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REVISED STRUCTURE FOR FIVE ACETOPHENONES FROM *CYNANCHUM TAIWANIANUM*

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Key Word Index—*Cynanchum taiwanianum*; Asclepiadaceae; acetophenones; biacetophenone dimer; cynandiones A–D; cynanchone A.

Abstract—The structures of the acetophenones cynandione A–D and cynanchone A isolated from *Cynanchum taiwanianum* have been revised following re-examination of their NMR spectral properties. Copyright © 1997 Elsevier Science Ltd

INTRODUCTION

In previous papers [1, 2] we have reported the isolation and structural elucidation of five novel acetophenones, cynandione A–D (**1′**–**4′**) and cynanchone A (**5′**). In a continuing study of the cytotoxic principles of this species, a 2,5-dihydroxyacetophenone (**6**) has been isolated. Examination of the NMR spectral properties of **1′**–**5′** and **6** shows that the chemical shifts of the A ring of **1′**–**5′** were in agreement with those of the corresponding data for **6** (Table 1); therefore, the characterizations of **1′**–**5′** are incorrect. In the present paper, we report revised structures for **1′**–**5′**.

RESULTS AND DISCUSSION

The chemical shifts for the A and B rings of **1** were in agreement with the corresponding data for **6**, 2,4-dihydroxyacetophenone (**7**) [3] and published data [4]. By comparing the aromatic proton chemical shifts of **1** and its peracetate (**1a**) (Table 1), it was found that the signal at δ 6.49 experienced a significant downfield shift of +0.82 ppm, whereas the signal at δ 7.78 only showed a slight downfield shift of +0.17 ppm. The other aromatic proton signals of **1** at δ 6.79 and 6.94 showed almost the same significant downfield shift, +0.46 and +0.45 ppm (Table 1), respectively, which is in accordance with the acetylation of hydroxyl groups in the *para* or *ortho* positions to the respective proton [5]. Based on the above evidence, **1′** was revised to be 2,3′-diacetyl-3,6,2′,6′-tetrahydroxybiphenyl (**1**). The two-dimensional spectrum of **1a** (Fig. 1) also supported this revision.

In the ^{1}H NMR spectra of **2**–**5**, the *ortho* coupled aromatic proton signals of the A ring, were all similar to those of the corresponding signals in **1**. The two-dimensional NMR spectra of **2**, **4** and **5** (Fig. 1) also indicated that structures **2′**, **4′** and **5′** should be revised to be **2**, **4** and **5**, and established the revision of ^{13}C NMR spectral assignments (Table 1). The ^{13}C NMR spectrum of **3** was assigned by comparison with those of corresponding data for **2** and **4**, and also indicated that the structure of **3′** should be revised to be **3**. The mass spectrum of revised structures (Scheme 1) also supported the revision of structures **1′**–**5′** to **1**–**5**.

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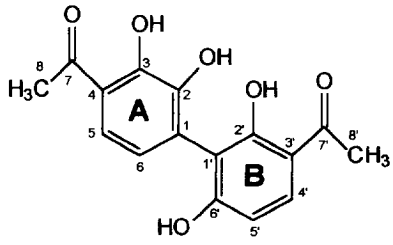

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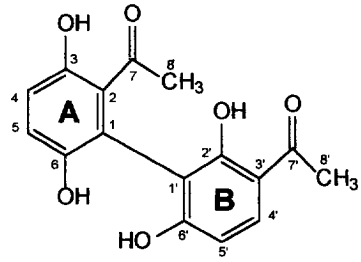

