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Two New Aporphine Alkaliods from *Fissistigma bracteolatum*

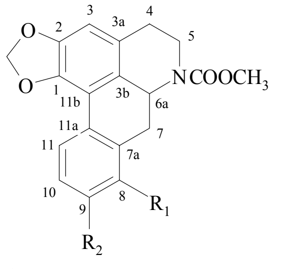
Yu DENG, Jin CHEN, Feng E WU*

Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041

Abstract: 1,2-methylenedioxy-9-methoxy-N-methoxycarbonyl-aporphine and 1,2-methylenedioxy -8,9-dimethoxy-N-methoxycarbonyl-aporphine, two new alkaloids possessing a N-(methoxy carbonyl) group have been isolated from the stems of *Fssistigma bracteolatum*. Their structures were established on the basis of spectral analysis.

Keywords: *Fissistigma bracteolatum*, aporphine, 1,2-methylenedioxy-9-methoxy-N-methoxy carbonyl-aporphine, 1,2-methylenedioxy -8,9-dimethoxy-N-methoxycarbonyl-aporphine.

Fissistigma bracteolatum Chatt., which is distributed in Yunan Province, is a Chinese medicine herb for the treatment of contusions and strains[1]. This species has not been studied chemically before. The present paper reports the structures of two new aporphine alkaloids, 1,2-methylenedioxy-9-methoxy-N-methoxycarbonyl-aporphine (**1**) and 1,2-methylenedioxy -8,9-dimethoxy-N-methoxycarbonyl-aporphine (**2**) from the stems of *Fissistigma bracteolatum.*



	R_1	R_2
1	H	OCH_3
2	OCH_3	OCH_3
3	H	H

Compound **1**, white power, mp 174-176°C, $[\alpha]_D^{20}$ –281.7 (c 0.01, $CHCl_3$), showed positive reaction to Dragendorff's test. The HREIMS showed the molecular formula $C_{20}H_{19}NO_5$ (found 353.1256, calcd. 353.1263). EIMS spectrum gave a molecular ion peak at *m*/*z* 353 $[M]^+$ (96) and fragment ion peaks at *m*/*z* 338 (16), 266 (90), 265 (100), 165 (26), 88 (17), 59 (47). An aporphine skeleton was suggested by UV $\lambda_{max}(\lg\varepsilon)$ at λ 215 (4.38), 239 (4.03), 282 (4.24), 325 nm (3.41)[2]. The IR band at 1697 cm^{-1} and a signal at δ 155.9 ppm in the ^{13}CNMR spectrum indicated that a N-carbamate group was present[3]. The H-5 correlated to carbonyl in HMBC also indicated that the carbonyl bonded to the nitrogen atom. These assignments were also supported by comparison

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*E-mail: FEWu@cib.ac.cn

Table 1 ^{1}H-(300MHz) and ^{13}C-(75MHz) NMR spectral data for **1** ,**2** ($CDCl_3$, δ in ppm, J Hz)

Number of C / H		δ_H		δ_C	
		1	**2**	**1**	**2**
1				142.3	142.5
2				146.8	146.7
3		6.54, s, 1H	6.56, s, 1H	106.7	106.9
3a				127.8	127.9
3b				124.9	125.0
4	H-4a	2.60, m, 1H	2.58, m, 1H	30.4	30.3
	H-4b	2.87, m, 1H	2.82, m, 1H		
5	H-5a	3.00, m 1H	2.99, m, 1H	39.2	39.1
	H-5b	4.42, m, 1H	4.41, m, 1H		
6a		4.85, m, 1H	4.76, m, 1H	51.7	51.6
7	H-7a	2.87, m, 1H	2.52, m, 1H	35.2	27.9
	H-7b	2.87, m, 1H	3.50, m, 1H		
7a				137.6	130.3
8		6.81, d (2.5), 1H		113.9	146.2
9				159.1	152.3
10		6.86, dd (8.5, 2.5), 1H	6.88, d (8.7), 1H	112.6	110.4
11		8.03, d (8.5), 1H	7.84, d (8.7), 1H	128.5	123.5
11a				123.6	124.3
11b				117.3	117.4
OCH_2O		6.06 and 5.95, d (1.3), each 1H	6.07 and 5.95, d (1.2), each 1H	100.8	100.8
8-OCH_3			3.83, s, 3H		60.9
9-OCH_3		3.84, s, 3H	3.91, s, 3H	55.3	55.8
N-$COOCH_3$		3.79, s, 3H	3.77, s, 3H	52.7	52.6
C=O				155.9	156.9

