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FOUR SESQUITERPENES FROM THE INSECTICIDAL PLANT *CELASTRUS ANGULATUS*

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Key Word Index—*Celastrus angulatus*; Celastraceae; sesquiterpenes; dihydro-β-agarofuran derivatives; insect antifeedant.

Abstract—The structures of four new highly esterified sesquiterpenes isolated from the insecticidal plant *Celastrus angulatus* were elucidated on the basis of spectral analysis, including 2D-NMR spectroscopy, especially long range ^{1}H–^{13}C correlation.

INTRODUCTION

Celastrus angulatus Maxim. has been used as a natural insecticide for a long time in China [1]. We recently reported on the isolation of 15 new sesquiterpenes based on the dihydro-β-agarofuran skeleton from this plant, and antifeedant effects against some insects were shown [2–7]. In recent years, compounds of this type have also attracted interest as a consequence of their cytotoxic and antitumour promoter activities [8–11]. Further investigation of *C. angulatus* has led to the isolation of four new sesquiterpenes (**1**–**4**). In the structural elucidation of these sesquiterpenes, it is difficult to determine the linkage sites of the respective ester groups because more than three kinds of acids are involved in ester formation. This problem can be solved conveniently by using long range ^{1}H–^{13}C correlation (COLOC) techniques.

RESULTS AND DISCUSSION

The chloroform fraction of the acetone extract of the root-bark of *C. angulatus* was subjected to repeated chromatography (CC and HPLC) to afford compound **1**. Its IR spectrum revealed the characteristic absorptions of ester carbonyl at 1730 cm^{-1} and hydroxyl at 3500 cm^{-1}. The mass spectrum exhibited peaks due to the loss of methyl, acetic acid and isobutyric acid units: *m/z* 679 $[M - Me]^+$, 634 $[HOAc]^+$ and 606 $[(M - C_3H_7COOH)]^+$. It contained also fragmentation ions attributable to the presence of furoylate (*m/z* 95), isobutyrate (*m/z* 71) and acetate (*m/z* 43) groups [12]. The ^{1}H and ^{13}C NMR spectra (Table 1) indicated the presence of six ester groups (ester carbonyls at δ160.9, 169.4, 169.6, 169.7, 175.6 and 176.8): three acetate esters (δ_H 1.85, 1.63, 1.56; δ_C 21.4, 21.1, 20.5), one furoylate ester (δ_H 7.94 *s*, 6.62 *bs*, 6.78 *bs*; δ_C 149.0, 118.0, 109.8, 144.0) and two isobutyrate esters (δ_H 1.29 *d*, 1.28 *d*, 1.24 *d*, 1.20 *d*, 2.67 *m*, 2.78 *m*; δ_C 19.0, 19.0, 34.1, 18.9, 18.7, 34.0). In addition, the ^{13}C NMR spectrum showed signals attributed to three methyls (δ29.6, 25.5, 24.5), two methylenes (δ65.5, 42.1), six oxygenated methines (δ68.1–75.6) and four quaternary carbons (δ91.5, 83.5, 70.0, 54.1). The ^{1}H NMR spectrum contained signals assignable to protons on the carbon atoms carrying the five secondary ester groups, i.e. δ6.42 (1H, *s*, H-6), 5.99 (1H, *s*, H-9), 5.82 (2H, *m*, H-1, 2), 5.60 (1H, *d*, J = 2.8 Hz, H-8) and a primary ester group, i.e. δ5.21, 5.02 (2H, AB_q, J = 12.7 Hz, H-11a, b) on the basis of the multiplicity and the ^{1}H–^{1}H COSY spectrum. These data suggested that **1** is a dihydro-β-agarofuran sesquiterpene substituted with six ester groups.

