Pergamon

0031-9422(95)00972-8

Phytochemistry, Vol. 42, No. 3, pp. 891–893, 1996

0031-9422/96 $15.00 + 0.00

TACCALONOLIDES FROM *TACCA PLANTAGINEA*

JIHUI SHEN, ZHONGLIANG CHEN* and YISHENG GAO

Shanghai Institute of Materia Medica, Academia Sinica, Shanghai 200031, China

(*Received in revised form* 21 *November* 1995)

Key Word Index—*Tacca plantaginea*; Taccaceae; taccalonolides L and M; steroidal lactones.

Abstract—Two new pentacyclic steroidal lactones, taccalonolides L and M, have been isolated from *Tacca plantaginea*. Their structures were established by spectroscopic methods.

INTRODUCTION

We previously reported that several pentacyclic steroidal bitter principles, the taccalolides, had been isolated from *Tacca plantaginea* [1–4]. Our continued interest in taccalonolides and its analogues prompted us to isolate the two minor constituents from the rhizome of the same plant. In the present paper, we report the isolation and structure determination of the two new compounds, taccalonolide L (**1**) and taccalonolide M (**2**).

RESULTS AND DISCUSSION

The rhizome of *Tacca plantaginea* was extracted with 5% ethanol. The diethyl ether soluble part of the ethanol extracted paste was separated by silica gel chromatography and preparative TLC. From the more polar fraction the two new compounds, **1** and **2**, were isolated and purified.

For **1**, EI- and FD-mass spectra did not give the molecular ion peak. Its IR spectrum showed the characteristic absorptions at 1810 and 1750 cm^{-1}, which indicated the presence of an enol γ-lactone. By comparison of **1** with taccalonolide A (**3**), the ^{1}H NMR spectrum of **1** was very similar to that of **3**, but showed two one-proton doublets for a methylene group at 4.17 (*d*, $J = 17.4$ Hz) and 3.95 (*d*, $J = 17.3$ Hz), and only three acetyl signals were observed. It was deduced that one acetyl group in **3** was replaced by an α-hydroxyacetyl group in **1**. To confirm this, the ^{13}C NMR spectrum of **1** showed a methylene triplet at δ 60.9.

Like **3**, the circular dichroic (CD) spectrum of **1** showed a negative Cotton effect ($\Delta\varepsilon$-1.46) at 279 nm, which indicated that the absolute configuration of **1** was the same as that of **3** [5].

With (**2**) the FD mass spectrum gave the $[M + 1]^{+}$ peak at *m/z* 619. Its IR spectrum showed absorptions at 1770 and 1735 cm^{-1}, which indicated the lack of an enol γ-lactone function. The ^{1}H NMR and ^{1}H–^{1}H 2D COSY spectra revealed the correlation between the H-6 signal (δ 4.16, *sbr*) and C_6–OH hydroxyl-proton signal (δ 3.14, *sbr*), which indicated the presence of the same A/B ring partial structure as that of taccalonolide K [4]. The H-12 signal appeared as a double doublet at δ 4.91 ($J = 3.0$ and 3.0 Hz), which suggested that **2** had the 11-desacetyl structure like that of taccalonolide E [3]. Owing to the 15-keto function, H-14 appeared in the ^{1}H NMR spectrum as a doublet which was downshifted (δ 3.01) more than that of the other known taccalonolides. The H-23 signal appeared in the ^{1}H NMR spectrum at δ 4.49, corresponding to the γ-lactone partial structure.

The stereochemistry at C-23 was determined as the *S*-configuration, H-23 had the β-position, and the hydroxyl group substituted at C-6 was elucidated as occupying the α-position. This was in accord with the NOE experimental results.

The two keto functions of **2** appeared in the ^{13}C NMR spectrum as two signals at δ 210.84 *s* and 205.83 *s*. We could predict that Cotton effects of the n-π^* of 7-one and 15-one would be negative and positive, respectively. By means of a Dreiding stereo molecular model, the CD spectrum of **2** was in exact agreement with this assumption, which indicated that B/C, C/D and D/E-rings were transfused. Hence, the structure of taccalonolide M was further confirmed as shown by **2** [5].

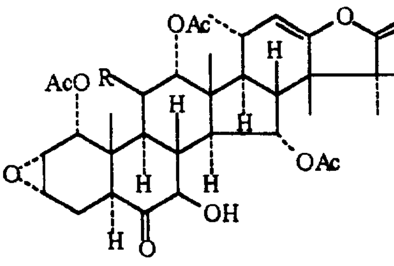
EXPERIMENTAL

IR spectra were recorded on a PE-599B spectrophotometer, ^{1}H and ^{13}C NMR spectra were measured on Bruker AM-400 and Ac-80 spectrometers, and mass spectra were taken on a Hitachi M-80 spectrometer.

