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A New Diels-Alder Type Adduct and a New Flavone from the Stem and Root Bark of *Morus mongolica*

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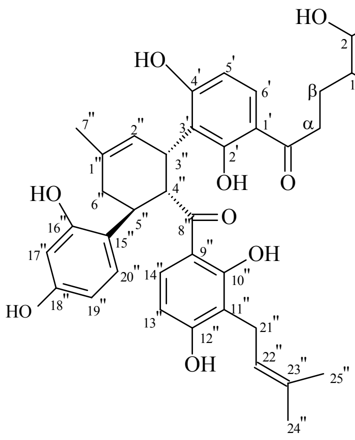
Abstract: A new Diels-Alder type adduct mongolicin G (**1**) and a new flavone 5′-(1″, 1″-dimethylallyl)-5,7,2′,4′-tetrahydroxyflavone (**2**) were isolated from the stem and root bark of *Morus mongolica*. Their structures were determined by spectroscopic analysis and chiroptical methods.

Keywords: *Morus mongolica*, Diels-Alder type adduct, mongolicin G, flavone, 5′-(1″,1″-dimethylallyl)-5,7,2′,4′-tetrahydroxyflavone.

Mulberry tree belongs to the economically and medically important plant in genus *Morus*, because its leaves are an indispensable food for silk worms, and its root barks were used to treat diabetes, arthritis, and rheumatism in Chinese herbal medicine[1]. The genus *Morus* comprises sixteen species and eleven of them in China. Many compounds, such as Diels-Alder type adducts and chalcone derivatives, were isolated from the genus. In an ongoing investigation on the stem and root bark of *Morus mongolica*, two new compounds (**1** and **2)** have been isolated. In this paper, the structural elucidation of the two new compounds was presented.



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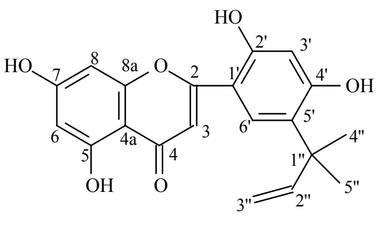

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Table 1 ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectral data for **1** and **2** in acetone-d_6, δ, ppm

NO.	1		HMBC correlations	NO.	2		HMBC correlations
	δ_H	δ_C			δ_H	δ_C	
1		118.4		2		162.6	
2		156.1		3	7.16,s	107.4	C-2,4a,1′
3	6.39,d,(2.5)	102.8	C-1,5	4		182.5	
4		157.1		4a		103.8	
5	6.25,dd,(8.5,2.5)	106.8	C-1,3	5		162.2	
6	6.91,d,(8.5)	130.7	C-2,4,β	6	6.19,d,(2.1)	99.1	C-8,4a
α	3.15, m, 2H	38.5	C-β,C=O	7		165.9	
β	2.84,t,(7.5),2H	25.5	C-1,2,C=O	8	6.43,d,(2.1)	94.2	C-6,4a
C=O		205.3		8a		158.2	
1′		112.6		1′		109.0	
2′		163.0		2′		157.8	
3′		115.5		3′	6.66,s	104.9	C-1′,5′
4′		163.8		4′		160.2	
5′	6.33,d,(9.0)	109.6	C-1′,3′	5′		126.4	
6′	7.69,d,(9.0)	130.7	C-2′,4′,C=O	6′	7.80,s	127.5	C-2,2′,4′,1″
1″		134.1		1″		40.2	
2″	5.67,brs	122.7	C-3′,3″,4″,7″	2″	6.29,dd,(17.4, 10.5)	148.1	C-1″,4″,5″
3″	4.10,brs	31.9	-	3″	4.97,m,2H	109.9	C-1″,2″
4″	4.66,t,(4.5)	46.7	C-2″,3″,6″	4″	1.50,s,3H	26.7	C-1″,5′
5″	3.79,brs	35.9	C-1″,20″	5″	1.50,s,3H	26.7	C-1″,5′
6″	2.50,brd,(18.5) 2.23,m	31.7	C-2″,4″,7″				
7″	1.94,s, 3H	23.2	C-2″,6″				
8″		208.5					
9″		112.4					
10″		164.0					
11″		115.2					
12″		163.5					
13″	6.45,d,(9.0)	107.9	C-9″,11″				
14″	8.38,d,(9.0)	131.4	C-8″,10″,12″				
15″		121.1					
16″		155.8					
17″	6.55,d,(2.0)	103.0	C-15″,19″				
18″		157.3					
19″	6.31,dd,(8.5,2.0)	106.9	C-15″,17″				
20″	6.97,d,(8.5)	128.1	C-5″,16″,18″				
21″	3.28,d,(7.0),2H	21.6	C-10″,12″, 23″				
22″	5.20,t,(7.0)	122.6	C-24″,25″				
23″		130.7					
24″	1.61,s,3H	25.2	C-25″				
25″	1.74,s,3H	17.2	C-24″				

