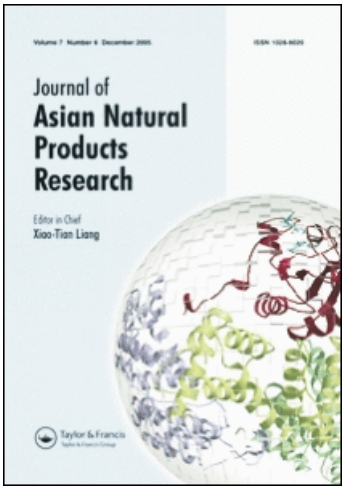

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A NEW COMPOUND FROM *GASTRODIA ELATA* BLUME

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A new compound, α-acetylamino-phenylprophyl α-benzoylamino-phenylpropionate (**1**) and a known compound 4-hydroxybenzyl β-sitosterol ether (**2**), were isolated from the tubers of *Gastrodia elata* Blume and their structures were elucidated by spectral data.

Keywords: *Gastrodia elata*; α-Acetylamino-phenylpropyl α-benzoylamino-phenylpropionate; 4-Hydroxybenzyl β-sitosterol ether; Spectral data

INTRODUCTION

The isolation and identification of the main constituents from the tubers of *Gastrodia elata* Blume have been reported previously. Our investigation on the tubers led to the isolation of a new compound α-acetylamino-phenylpropyl α-benzoylamino-phenylpropionate (**1**) and a known compound 4-hydroxybenzyl β-sitosterol ether (**2**). Here we report their isolation and structure elucidation.

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were determined on a X-4 micromelting apparatus and are uncorrected; ^{1}H, ^{13}C NMR and 2D NMR were recorded on Varian UNITY INOVA 500 and Bruker AM-500 instruments (500 MHz for ^{1}H and 125 MHz for ^{13}C) in $CDCl_3$, with TMS as internal standard. ^{1}H and ^{13}C NMR assignments were supported by $^{1}H-^{1}H$ COSY, DEPT, HMQC and HMBC experiments. EIMS were performed with Hitachi M-80 and Hitachi M-4100H spectrometers.

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Plant Material

The tubers of *Gastrodia elata* BLUME were collected in Sichuan province, China and authenticated by professor Z.W. Xe, Institute of Chinese Materia Medica, China Academy of Traditional Chinese Medicine, Voucher specimens are deposited in the same Institute.

Extraction and Isolation

The air-dried tubers (10 kg) were extracted with 95% EtOH and the extracts after concentration were dilated with water and partitioned with Et_2O. the Et_2O extract (60 g) was subjected to repeated column chromatography over silica gel, using petroleum-EtOAc mixtures in increasing polarity as eluent. 4-hydroxybenzyl β-sitosterol ether(25 mg) was obtained in petroleum-EtOAc (10:1) elution. α-acetylamino-phenylpropyl α-benzoylamino-phenylpropionate (12 mg) were obtained from fractions eluted by petroleum-EtOAc (6:1) and purified by a column chromatography over ODS, using 80% MeOH as eluent.

α-acetylamino-phenylpropyl α-benzoylamino-phenylpropionate. This was obtained as white crystal, mp 193–195°C EIMS, see (Fig. 5), CIMS *m/z*: 445 ($M^+ + H$), ^1H and ^{13}C NMR data, see Tables I–III.

4-hydroxybenzyl β-sitosterol ether. This was obtained as white crystals, mp 228–231°C EIMS *m/z* (%): 520 (1.3M^+), 414 (11.3), 413 (10.3), 413 (10.3), 399 (10.5), 398 (27.4), 328 (4), 303 (5), 255 (6), 213 (5), 159 (8), 107 (100). CIMS *m/z*: 521 ($M^+ + H$). HREIMS, see (Fig. 6), ^1H and ^{13}C NMR data, see Tables IV and V.

TABLE I NMR spectral data of group **A**

Atom No.	*C*	*H*
1	136.6, s	–
2	129.3, d	7.20–7.32 (5H, m)
3	128.8, d	
4	127.1, d	
5	128.8, d	
6	129.3, d	
7	38.4, t	(a) 3.22 (1H, dd, $J = 13.5, 5.7$ Hz)
		(b) 3.06 (1H, dd, $J = 13.5, 8.5$ Hz)
8	55.0, d	4.75 (1H, m)
9	170.2, s	–
10	–	6.72 (1H, d, $J = 7.8$ Hz)