The positions of the ester groups were established unambiguously by using COLOC experiments. The carbonyl ^{13}C signal at δ160.9 showed long range correlations with the ^{1}H signals at δ5.99 (H-9) and 6.62 (H-4′). Thus, the furoyl group must be located on C-9. The long range couplings of the carbonyl signals at δ169.4, 169.6 and 169.7 with the proton signals at δ6.42 (H-6) and 5.82 (H-1, 2) and the acetyl methyl signals at δ1.85, 1.63 and 1.56 indicated the presence of acetyl groups on C-6, C-1 and C-2. The last two carbonyl ^{13}C signals at δ175.6 and 176.8 were correlated with the ^{1}H signals at δ5.60 (H-8), 2.67 (H-22), 1.29 (H-20), 1.24 (H-21) and 5.21, 5.02 (H-11a, b), 2.78 (H-18), 1.28 (H-16) and 1.20 (H-17), respectively. Thus, the two isobutyryl groups had to be situated on

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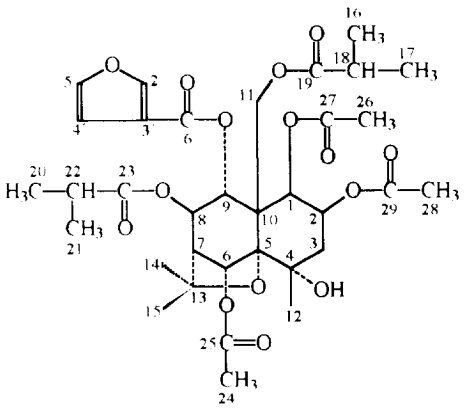

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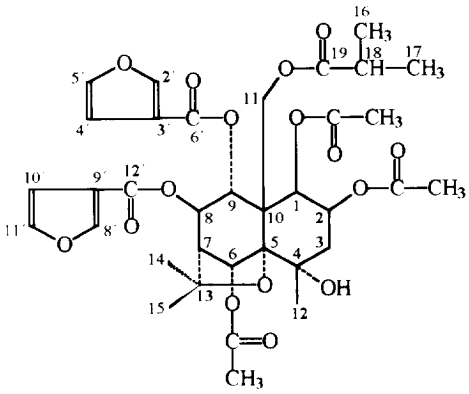

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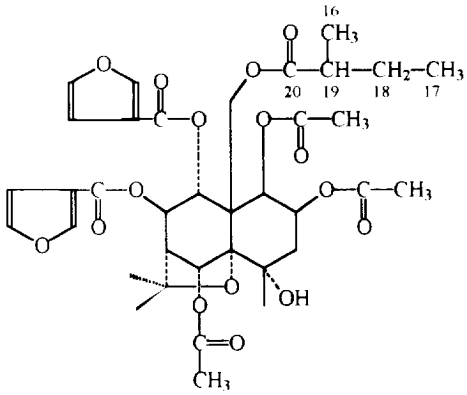

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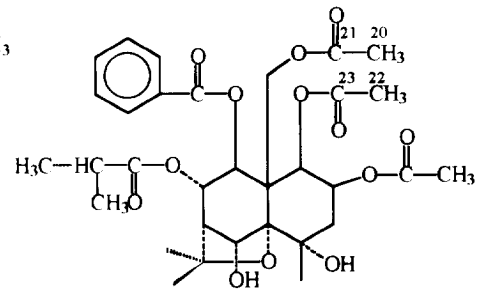

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C-8 and C-11. Therefore, a planar structure for **1** was established.

The relative stereochemistry of **1** was confirmed via the NOE difference spectra. When the H-11b signal was irradiated, an increase (16.3%) of the H-6 signal intensity and an increase (6.28%) of the H-12 signal intensity occurred. On irradiation of the H-1 and H-2 signal, the intensity of the H-3_{ax} signal was increased, while on irradiation of the H-11a signal, the intensity of the H-9 signal was increased (6.9%). In the ^{1}H NMR spectrum of **1**, H-9 appeared as singlet. This is due to the angle 8α, 9β adjacent to 90° as reported in the literature [13]. These results indicated that the orientations of the protons attached to the oxygen-bearing carbon atoms were H-1_{ax}, H-2_{eq}, H-6_{ax}, H-8_{eq} and H-9_{eq}. Considering the above data for **1** the structure was elucidated to be 1β, 2β,6α-triacetoxy-4α-hydroxy-8β,11-diisobutyryloxy-9α-furoyloxydihydro-β-agarofuran.