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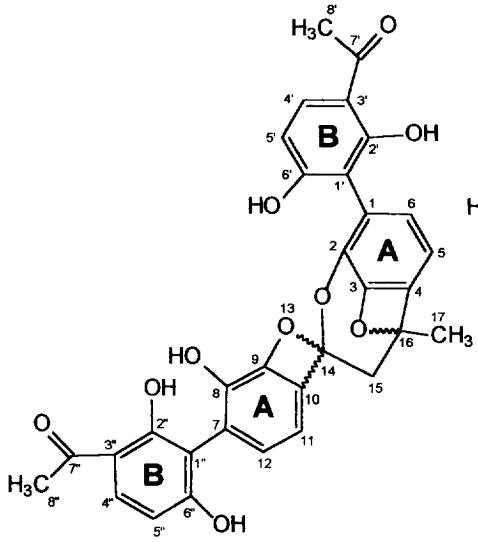
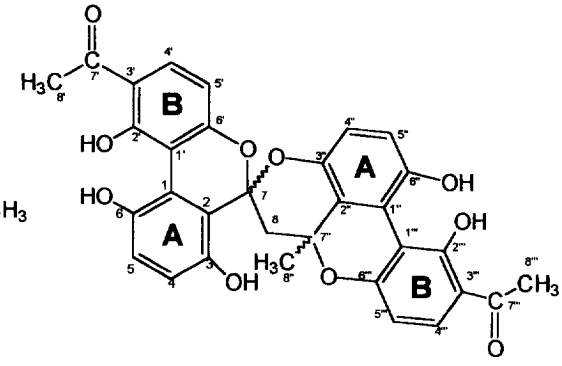
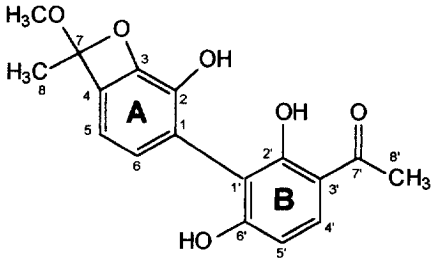


2' - 4'



2 - 4



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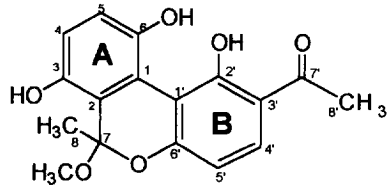

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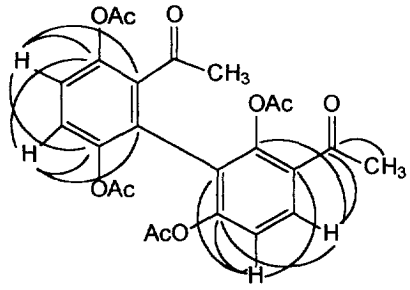
Table 1. NMR data of compounds **1**–**7**