Signal assignments are based on 2D-NMR (^{1}H-^{1}H COSY, HMQC and HMBC) spectra.

with the spectral data of romucosine **3**[3]. In the NMR spectra of compound **1**, the shifts of A and B rings are similar to those of romucosine. The ^{1}HNMR spectrum showed the presence of a methylenedioxy (δ 6.06 and 5.95, each 1 H, J=1.3Hz,), a methoxyl (δ 3.84, s, 3H), and methoxycarbonyl group (δ 3.79, s, 3H). The ^{1}HNMR also showed a typical singlet at δ 6.54 (s, 1H, H-3), which revealed the methylenedioxy was located at C-1 and C-2. The signals at δ 8.03 (d, 1H,J=8.5Hz, H-11), 6.86 (dd, 1H, J=8.5, 2.5Hz, H-10), 6.81 (d, 1H, J=2.5Hz, H-8) showed that there existed two *ortho* coupled protons and one *meta* coupled proton at ring D. The ^{13}CNMR spectrum showed the chemical shift of carbonyl carbon at δ 155.9, twelve aromatic carbon atoms between δ 159.1 and 106.7, a methylenedioxy carbon atom at 100.8, a methoxyl carbon atom at δ 55.3, as well as one carboxylic methyl carbon at δ 52.7. The correlation between H-7 and C-8, between H-8, H-10, H-11, OMe and C-9 in HMBC revealed that the methoxyl group was situated at C-9 position. So compound **1** was elucidated as 1,2-methylenedioxy-9-methoxy-N-methoxycarbonyl-aporphine and its ^{1}H- and ^{13}C- NMR spectra (**Table 1**) were completely assigned by detailed 2D-NMR experiments.

Compound **2**, white power, mp 190-192°C, $[\alpha]^{20}_{D}$ δ–265.2 (c 0.01, $CHCl_3$), showed positive reaction to Dragendorff's test. The HREIMS showed the molecular formula $C_{21}H_{21}NO_6$ (found 383.1353, calcd. 383.1369). EIMS spectrum gave a molecular ion peak at *m/z* 383 $[M]^+$ (100) and fragment ion peaks at *m/z* 368 (6), 308 (8), 296 (40), 295

(82), 265 (8), 88 (10), 59 (25). An aporphine skeleton was suggested by UV λ_{max} (lgε) at λ 218 (4.47), 239 (4.09), 282 (4.24), 322 nm (3.56)[2]. The IR band at 1692 cm^{-1} and a signal at δ 156.9 ppm in the ^{13}CNMR spectrum indicated the presence of a N-carbamate group[3]. The H-5 correlated to carbonyl in HMBC also indicated that the carbonyl bonded to the nitrogen atom. Except for one more methoxy in **2**, the ^{1}H and ^{13}CNMR spectra of **2** were similar to those of **1**. The correlation between H-7, H-10, one OCH_3 and C-8, between H-10, H-11, another OCH_3 and C-9 in HMBC, as well as the *ortho* coupling between H-11 and H-10 (J=8.7Hz) in ^{1}HNMR revealed that the two methoxyl groups were situated at C-8, C-9 position respectively. So compound **2** was elucidated as 1,2-methylenedioxy-8, 9-dimethoxy-N-methoxycarbonyl- aporphine and its ^{1}H- and ^{13}C-NMR spectra (**Table 1**) were completely assigned by detailed 2D-NMR experiments.

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