The dry powdered plant material (20 kg) was treated as in the previous report [3]. After CC, the Et_2O–MeOH (9:1) of the Et_2O extract was further sepd. by prep. TLC and/or repeated CC, using the solvent systems as follows: cyclohexane–EtOAc (1:3), $CHCl_3$–EtOH (19:1) and EtOAC–EtOH (19:1). Finally, **1** (30 mg) and **2** (50 mg) were obtained.

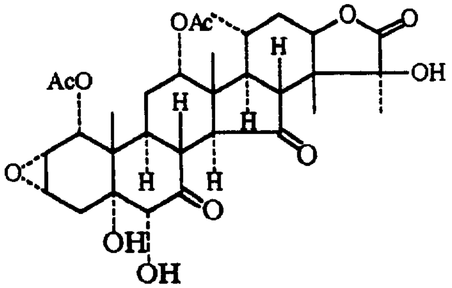
---

*Author to whom correspondence should be addressed.



1 R=OCOCH₂OH

3 R=OAc



2

Compound **1**. Mp 200°, recrystallization from $CHCl_3$, $C_{36}H_{46}O_{15}$. $[\alpha]_D^{22} = +33.92°$ (*c* 0.0029, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}. 3470 (OH), 1810, 1750 (CO), 1250. ^1H NMR ($CDCl_3$, 400 MHz): see Table 1. ^1H NMR (CD_3COD_3, 400 MHz): 4.83 (1H, *d*, $J = 5.5$ Hz, H-1), 3.42 (1H, *dd*, $J = 5.0$, 4.0 Hz, H-2), 3.37 (1H, *m*, H-3), 2.25 (1H, *m*, H_a-4), 2.02 (1H, overlapped by the peak of solvent, H_b-4), 2.86 (1H, *dd*, $J = 6.0$, 10.0 Hz, H-5), 4.19 (1H, *dd*, $J = 10.5$, 1.0 Hz, H-7), 1.90 (1H, *dd*, $J = 11.0$, 10.5 Hz, H-8), 2.93 (1H, *dd*, $J = 11.5$, 11.5 Hz, H-9), 5.43 (1H, *dd*, $J = 3.0$, 11.5 Hz, H-11), 5.29 (1H, *d*, $J = 3.0$ Hz, H-12), 2.58 (1H, *dd*, $J = 10.0$, 9.5 Hz, H-14), 5.52 (1H, *dd*, $J = 10.0$, 9.5 Hz, H-15), 2.53 (1H, *dd*, $J = 10.0$, 13.5 Hz, H-16), 1.92 (1H, H-17), 1.08 (3H, *s*, H-18), 0.82 (3H, *s*, H-19), 2.23 (1H, *m*, H-22), 1.66 (3H, *s*, H-27), 1.34 (3H, *s*, H-28), 1.93 (3H, *s*, CH_3CO_2), 2.16 (3H, *s*, CH_3CO_2), 2.21 (3H, *s*, CH_3CO_2), 4.15 (1H, *d*, $J = 17.4$ Hz, $-CH_2-$), 3.86 (1H, *d*, $J = 17.5$ Hz, $-CH_2-$). ^{13}C NMR ($CDCl_3$, 90 MHz): see Table 2. ^{13}C NMR (CD_3COCD_3, 80 MHz): 210.82, 178.31, 173.17, 171.95, 170.71, 170.52, 155.78, 111.12, 79.76, 75.68, 74.70, 73.63, 72.74, 72.21, 60.90, 55.14, 52.75, 52.00, 51.02, 50.36, 49.51, 43.81, 43.66, 43.56, 42.57, 40.97, 31.33, 25.64, 22.51, 22.01, 20.97, 20.90, 20.61, 20.29, 13.38, 12.80. CD(EtOH): $\Delta\varepsilon$ (nm): 12.86 (201), −13.16 (228), −1.46 (279).

