

A Novel Dimeric Coumarin from *Clausena lenis*

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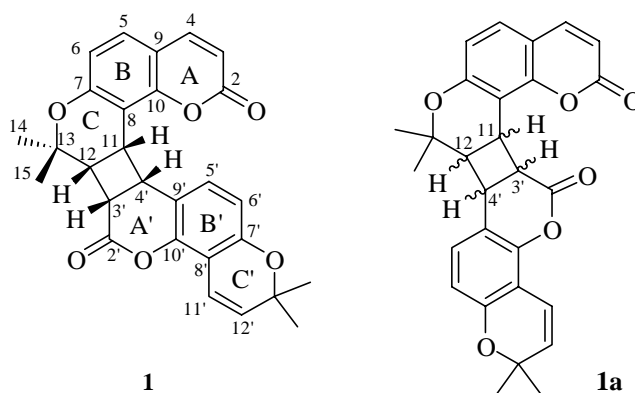
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Abstract: A novel dimeric coumarin (**1**), a dimeric of seselin named diseselin A, was isolated from the aerial part of *Clausena lenis*. The structure was elucidated based on the MS, 1D and 2D NMR data.

Keywords: *Clausena lenis*, coumarin, diseselin A, seselin, dimer.

Clausena lenis Drake (Rutaceae) is a shrub growing in Yunnan Province. Leaves and barks of this plant have been used for the treatment of dysentery, and arthritis¹. Previous researches revealed that this genus contained *O*-terpenoidal coumarins²⁻¹⁰. The chemical constitutions of *C. lenis* were not investigated before this work. Herein we reported the isolation of a new dimeric coumarin (**1**) named diseselin A, a dimer of seselin¹¹⁻¹⁴ from the ethanol extract of the aerial part of *C. lenis* collected in Xishuangbanna, Yunnan Province. The structure was elucidated on the basis of 1D and 2D NMR experiments

Figure 1 The relative configurations of the new dimeric coumarin **1**

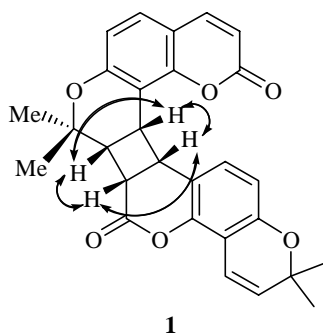


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(HMQC, HMBC, and ^1H - ^1H COSY). The relative configuration of **1** was established by the analysis of the NOE effects. This type of dimeric coumarin was firstly isolated from the genus *Clausena*.

Compound **1** was determined to have the molecular formula $\text{C}_{28}\text{H}_{24}\text{O}_6$ based on the high resolution EIMS (at m/z 456.1579 $[\text{M}]^+$, calcd: 456.1573). The ^1H NMR spectra showed a typical AB system characteristic signals of a coumarin lactone at δ_{H} 6.32, 7.68 (d, $J = 9.6$, each 1H) assigned to H-3, H-4 (**Table 1**)²⁻¹⁰. The ^{13}C NMR spectra (**Table 1**) showed 28 signals for four methyl, twelve methine, twelve quaternary carbons including two oxygen-substituted quaternary ones at δ 76.1 and 76.6, respectively. Analyzing the ^{13}C NMR and EIMS data suggested that **1** was a dimer of seselin¹¹⁻¹⁴. EIMS of **1** exhibited an $[\text{M}]^+$ peak at m/z 456 and the base peak at m/z 228 which corresponded to $\text{C}_{14}\text{H}_{12}\text{O}_3$. The ^1H and ^{13}C NMR spectra (**Table 1**) suggested that **1** was a dimer composed of two molecular seselins linked between rings C and A' through C-C bonds. However, this dimer could be in two forms, **1** and **1a** (**Figure 1**). The ^1H - ^1H COSY spectra, δ 3.70 showed the linear coupling relationship with 3.18, δ 3.18 showed the coupling relationship with 3.70 and 3.54, δ 3.54 showed the coupling relationship with 3.18 and 3.33, δ 3.33 showed the coupling relationship with 3.54, which revealed the juncture of those four protons: δ 3.70— δ 3.18— δ 3.54— δ 3.33. In HMBC, δ_{H} 3.70 (H-11) had the ^1H - ^{13}C long-range correlations with δ_{C} 35.7d (C-3'), 39.5d (C-4'), 44.8d (C-12), 111.9s (C-8), and 156.3s (C-7), δ 3.18 (H-12) had the ^1H - ^{13}C long-range correlations with δ_{C} 37.4d (C-11), 111.9s, and 166.5s (C-2'). For ring A', δ_{H} 3.54 (H-3') had the ^1H - ^{13}C long-range correlations with δ_{C} 44.8d (C-12), 76.1s (C-13), 113.8s (C-9'), and 166.5s (C-2'), and the proton δ 3.33 (H-4') had ^1H - ^{13}C long-range correlations with δ_{C} 37.4d, 44.8d, 111.9s, 113.8s, 129.7d (C-5'), and 146.2s (C-10'). Thus, protons at δ 3.70, δ 3.18, δ 3.54 and δ 3.33 were signed to H-11, H-12, H-3' and H-4', respectively, confirming this dimer must be **1** in stead of **1a**.