TABLE II NMR spectral data of group **B**

Atom No.	*C*	*H*
1′	136.7, s	–
2′	129.1, d	7.07 (1H, m)
3′	128.6, d	7.16 (1H, m)
4′	126.7, d	7.14 (1H, m)
5′	128.6, d	7.16 (1H, m)
6′	129.1, d	7.07 (1H, m)
7′	37.4, t	2.75 (2H, m)
8′	49.4, s	4.35 (1H, m)
9′	64.6, t	(a) 3.93 (1H, dd, $J = 11.2, 4.8$ Hz)
		(b) 3.82 (1H, dd, $J = 11.2, 4.3$ Hz)
10′	–	5.91 (1H, d, $J = 7.8$ Hz)

TABLE III NMR spectral data of group **C**

Atom No.	*C*	*H*
1″	133.6, s	–
2″	127.0, d	7.71 (1H, m)
3″	128.6, d	7.44 (1H, m)
4″	131.9, d	7.53 (1H, tt, $J = 7.6, 1.1$ Hz
5″	128.6, d	7.44 (1H, m)
6″	127.0, d	7.71 (1H, m)
7″	167.1, s	–

RESULTS AND DISCUSSION

Compound **1** was assigned the molecular formula $C_{27}H_{28}N_2O_4$ (HRMS, $[M^+] = m/z$ 444.2032, calcd: 444.2049). The ^{1}H NMR spectrum of **1** showed the presence of three monosubstituted phenyls (δ_H 7.20–7.32 (5H, m); 7.07 (2H, m), 7.16 (2H, m), 7.14 (1H, m); δ_H 7.71 (2H, m), 7.44 (2H, m), 7.53 (1H, tt, $J = 7.6$, 1.1 Hz)) and two secondary amino

TABLE IV The ^{13}C NMR spectral data of compound **2** and β-sitosterol

Carbon	*Compound* **2**	*β-sitosterol*
1	37.3 t	37.3 t
2	26.1 t	26.1 t
3*	78.3 d	71.8 d
4	39.2 t	42.3 t
5	141.0 s	140.7 s
6	121.5 d	121.7 d
7	32.0 t	32.0 t
8	31.9 d	31.9 d
9	50.2 d	50.1 d
10	36.9 s	36.5 s
11	21.1 t	21.1 t
12	39.8 t	39.8 t
13	42.3 s	42.8 s
14	56.8 d	56.8 d
15	24.2 t	24.8 t
16	28.2 t	28.5 t
17	56.1 d	56.0 d
18	19.4 q	19.4 q
19	11.9 q	11.9 q
20	36.1 d	36.1 d
21	18.8 q	18.8 q
22	33.9 t	33.9 t
23	28.4 t	28.4 t
24	45.8 d	45.8 d
25	23.0 t	23.1 t
26	12.0 q	12.0 q
27	29.1 d	29.1 d
28	19.0 q	19.0 q
29	19.8 q	19.8 q
1′	131.3 s	–
2′	129.4 d	–
3′	115.2 d	–
4′	154.9 s	–
5′	115.2 d	–
6′	129.4 d	–
7′	69.5 t	–

TABLE V The ^{1}H NMR spectral data of compound **2**

Atom No.	*H*
1a	1.03 (1H, m)
1b	1.85 (1H, m)
2	1.15 (2H, m)
3	3.26 (1H, m)
4a	2.27 (1H, m)
4b	2.40 (1H, m)
6	5.34 (1H, m)
7a	1.48 (1H, m)
7b	1.96 (1H, m)
8	1.50 (1H, m)
9	0.91 (1H, m)
11	1.47 (2H, m)
12a	1.16 (1H, m)
12b	2.0 (1H, m)
14	0.98 (1H, m)
15a	1.06 (1H, m)
15b	1.58 (1H, m)
16a	1.26 (1H, m)
16b	1.83 (1H, m)
17	1.10 (1H, m)
18	1.03 (3H, s)
19	0.68 (3H, s)
20	1.35 (1H, m)
21	0.92 (3H, d, $J = 6.6$)
22a	1.02 (1H, m)
22b	1.33 (1H, m)
23a	1.53 (1H, m)
23b	1.93 (1H, m)
24	0.93 (1H, m)
25	1.25 (2H, m)
26	1.20 (3H, t, $J = 7.3$)
27	1.66 (1H, m)
28	0.81 (3H, d, $J = 6.9$ Hz)
29	0.81 (3H, d, $J = 6.9$ Hz)
2′	7.22 (1H, d, $J = 8.6$ Hz)
3′	6.79 (1H, d, $J = 8.6$ Hz)
5′	6.79 (1H, d, $J = 8.6$ Hz)
6′	7.22 (1H, d, $J = 8.6$ Hz)
7′	4.73 (2H, s)