Compound **1** was obtained as yellowish amorphous powder, $[\alpha]_{D}^{25}$ +166 (c 0.091, MeOH). The HR-FAB-MS indicated a molecular ion at *m/z* 680.2629 $[M^{+}]$ (calcd. 680.2621) corresponding to a molecular formula of $C_{40}H_{40}O_{10}$. Its IR spectrum revealed the presence of hydroxy (3315 cm^{-1}), carbonyl (1701 cm^{-1}), and aromatic rings (1616 cm^{-1}). The UV absorptions, maxima at 208 and 287 nm, indicated the presence of a conjugated system in the structure. The ^{1}H and ^{13}C NMR spectral data of **1** exhibited structural feature of a Diels-Alder type adduct. The ^{1}H NMR spectrum of **1** showed signals of a γ, γ-dimethylally group at δ 1.61, 1.74 (s, each 3H), 3.28 (d, 2H, *J* = 7.0 Hz) and 5.20 (t, 1H, *J* = 7.0 Hz) and the following signals of the protons: two double doublets, δ 6.31 (dd, 1H, *J* = 8.5, 2.0 Hz, H-19″) and 6.25 (dd, 1H, *J* = 8.5, 2.5 Hz, H-5); six *ortho* coupled doublets, δ 6.97 (d, 1H, *J* = 8.5 Hz, H-20″), 6.45 (d, 1H, *J* = 9.0 Hz, H-13″), 8.38 (d, 1H, *J* = 9.0 Hz, H-14″), 6.33 (d, 1H, *J* = 9.0 Hz, H-5′), 7.69 (d, 1H, *J* = 9.0 Hz, H-6′), 6.91 (d, 1H, *J* = 8.5 Hz, H-6); two *meta* coupled doublets, δ 6.55 (d, 1H, *J* = 2.0 Hz, H-17″), 6.39 (d, 1H, *J* = 2.5 Hz, H-3); multiplets of ethylene protons, δ 3.15 (m, 2H, H-α), 2.84 (t, 2H, *J* = 7.5 Hz, H-β). These data suggested that **1** comprised two 1,2, 4-trisubstituted and two 1,2,3,4-tetrasubstituted benzene rings and an ethylene group moieties. The ^{13}C NMR spectrum revealed the presence of 10 aliphatic carbons besides 30 aromatic and olefinic carbons. All the ^{1}H and ^{13}C NMR assignments together with the HMBC correlations were listed in **Table 1**. Comparison of ^{1}H and ^{13}C NMR data of **1** with those of kuwanon J[2] revealed the structure of **1** was same as the latter, except for an α, β saturated ketone in **1**, instead of an α, β unsaturated ketone in kuwanon J. The HMBC correlations also supported the structure of **1** as illustrated. The 3″-4″-*cis*, 4″-5″-*trans* relative configuration on the methycyclohexene-substituted ring was assigned by the coupling constant ($J_{3''\mathrm{H}\text{-}4''\mathrm{H}} = J_{4''\mathrm{H}\text{-}5''\mathrm{H}} = 4.5$ Hz)[2] and the positive optical rotation[3]. What′s more, the absolute configuration of compound **1**was 3″*S*, 4″*R*, 5″*S* with positive Cotton effect at 280 nm[3].

Compound **2** was obtained as yellowish powder. The molecular formula of **2** was determined by HR-EI-MS at *m/z* 354.1110 [M^{+}] (calcd. 354.1103) corresponding to a molecular formula of $C_{20}H_{18}O_6$. The IR spectrum of **2** showed absorption bands at 3434, 1653 and 1616 cm^{-1} assignable to hydroxyl, conjugated carbonyl and benzene ring. The ^{1}H NMR spectrum of **2** exhibited signals of an α, α-dimethylally group at δ 1.50 (s, 6H), 4.97 (m, 2H) and 6.29 (dd, 1H, *J* = 17.4, 10.5 Hz) and the following signals of the protons: two *meta* coupled doublets, δ 6.19 (d, 1H, *J* = 2.1 Hz, H-6), 6.43 (d, 1H, *J* = 2.1 Hz, H-8); three single signals, δ 6.66 (s, 1H, H-3′), 7.80 (s, 1H, H-6′) and 7.16 (s, 1H, H-3). The ^{13}C NMR spectrum revealed the presence of 3 aliphatic carbons besides 17 aromatic and olefinic carbons. Total ^{1}H and ^{13}C NMR assignments together with the HMBC correlations were listed in **Table 1**. In the HMBC spectrum, CH long-range correlations revealed an α, α-dimethylally group at C-5′. Thus, compound **2** was assigned as 5′-(1″,1″-dimethylallyl)-5,7,2′,4′-tetrahydroxyflavone.

Acknowledgments

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