Compound **2**. Mp 235–237°, recrystallization from $CHCl_3$ or EtOH. FD-MS *m/z*: 619 $[M + 1]^+$ (100%), $C_{32}H_{42}O_{12}$. $[\alpha]_D^{22} = +54.73°$ (*c* 0.0053, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3480 (OH), 1770, 1735 (O), 1250. ^{13}C NMR (Me_2CO-d_6, 90 MHz): 210.84 *s*, 205.83 *s*, 178.45

Table 1. ^1H NMR spectral data for compounds **1** and **2** (400 MHz, $CDCl_3$)

Carbon	1	2
1	4.70 *d* (5.5)	4.73 *d* (5.0)
2	3.42 *dd* (5.5, 4.0)	3.72 *dd* (5.0, 4.0)
3	3.37 *ddd* (4.0, 2.0, 2.0)	3.57 *dd* (4.0, 2.0)
4	2.18 *m*	2.66 *dbr* (16.0)
5	2.75 *dd* (6.0, 10.0)	2.1 *dd* (16.0, 2.0)
6		4.16 *s*
7	3.99 *dd* (12.0, 2.5)	
8	1.70 *dd* (11.0, 11.5)	2.57 *dd* (10.5, 10.0)
9	2.72 *dd* (11.5, 11.0)	2.46 *ddd* (13.5, 10.5, 4.0)
11	5.40 *dd* (11.5, 2.5)	1.58 *ddd* (15.0, 4.0, 3.0)
		1.68 *ddd* (15.0, 13.5, 3.0)
12	5.27 *d* (2.5)	4.91 *dd* (3.0, 3.0)
14	2.43 *dd* (10.0, 10.0)	3.01 *d* (10.0)
15	5.51 *dd* (9.5, 9.5)	
16	2.41 *dd* (10.0, 10.0)	1.93 *d* (14.0)
17	1.78 *dd* (13.5, 10.0)	2.06 *dd* (14.0, 13.0)
18	0.98 *s*	0.76 *s*
19	0.76 *s*	1.16 *s*
20	2.17 *m*	1.88 *m*
21	0.88 *d* (8.0)	1.0 *d* (5.0)
22	5.05 *d* (1.0)	1.75 *ddd* (12.5, 5.0, 4.0)
		1.90 *m*
23		4.49 *dbr* (4.0)
27	1.62 *s*	1.52 *s*
28	1.33 *s*	1.42 *s*
Ac	2.16 *s*, 2.11 *s*, 1.97 *s*	2.09 *s*, 1.98 *s*
$HOCH_2$	4.17 *d* (17.5)	
	3.95 *d* (17.5)	

Table 2. ^{13}C NMR spectral data for compound **1** (90 MHz, $CDCl_3$)

Carbon	δ	Carbon	δ
1	72.6	19	12.9
2	49.5	20	30.6
3	52.1	21	13.3
4	21.3	22	111
5	42.1	23	154.5
6	209.7	24	50.1
7	75.1	25	79.1
8	42.9	26	178
9	40	27	25.3
10	43	28	20.6
11	71.3	COO	172.2
12	73.8		172
13	43.1		169.9
14	54.3	CH_3(OAc)	22.4
15	72.3		20.8
16	51.1		20.6
17	48.7	CH_2OH	60.9
18	20.1		

s, 170.57 *s*, 170.31 *s*, 86.46 *d*, 81.30 *s*, 78.42 *d*, 75.86 *s*, 73.97 *d*, 73.01 *d*, 55.42 *d*, 55.33 *d*, 53.17 *d*, 51.41 *d*, 49.06 *s*, 43.77 *d*, 43.00 *s*, 42.16 *s*, 42.02 *d*, 37.57 *d*, 31.01 *t*, 29.77 *t*, 27.61 *d*, 25.78 *t*, 23.28 *q*, 21.03 *q*, 20.71 *q*, 20.26 *q*, 19.42 *q*, 15.58 *q*, 13.45 *q*. CD(EtOH): $\Delta\varepsilon$(nm): −1.14 (214), −0.56 (268), +3.5 (306.5).

Acknowledgements—This research programme was supported by the Chinese National Fund of Natural Sciences. We are grateful to Prof. Min-quin Chen, Department of Chemistry, Fudan University, Shanghai, for X-ray crystallographic analysis.

REFERENCES

1. Chen, Z., Wang, B. and Chen, M. (1987) *Tetrahedron Letters* **28**, 1673.
2. Chen, Z., Wang, B. and Shen, J. (1988) *Phytochemistry* **27**, 2999.
3. Shen, J., Chen, Z. and Gao, Y. (1991) *Chin. J. Chem.* 93.
4. Chen, Z., Shen, J. and Gao, Y. (1989) *Heterocycles* **29**, 2103.
5. Mi, J., Chen, Z. and Shen, J. (1994) *Acta Pharm. Sinica* **29**, 111.