Figure 2 The selected NOE of the new dimeric coumarin **1**



In the NOE experiment (**Figure 2**), some NOE effects were observed between δ_{H} 3.18 (H-12) and 3.70 (H-11), and between δ_{H} 3.18 (H-12) and 3.54 (H-3'), which suggested that H-11, H-12, and H-3' were both in β -form. On the other hand, there were presence NOE effects between δ_{H} 3.33 (H-4') and 3.70 (H-11), and between δ_{H} 3.33 (H-4') and 3.54 (H-3') (**Figure 2**), which revealed that H-4', H-11, and H-3' all were in β -

form. So, the structure and relative configuration of **1** were identified to be as shown in **Figure 1** and **Figure 2**.

Table 1 The ^1H and ^{13}C NMR assignments for **1** in CDCl_3 (δ ppm, J_{HZ})

C	^1H	^{13}C	^1H - ^1H COSY	HMBC
2	/	160.8s	/	/
3	6.32 (d, 9.6)	113.4d	7.68 (H-4)	C-2, C-9
4	7.68 (d, 9.6)	144.0d	6.32 (H-3)	C-2, C-5, C-10
5	7.33 (d, 8.6)	127.4d	6.90 (H-6)	C-4, C-7, C-10
6	6.90 (d, 8.6)	115.5d	7.33 (H-5)	C-8, C-10
7	/	156.3s	/	/
8	/	111.9s	/	/
9	/	113.2s	/	/
10	/	153.6s	/	/
11	3.70 (d, 8.6)	37.4d	3.18 (H-12)	C-7, C-8, C-12, C-3', C-4'
12	3.18 (t, 8.6)	44.8d	3.54 (H-3'), 3.70 (H-11)	C-8, C-11, C-2'
13	/	76.1s	/	/
14	1.53 (s, 3H)	25.2q	/	C-12, C-13, C-15
15	1.10 (s, 3H)	23.5q	/	C-12, C-13, C-14
2'	/	166.5s	/	/
3'	3.54 (t, 8.6)	35.7d	3.18 (H-12) 3.33 (H-4')	C-12, C-13, C-2', C-9'
4'	3.33 (d, 8.6)	39.5d	3.54 (H-3')	C-8, C-11, C-12, C-5', C-9', C-10'
5'	7.70 (d, 8.4)	129.7d	6.81 (H-6')	C-4', C-7', C-10'
6'	6.81 (d, 8.4)	114.5d	7.70 (H-5')	C-7', C-8', C-9'
7'	/	153.6s	/	/
8'	/	110.2s	/	/
9'	/	113.8s	/	/
10'	/	146.2s	/	/
11'	6.78 (d, 10.1)	116.2d	5.69 (H-12')	C-7', C-13'
12'	5.69 (d, 10.1)	131.0d	6.78 (H-11')	C-8', C-13'
13'	/	76.6s	/	/
14'	1.48 (s, 3H)	28.3q	/	C-12', C-13', C-15'
15'	1.45 (s, 3H)	28.3q	/	C-12', C-13', C-14'

^a ^1H and ^{13}C NMR spectra were obtained at 400 and 100 MHz, respectively, and assigned by the ^1H - ^1H COSY, HMQC and HMBC experiments.

^b Coupling constants were presented in Hertz, unless otherwise indicated, all proton signals integrate to 1H.

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