	1 (CD_3OD)*		**1a** ($CDCl_3$)*†			**2** (pyridine-d_5)*‡		**3** (pyridine-d_5)*		**4** ($CDCl_3$)†		**5** ($CDCl_3$)†		**6** (acetone-d_6)†		**7** (DMSO-d_6)§	
C	δ_C	δ_H	δ_C	δ_H	C	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	128.1″		122.4″		1	122.0**		122.0**		122.8**		118.9		120.7		112.8	
2	120.6		135.8		2	117.5		117.8		115.0		115.3		156.5		164.9	
3	152.6		144.1		3	149.1		148.9		147.6	8.27 (OH)	147.1	8.21 (OH)	119.5	6.78 *d*	102.3	6.25 *d*
4	118.5	6.79 *d*	124.3	7.25 *d*	4	122.1	7.39 *d*	122.2	7.41 *d*	122.8	7.14 *d*	122.0	7.03 *d*	125.9	7.00 *d*	164.2	
5	122.0	6.94 *d*	125.0	7.37 *d*	5	119.6	7.29 *d*	119.5	7.31 *d*	120.4	7.10 *d*	118.9	6.92 *d*	150.6		108.1	6.37 *dd*
6	149.3		145.9		6	147.8		147.9		150.7	8.95 (OH)	146.0	7.50 (OH)	116.4	7.22 *d*	133.6	7.74 *dd*
7	207.7		199.4		7	101.3		100.9		102.6		104.7		205.9		205.6	
8	31.2	2.18 *s*	30.7	2.07 *s*	8	41.1	3.30 *d*	46.1	3.43 *d*	44.4	2.77 *d*	24.0	1.60 *s*	26.9	2.58 *s*	26.2	2.52 *s*
9							4.85 *d*		5.08 *d*		2.93 *d*						
10					1′	112.6		112.4		111.5		110.9					
11					2′	158.7		158.9		158.2	15.6 (OH)	158.5	15.6 (OH)				
12					3′	116.8		115.5		114.7		115.0					
14					4′	133.2	7.78 *d*	133.0	7.74 *d*	132.1	7.70 *d*	131.8	7.77 *d*				
15					5′	110.8	6.84 *d*	120.1	6.79 *d*	111.3	6.58 *d*	110.9	6.74 *d*				
16					6′	160.7		161.3		161.0		159.0					
17					7′	205.1		205.0″		204.2″		204.6					
1′	114.8″		122.5″		8′	26.4″	2.53 *s*	26.3	2.55 *s*	26.3	2.68 *s*	26.2	2.68 *s*				
2′	164.0		147.8		1″	113.1		113.3		114.7							
3′	113.4		128.7		2″	120.9		122.0**		122.8**							
4′	134.3	7.78 *d*	131.0	7.95 *d*	3″	149.1		142.3**		147.6							
5′	109.0	6.49 *d*	120.1	7.31 *d*	4″	118.9	6.97 *d*	111.2	6.85 *d*	120.3	7.02 *d*						
6′	164.0		152.0		5″	121.0	7.17 *d*	120.6	7.20 *d*	120.5	7.08 *d*						
7′	204.9		196.4		6″	143.1		143.2		146.1	7.40 (OH)						
8′	26.6	2.56 *s*	29.0	2.56 *s*	7″	75.6		75.2		72.8							
1″					8″	24.8	2.00 *s*	26.2	1.79 *s*	25.6	1.40 *s*						
2″					1‴	114.1		114.0		115.0							
3″					2‴	157.9		157.8		158.2	15.6 (OH)						
4″					3‴	115.7		116.6		114.7							
5″					4‴	132.6	7.83 *d*	132.4	7.81 *d*	131.8	7.74 *d*						
6″					5‴	111.6	6.80 *d*	111.6	6.47 *d*	111.5	6.45 *d*						
7″					6‴	159.2		159.0		158.2							
8″					7‴	205.1		205.1″		205.2″							
					8‴	26.7	2.57 *s*	26.7	2.58 *s*	26.2	2.68 *s*						
OCH_3												51.6	3.52 *s*				

(**1a**) OCOMe 20.6, 20.7(2), 20.8, 2.06, 2.08, 2.12, 2.30
OCOMe 168.0, 168.4, 168.8, 169.1

* The number of directly attached protons to each individual carbon atom was verified using the DEPT pulse sequence.
† Signals obtained by HMQC, HMBC and NOESY techniques.
‡ Signals obtained by HMQC and HMBC techniques.
§ Data from ref. [3].
″ Signals may be reversed in each column.
** Signals may be revised.



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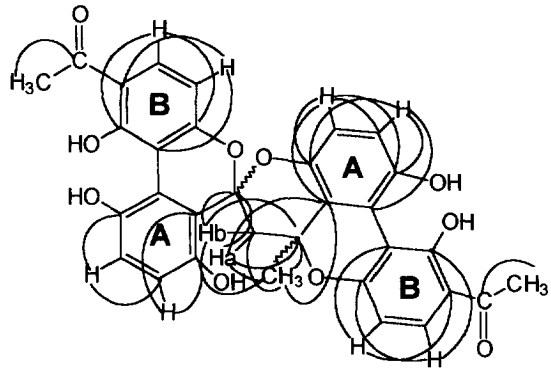

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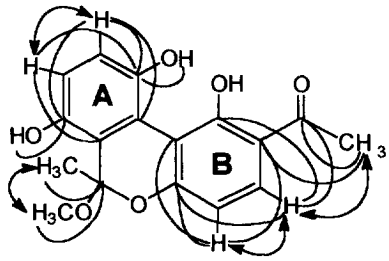

