of 3'(*R*)-angeloyloxy-3',4'-dihydro-seselin, namely selinidin, whose rotation value was  $[\alpha]_{\text{D}} -24.0$  ( $\text{CHCl}_3$ ) and  $+20.3$  (1,4-dioxane), as reported by Seshadri and others [6,7]. So secryptotaenin A (**1**) should be the optical isomer of selinidin and determined as 3'(*S*)-angeloyloxy-3',4'-dihydro-seselin.

## 3. Experimental

### 3.1 General experimental procedures

Melting points were uncorrected. Optical rotations were taken on a JASCO-20C polarimeter. UV spectra were obtained on a Shimadzu UV-2401 spectrometer. IR spectra were recorded on a Bio-Rad FTS-135 spectrometer with KBr pellets.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained on a Bruker AM-400 spectrometer with TMS as an internal standard. ESIMS and HRESIMS were recorded on a VG Auto Spec-3000 spectrometer.

### 3.2 Plant material

The roots of *Selinum cryptotaenium* were collected in Songming county, Yunnan Province, China, in October 1996. A voucher specimen (960175), identified by Professor Q.X. Liu, is deposited in the herbarium of Yunnan College of Traditional Chinese Medicine.

### 3.3 Extraction and isolation

Dried and powdered roots (1.7 kg) of *Selinum cryptotaenium* were extracted with 95% EtOH ( $61 \times 3$  times) under reflux. The extract was concentrated under vacuum to afford a brown-red residue (360 g). The residue was dissolved in water, and partitioned with EtOAc ( $0.5 \text{ l} \times 3$  times). The EtOAc extract (brown residue, 85 g) was subjected to silica gel column

chromatography, and eluted with cyclohexane–EtOAc mixture containing an increasing amount of EtOAc (100:5–100:100), to furnish fractions A–C. The fractions were further submitted to repeated column chromatography on silica gel, eluting with cyclohexane–EtOAc (100:10–100:25) and  $\text{CHCl}_3$ –MeOH (100:5–100:20) to afford **1** (72 mg), **2** (140 mg), **3** (170 mg), **4** (25 mg), **5** (1.0 g), **6** (1.22 g), **7** (170 mg), **8** (107 mg), **9** (1.5 g), **10** (70 mg), **11** (25 mg), **12** (146 mg), **13** (121 mg) and **14** (82 mg), respectively.

**3.3.1 Secryptotaenin A (1).**  $\text{C}_{19}\text{H}_{20}\text{O}_5$ , colourless glassy mass,  $[\alpha]_{\text{D}}^{28} + 6.2$  (c 0.13,  $\text{CHCl}_3$ ) and  $[\alpha]_{\text{D}}^{17} - 9.2$  (c 0.25, 1,4-dioxane). UV (EtOH)  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 328 (4.09), 258 (3.49), 240 (3.67). IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 2980, 2930, 1730, 1606, 1490, 1456, 1230, 1150, 1110. ESIMS  $m/z$ : 328  $[\text{M}]^+$ , 228, 213 (100), 83, 55; HRESIMS  $[\text{M} + \text{Na}]^+ m/z$ : 351.1216 (calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_5\text{Na}$ , 351.1203).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.67 (1H, d,  $J = 9.5$  Hz, H-4), 7.29 (1H, d,  $J = 8.6$  Hz, H-5), 6.77 (1H, d,  $J = 8.6$  Hz, H-6), 6.17 (1H, d,  $J = 9.5$  Hz, H-3), 5.07 (1H, t,  $J = 5.2$  Hz, H-3'), 3.24 (1H, dd,  $J = 17.8, 5.2$  Hz, 4'-Ha), 2.95 (1H, dd,  $J = 17.8, 5.2$  Hz, 4'-Hb), 1.50 and 1.46 [each 3H, s, 2'-gem ( $\text{CH}_3$ )<sub>2</sub>]; 3'-angeloyloxy: 6.07 (1H, q,  $J = 7.2$  Hz), 1.90 (3H, d,  $J = 7.2$  Hz), 1.88 (3H, br.s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 159.9 (s, C-2), 155.5 (s, C-7), 152.6 (s, C-9), 143.2 (d, C-4), 126.2 (d, C-5), 114.8 (d, C-6), 111.6 (d, C-3), 111.2 (s, C-10), 106.3 (s, C-8), 75.8 (s, C-2'), 68.8 (d, C-3'), 24.1 (t, C-4'), 22.3 and 20.4 [q, 2'-gem ( $\text{CH}_3$ )<sub>2</sub>]; 3'-angeloyloxy: 165.8 (s), 138.3 (d), 126.6 (s), 14.9 (q), 26.5 (q).

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