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Two novel cyclopentenones from *Fissistigma oldhamii*

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Abstract

Two novel cyclopentenones, stigmahamone I (**1**) and stigmahamone II (**2**), have been isolated from the seeds of *Fissistigma oldhamii*. The structures of **1** and **2** were elucidated by spectroscopic methods. © 2000 Elsevier Science Ltd. All rights reserved.

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Our laboratory has reported a series of studies on *Fissistigma* species. In these previous papers, such species were found to contain alkaloids,[1–6] a novel furanone-fissohamione,[7] and a number of flavonoids were reported by Shang et al.[8,9] *Fissistigma oldhamii* (Hemsl.) Merr. (Annonaceae) is a perennial shrub, which is distributed mainly in southern China and Taiwan. As a folklore medicine, this plant is used for liver protection, anti-inflammatory and anti-arthritic effects, and anti-tumor action.[10] In a preliminary bioassay, the methanolic extract of *F. oldhamii* also showed significant activity in antiplatelet aggregation. In order to understand the chemotaxonomy and search for the new plant bioactive agents, phytochemical investigation was consequently undertaken. In this study, we have isolated two novel cyclopentenones, stigmahamone I (**1**) and stigmahamone II (**2**), from the methanolic extract of the seeds of *F. oldhamii*. The structures of **1** and **2** were elucidated by spectroscopic methods.

Specimens of *F. oldhamii* were collected from Taichung, Taiwan in August 1989. The methanolic extract (12 g) was directly separated by column chromatography using 1:2 EtOAc:*n*-hexane as an eluent to obtain a fraction, which was further purified by preparative TLC to yield **1** (0.008% dry wt, EtOAc:*n*-hexane, 1:3, R_f=0.55) and **2** (0.003% dry wt, EtOAc:*n*-hexane, 1:2, R_f=0.44).

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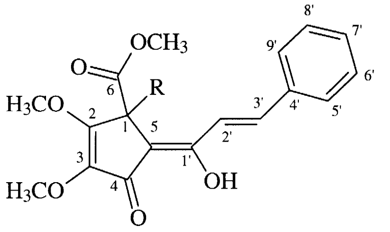

1 R = OCH_3

2 R = OH

Stigmahamone I (**1**) was obtained as a yellow oil, $[\alpha]_D$=+13.2 (*c* 0.11, $CHCl_3$). The molecular formula, $C_{19}H_{20}O_7$, was confirmed by high-resolution mass spectroscopic measurement (*m/z* 361.1289 $[M+H]^+$, calcd: 361.1287). The UV spectrum of **1** had absorptions at 217, 282 and 377 nm. In the IR spectrum, absorption bands attributable to hydroxyl (3477 cm^{-1}) and carbonyl (1755, 1650 cm^{-1}) groups were observed. The presence of a methoxycarbonyl group was substantiated by its EIMS (*m/z* 301 $[M-59]^+$) spectrum. The ^1H NMR spectrum of **1** (see data in Table 1) indicated the presence of signals corresponding to four methoxyl groups (one methoxyl signal was significantly shielded at δ 3.22), two *trans* alkene protons (d, J=16.0 Hz), one mono-substituted aromatic ring and one phenolic hydroxyl group which was strongly hydrogen bonded. The ^{13}C NMR and DEPT experiments (see data in Table 1) further confirmed the presence of seven methines, eight quaternary carbons (including two carbonyl at δ 192.76 and 169.42), and four methoxyl signals. The above-mentioned data indicate the structure of **1** is a cyclopentenone, which is in agreement with those reported in the literature,[11] with a cinnamoyl side chain, a methoxycarbonyl group, three methoxyl groups and a hydrogen-bonded hydroxyl group, respectively.

Table 1

^{13}C NMR (100 MHz, $CDCl_3$) and ^1H NMR (400 MHz) data for **1** and **2**

Position	**1**		**2**	
	δ_C	δ_H, J (Hz)	δ_C	δ_H, J (Hz)
1'	161.32		161.57	
2'	117.56	6.88, *d* (16)	117.48	6.61, *d* (16)
3'	139.19	7.50, *d* (16)	138.75	7.47, *d* (16)
4'	135.33		135.37	
5', 9'	128.03	7.55, *m*	127.86	7.49, *m*
6', 8'	128.84		128.85	
7'	129.77	7.37, *m*	129.69	7.36, *m*
1	81.08		75.22	
2	159.54		160.49	
3	138.24		136.12	
4 (CO)	192.76		193.21	
5	104.10		107.89	
6	169.42		173.12	
OMe-1	50.88	3.22, *s*		
OMe-2	59.42	4.15, *s*	59.95	4.17, *s*
OMe-3	59.97	4.01, *s*	60.00	3.99, *s*
OMe-6	53.25	3.76, *s*	54.03	3.79, *s*
OH-1'		12.30, *br s*		12.15, *br s*