groups (δ_H 5.91 (1H, d, $J = 7.8$ Hz), 6.72 (1H, d, $J = 7.8$ Hz)). The EIMS spectrum of **1** exhibited the presence of benzoyl and benzyl moities by the fragments at *m/z* 105 and 91. Furthermore, the $^{1}H-^{1}H$ COSY and $^{13}C-^{1}H$ COSY spectra of **1** exhibited the presence of structural fragments of group A–C (Figs. 1–3 and Tables I–III) and an acetyl (δ_H 2.03, 3H, s; δ_C 20.8, q, 170.8, s). The fragmental peak at *m/z* 252.1006 ($C_{16}H_{14}N_1O_2$) and the long-range $^{13}C-^{1}H$ correlation between H-10 and C-7″ indicated that the benzoyl was connected with N-10. The HMBC (Fig. 4) and HRMS (Fig. 5) spectra provided further conclusive structural evidence for compound **1**. Therefore, the structure of **1** was determined as α-acetylamino-phenylpropyl α-benzoylamino-phenylpropionate (Figs. 4 and 5).

Compound **2** was assigned the molecular formula $C_{36}H_{56}O_2$ (HRMS, $[M^+] = m/z$ 520.4279, calcd: 520.4280). The ^{1}H NMR and ^{13}C NMR spectra of **2** exhibited the presence a steroidal skeleton (δ_H 1.0 (3H, s), 0.68 (3H, s), 0.92 (3H, d, $J = 6.6$), 1.20 (3H, t, $J = 7.3$), 0.81 (6H, d, $J = 6.9$); δ_C 19.4 (q), 11.9 (q), 18.8 (q), 12.0 (q), 19.0 (q), 19.8 (q)) and a 4-hydroxy-benzyloxy (δ_H 7.22 (2H, d, $J = 8.6$ Hz), 6.79 (2H, d, $J = 8.6$ Hz), 4.73 (2H, s); δ_C 131.3 (s), 129.4 (2c,d), 115.2 (2c,d), 154.9 (s), 69.5 (t)). Comparing the ^{13}C NMR spectrum

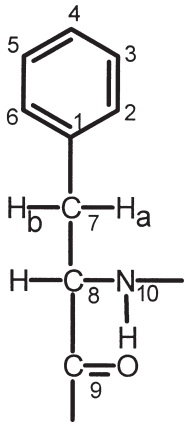

FIGURE 1 Structure of group A.

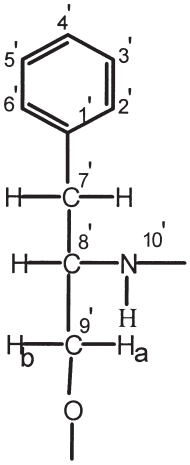

FIGURE 2 Structure of group B.

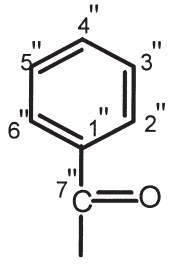

FIGURE 3 Structure of group C.

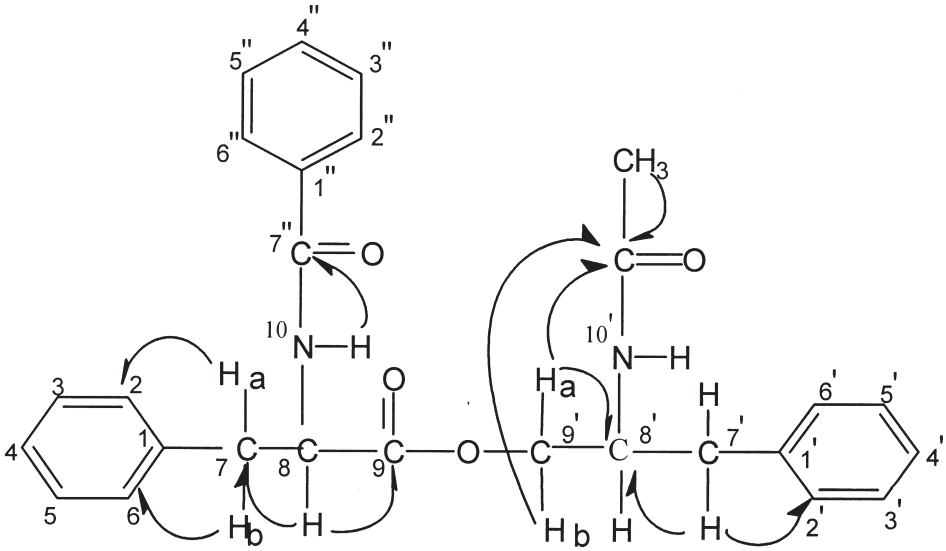

FIGURE 4 Selected HMBC correlations of compound **1**.