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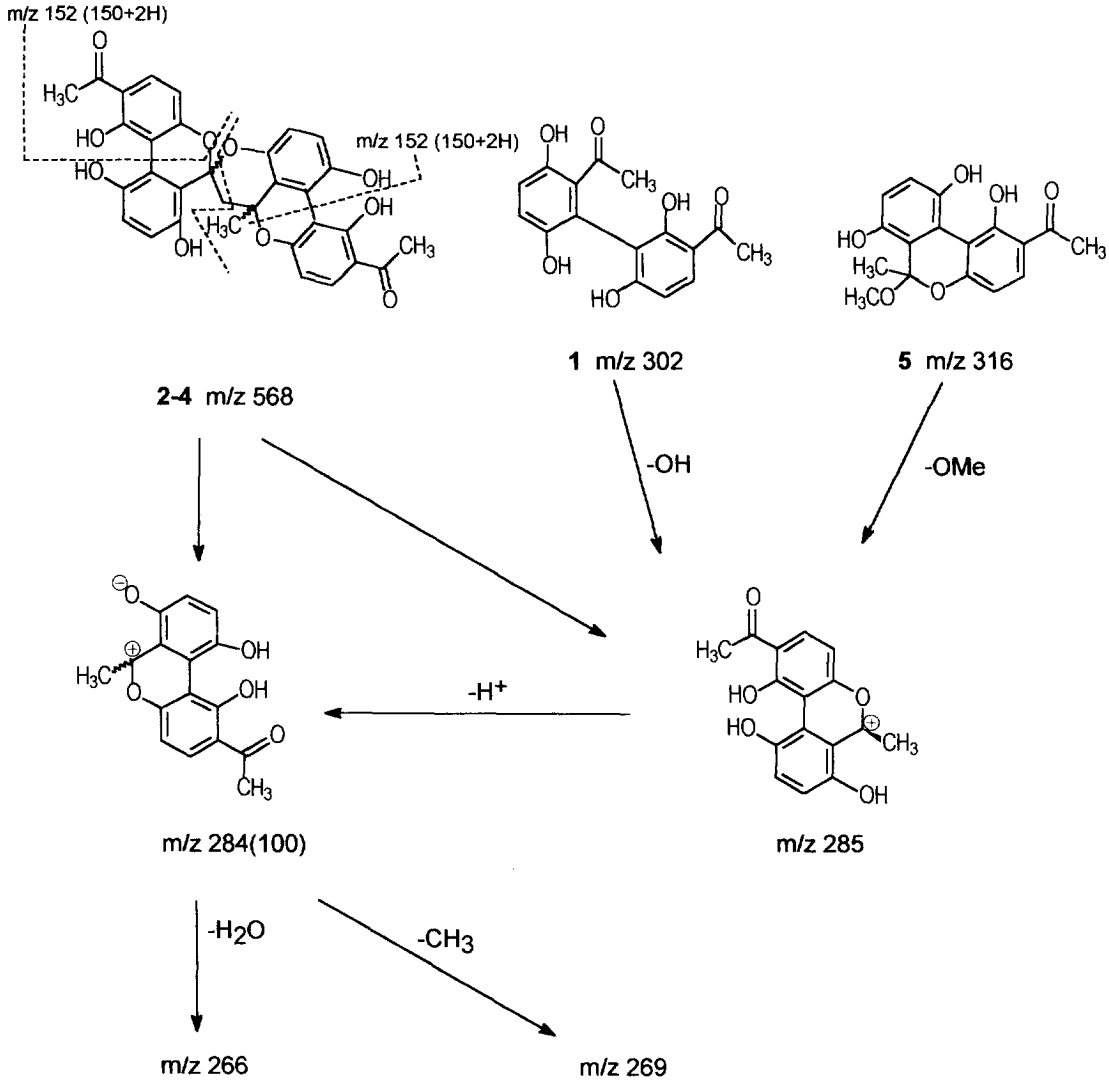
Fig. 1. (——) HMBC of compounds **1**, **2** and **5** and (←——→) NOESY of **5**.



Scheme 1. Mass spectral fragmentation of compounds **1**–**5**.

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