Further confirmation of the structural assignment was obtained by means of two-dimensional NMR experiments. The sequential correlations of HMBC were successfully established as shown in Fig. 1. When compared with literature data[11,12] the above results support the structure of **1** as a novel methyl 5-((2′*E*)-1′-hydroxy-3′-phenylprop-2′-enylidene)-1,2,3-trimethoxy-4-oxocyclopent-2-enecarboxylate, which is provisionally named stigmahamone I.

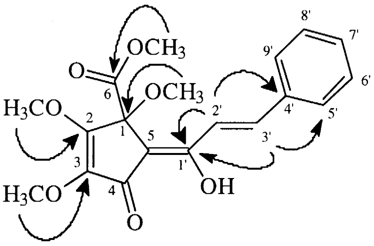

Fig. 1. Key HMBC correlations of stigmahamone I (**1**)

Stigmahamone II (**2**) was isolated as a pale yellow oil, $[\alpha]_D$=+15.9 (*c* 0.07, $CHCl_3$). The molecular formula $C_{18}H_{18}O_7$ was deduced by high-resolution mass spectroscopic measurement (*m/z* 347.1120 $[M+H]^+$, calcd: 347.1131). In the mass spectrum, the appearance of peaks at *m/z* 287 $[M-59]^+$ corresponded to the loss of a methoxycarbonyl group. Its UV and IR spectra were similar with the pattern in the spectra of **1**. Compound **2** also exhibited a similar ^{1}H NMR spectrum to **1** (see data in Table 1) but lacked the signal of the most upfield methoxyl group (δ 3.22). The ^{13}C NMR spectrum (see data in Table 1) showed signals for seven methines, eight quaternary carbons (including two carbonyl at δ 192.76 and 169.42), and three methoxyl groups. Therefore, we can determine that **2** also possesses a cyclopentenone skeleton. Further confirmation of the structural assignment was also made by HMBC experiments and by comparison with **1**. The above results support the structure of **2** as a novel methyl 5-((2′*E*)-1′-hydroxy-3′-phenylprop-2′-enylidene)-2,3-dimethoxy-4-oxocyclopent-2-enecarboxylate, which is provisionally named stigmahamone II. Further chemical examination of this Annonaceae plant is now under way in our laboratory.

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References

1. Lu, S. T.; Wu, Y. C. *Heterocycles* **1983**, *20*, 813–815.
2. Lu, S. T.; Wu, Y. C.; Leou, S. P. *Phytochemistry* **1985**, *24*, 1829–1834.
3. Wu, Y. C.; Lu, S. T.; Wu, T. S.; Lee, K. H. *Heterocycles* **1987**, *26*, 9–12.
4. Wu, Y. C.; Kao, S. C.; Huang, J. F.; Duh, C. Y.; Lu, S. T. *Phytochemistry* **1990**, *29*, 2387–2388.
5. Chia, Y. C.; Chang, F. R.; Li, C. M.; Wu, Y. C. *Phytochemistry* **1998**, *48*, 367–369.
6. Chia, Y. C.; Chang, F. R.; Wu, Y. C. *J. Nat. Prod.* **1998**, *61*, 1430–1432.
7. Chia, Y. C.; Chang, F. R.; Wu, Y. C. *Tetrahedron Lett.* **1999**, *40*, 7513–7514.
8. Shang, L. J.; Zhao, B. T.; Hao, X. J. *Yunnan Zhiwu Yanjiu* **1994**, *16*, 191–195.
9. Hao, X. J.; Lu, Y.; Shang, L. J.; Zheng, Q. T. *Yunnan Zhiwu Yanjiu* **1995**, *5*, 143–145.
10. Wu, J. B.; Cheng, Y. D.; Kuo, S. C.; Wu, T. S.; Iitaka, Y.; Ebizuka, Y.; Sankawa, U. *Chem. Pharm. Bull.* **1994**, *42*, 2202–2204.
11. Schill, G.; Dietrich, B.; Fritz, H. *Liebigs Ann. Chem.* **1985**, *12*, 2477–2480.
12. Ng, S.; Lee, H. H.; Bennett, G. J. *Magn. Reson. Chem.* **1990**, *28*, 337–342.