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Studies on the Structure of Kansuinine A from *Euphorbia kansui*

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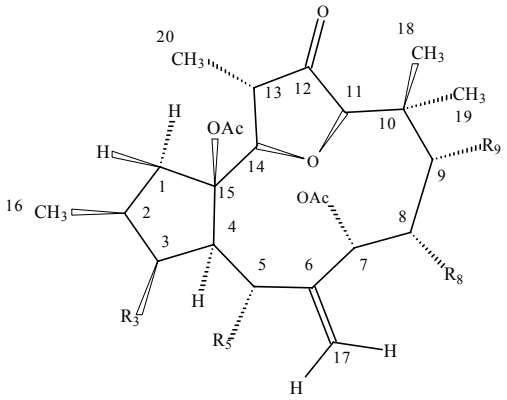
Abstract: Kansuinine A is a macrocyclic jatrophane diterpene that was isolated from *Euphorbia kansui*. Further investigation of the structure was revealed that the benzoyl group located at C-8 and the position of C-3 was the present of an acetyl group by means of HMQC, HMBC spectra.

Keywords: *Euphorbia kansui*, kansuinine A.

Euphorbia kansui is a famous chinese traditional medicine which containing the toxic and analgesic compounds, kansuinine A and B have been isolated from the root. Kansuinine A **1** is a jatrophane diterpene that had been elucidated by Hirata[1] and Uemura[2] with the chemical and spectroscopic means. The skeleton and stereostructure was determined, but the substituting groups at C-3, C-5, C-8 and C-9 were not proved. We reinvestigated the structure with HMQC, HMBC, ^{1}H-^{1}H COSY and NOESY spectra that showed the benzoyl at C-8, three acetyl groups at C-3, C-5 and C-9 respectively. The structure of kansuinine A was revised as **2**. In this paper the revised structure of kansuinine A **2** was described.

Figure 1 The structure of kansuinine A



1 R_3, R_5, R_8, R_9=3*OAc, 1*OBz
2 R_3=R_5=R_9=OAc, R_8=OBz

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Dried roots of *E. kansui* were extracted with 95% EtOH three times under reflux. The extract was condensed and dissolved in water, then partitioned successively with petroleum ether and EtOAc. The EtOAc extract was subjected to a silica gel column chromatography to yield **2**.

Table 1 ^{1}HNMR ^{13}CNMR HMBC and NOESY spectral data for kansuinine A **2** ($CDCl_3$, δ (J=Hz))

atom	^{1}H	^{13}C	^{1}H-^{1}HCOSY	HMBC	NOESY
1α	2.64dd(14.0,6.5)	40.0t	H-2,1β	C-2,4,3,15,14	H-20,2
1β	2.24d(14.0)		H-1α	C-16,2,15,14	H-16
2	2.11m	39.1d	H-16,1α,3	C-1,15,4	H-1α,4,3
3	5.59d(3.0)	74.4d	H-2,4	C-1,15,5	H-2,4
4	2.96br.s	51.8d	H-3,5		H-2,3
5	6.14br.s	69.8d	H-4,17a	C-4,7,3,15,6,5-OCO-	H-8,7,3-OAc
6		146.0s			
7	6.43s	68.5d	H-17a,17β,8	C-8,9,6,7-OCO-	H-8,5
8	6.03s	71.1d	H-7	C-10,9,6,8-OCO-	H-18,9,5,7
9	5.07s	82.4d		C-18,19,10,7,8,11,9-OCO-	H-18,8
10		41.5s			
11	4.13s	77.4d		C-18,19,10,9,12	H-19
12		213.3s			
13	2.31m	50.9d	H-20	C-20,15,14,12	
14		106.3s			
15		90.5s			
16	0.92d(6.5)	13.3q	H-2	C-1,3	H-1β,3-OAc
17α	5.22br.s	110.3t	H-17β,5,7	C-7	5-OAc
17β	5.13br.s		H-17α,7		H-17α
18	1.29s	18.7q		C-19,10,11,9	H-9,8
19	1.14s	22.1q		C-18,10,11,9	H-11
20	1.31d(7.0)	9.2q	H-13	C-13,14,12	H-1a
3-OAc		169.1s			H-16(Me)
	1.99s	21.9q		3-OCO-	
5-OAc		168.7s			
	1.95s	20.8q		5-OCO	
7-OAc		170.4s			
	2.17s	21.0q		7-OCO-	
8-OBz		165.3s			
1′		130.3s			
2′, 6′	8.04d(7.5)	128.3d	H-3′, 5′	C-3', 5', 8-OCO-	H-3′, 5′
3′, 5′	7.48t(7.5)	129.9d	H-2′, 6′, 4′	C-2', 6', 4', 8-OCO-	H-2′, 6′
4′	7.54t(7.5)	132.9d	H-3′, 5′	C-3', 5'	
9-OAc		169.5s			
	2.07s	20.4q		9-OCO-	
15-OAc		170.0s			
	2.09s	21.2q		15-OCO-	

Kansuinine A **2** obtained as colorless crystals, mp 200-202°C, [α]+29 (*c* 0.25, EtOH), and its formula $C_{37}H_{46}O_{15}$ (required:730.2843, found:730.2840) was determined by high-resolution mass spectrometry. In ^{1}H-NMR and HMQC spectral data were identical with those of **1** which showed the present of one benzoyl, five acetyls and one hydroxyl group. From HMBC and NOESY spectra, the skeleton of kansuinine A **2** was the same as that of **1**. The signal at δ 6.03 correlated with C-6 (δ 146.0), C-9(δ 82.4) and C-10(δ 41.5) and the carbonyl carbon (δ 165.3) of a benzoyl group respectively in

HMBC spectrum. So the signal at δ 6.03 was assigned as H-8 and the benzoyl group existed at C-8. In addition, the NOE effect was observed between C_{16}-Me (δ 0.92) and a acetyl group (δ 1.99) showing the present of a acetyl group at C-3 (**Table 1**). Therefore, the structure of kansuinine A was concluded to be **2**.

References

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