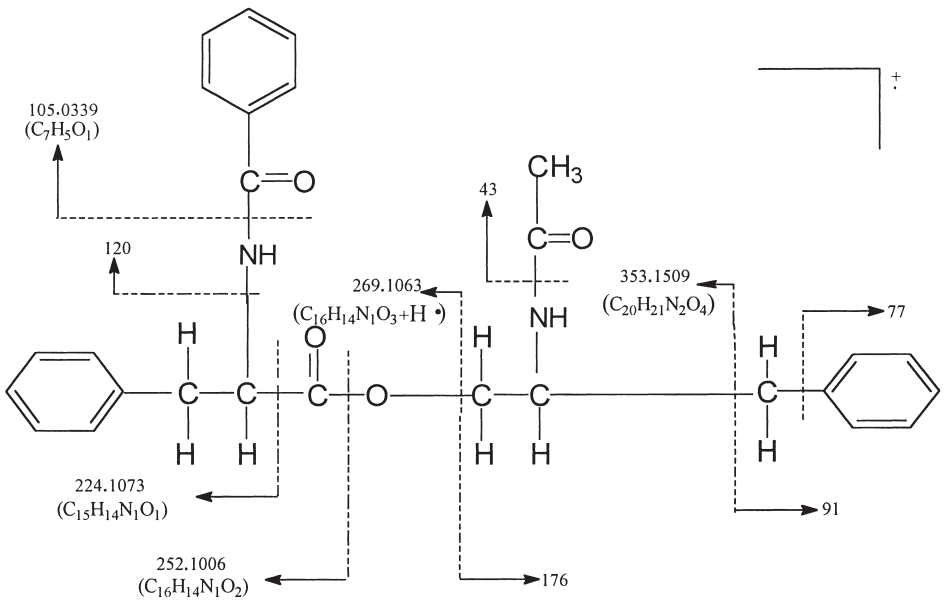

FIGURE 5 EIMS spectral fragment ions of compound **1**.

of compound **2** with that of β-sitosterol, it was found that the ^{13}C NMR spectral data of two compounds were very similar, except the data corresponding to 4-hydroxy-benzyloxy of compound **2**. In addition, the signal for C-3 of compound **2** was lower-field shifted by 6.5 ppm than the signal for C-3 of β-sitosterol. Therefore, the structure of compound **2** was deduced as 4-hydroxybenzyl β-sitosterol ether (Fig. 6). The long-range $^{13}C-^{1}H$ correlations (HMBC) and HRMS (Fig. 6) provided further conclusive structural evidence for compound **2**. It has been isolated from the same plant in 1998 [1].

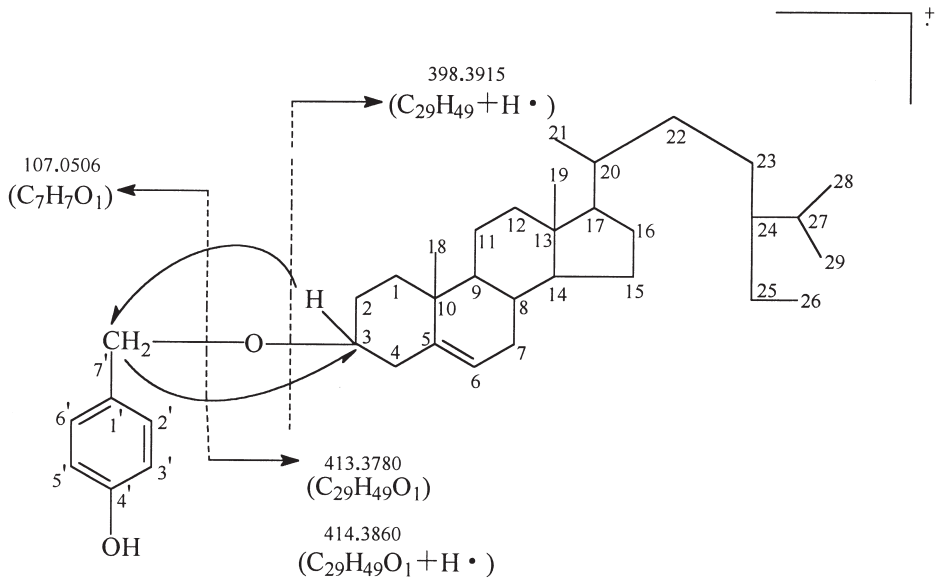

FIGURE 6 HREIMS spectral fragment ions and selected HMBC correlations of compound **2**.

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[1] Yun-Choi, H.S., Pyo and M.K., Park, K.N. (1998) *Arch Pharmacol Res.* **21**(3), 357–360.