Compound **2** was found to be spectroscopically similar to **1**. Its spectral data (Table 2) suggested the presence of three acetate esters, two furoylate esters and one isobutyrate ester and the 1β, 2β, 6α, 8β, 9α,11-hexaesterified dihydro-β-agarofuran parent. Close comparison of the ^{1}H and ^{13}C NMR spectra of **1** and **2** clearly revealed the furoylate at C-8 of **2** replacing an isobutyrate of **1**. In the same way as in **1** (COLOC experiment), the positions of the three acetate esters were shown to be situated at C-1, C-2 and C-6, the two furoylate esters at C-8 and C-9, and the one isobutyrate ester at C-11, respectively. Thus, the structure of **2** is 1β,2β,6α-triacetoxy-4α-hydroxy-8β,9α-difuroyloxy-11-isobutyryloxydihydro-β-agarofuran.

Compound **3** was found to be spectroscopically very similar to **2**. Close examination of the ^{1}H NMR spectrum of **3** clearly revealed the absence of an isobutyroyl function at C-11, as did the ^{13}C NMR data when compared with those for **2**. It was replaced by a 3-methyl-isobutyroyl group. All the remaining spectroscopic features of **3** were consistent with **2**. So, the structure of **3** was established to be 1β,2β,6α-triacetoxy-4α-hydroxy-8β, 9α-difuroyloxy-11-(3-methyl) isobutyroyloxydihydro-β-agarofuran.

Compound **4** was assigned as 1β,2β,11-triacetoxy-4α,6α-dihydroxy-8α-isobutyryloxy-9β-benzoyloxy-dihydro-β-agarofuran based on the followig data. The IR spectrum showed hydroxyl and ester group bands. The mass spectrum exhibited peaks due to the losses of methyl and acetic acid units: *m/z* 619 $[M - Me]^+$ and 574 $[HOAc]^+$ and fragmentation ions attributable to the presence of benzoate (*m/z* 105), isobutyrate (*m/z* 71) and acetate (*m/z* 43) groups: one benzoate ester [δ_H 7.83 *d*, 7.53 '*t*', 7.39 '*t*'; δ_C 128.7 (2 × CH), 129.5 (1 × C, 2 × CH), 133.4 (CH) and 165.8 (ester carbonyl)], one

Table 1. ^1H and ^{13}C NMR spectral data for compound **1** (in C_6D_6)

H	δ	J(Hz)	^1H–H COSY correlation with	C	δ (DEPT)	^3H–^{13}C COSY correlation with	Significant COLOC correlation with
1	5.82 *m*			1	68.1 (CH)*	H-1	
2	5.82 *m*		H-3a, b	2	70.8 (CH)*	H-2	
3a	2.03 *m*		H-3b/H-2	3	42.1 (CH_2)	H-3a, b	
3b	1.80 *m*		H-3a/H-2				
4				4	70.0 (C)		
5				5	91.5 (C)		
6	6.42 *s*		H-7 (w)	6	75.6 (CH)	H-6	
7	2.41 *d*	2.8	H-6 (w)/H-8	7	53.1 (CH)	H-7	
8	5.60 *d*	2.8	H-7/H-9 (w)	8	76.1 (CH)	H-8	
9	5.99 *s*		H-8 (w)	9	71.5 (CH)	H-9	
10				10	54.1 (C)		
11a	5.21 *d*	12.7	H-11b	11	65.6 (CH_2)	H-11a,b	
11b	5.02 *d*	12.7	H-11a				
12	1.43 *s*			12	29.6 (CH_3)	H-12	
13				13	83.5 (C)		
14	1.52 *s*			14	25.5 (CH_3)	H-14	
15	1.27 *s*			15	24.5 (CH_3)	H-15	
Fu							
2′	7.94 *s*		H-4′/H-5′	2′	149.0 (CH)	H-2′	
3′				3′	118.0 (C)		
4′	6.62 *bs*		H-2′/H-5′	4′	109.8 (CH)	H-4′	
5′	6.78 *bs*		H-2′/H-4′	5′	144.0 (CH)	H-5′	
6′				6′	160.9 (C)		H-9/H-4′
Bu							
16	1.28 *d*	7	H-18	16	19.0 (CH_3)	H-16	
17	1.20 *d*	7	H-18	17	19.0 (CH_3)	H-17	
18	2.78 *m*		H-16/H-17	18	34.1 (CH)	H-18	
19				19	176.8 (C)		H-11a, b/H-16, 17, 18
20	1.29 *d*	7	H-22	20	18.9 (CH_3)	H-20	
21	1.24 *d*	7	H-22	21	18.7 (CH_3)	H-21	
22	2.67 *m*		H-20/H-21	22	34.0 (CH)	H-22	
23				23	175.6 (C)		H-8/H-20, 21, 22
Ac							
24	1.85 *s*			24	21.4 (CH_3)	H-24	
25				25	169.4 (C)		H-6/H-24
26	1.63 *s*			26	21.1 (CH_3)	H-26	
27				27	169.6 (C)		H-1 (or H-2)/H-26
28	1.56 *s*			28	20.5 (CH_3)	H-28	
29				29	169.7 (C)		H-2 (or H-1)/H-28

*Assignments in the same vertical column may be reversed.
w: weak.

isobutyrate ester [δ_H0.87 *d*, 0.99 *d*, 2.32 *m*; δ_C18.5 (CH_3), 18.6 (CH_3), 34.1 (CH)] and three acetate esters [δ_H2.32 *s*, 2.06 s, 2.03 *s*; δ_C21.5 (CH_3), 21.0 (CH_3), 20.5 (CH_3)]. In addition, the ^{13}C NMR spectrum showed signals attributed to the remaining skeletal moiety: three methyls (δ24.3, 26.3 and 30.1), two methylenes (δ41.3 and 61.5), six methines (δ53.8, 67.5, 73.5, 75.0, 75.5 and 76.7) and four quaternary carbons (δ50.8, 72.2, 84.6 and 91.6). Thus, **4** is also a polyester dihydro-β-agarofuran sesquiterpene. On the basis of the multiplicity and the ^1H–^1H COSY spectrum, the signals at δ6.04, 5.60, 5.44, 5.36, 5.20, 4.76, 4.71 and 2.57 in the ^1H NMR spectrum of **4** were assigned to H-9, H-8, H-1, H-2, H-6, H-11a, b and H-7, respectively. The shifts of H-3, whose signals overlapped in the ^1H NMR spectrum, were ascertained by correlation with H-2. The relative stereochemistry of compound **4** was determined as H-1_{eq}, H-2_{eq}, H-6_{ax}, H-8_{ax} and H-9_{ax} according to the coupling constants of each proton ($J_{1,2}$ = 3.4 Hz, $J_{7,8}$ = 3.1 Hz, $J_{8,9}$ = 9.8 Hz) and by comparison with the data for angulatueoids A–D isolated from the same plant and for which X-ray data were available [4]. In order to determine the location of the ester groups, the COLOC spectrum of compound **4** was measured. Cross peaks were observed between the carbonyl carbon at δ165.8 and δ6.04 (H-9) and 7.83 (H-2′, 6′), and thus the benzoyl group must be located on

Table 2. ^1H and ^{13}C NMR spectral data for compound **2** (in $CDCl_3$)

H	δ	J(Hz)	^1H–^1H COSY correlation with	C	δ (DEPT)	^1H–^{13}C COSY correlation with	Significant COLOC correlation with
1	5.52 *m*			1	70.4 (CH)*	H-1	
2	5.52 *m*		H-3a, b	2	68.1 (CH)*	H-2	
3a	1.94 *m*		H-2/H-3b	3	42.1 (CH_2)	H-3	
3b	2.20 *m*		H-2/H-3a				
4				4	70.0 (C)		
5				5	91.4 (C)		
6	6.34 *s*		H-7	6	75.7 (CH)	H-6	
7	2.45 *d*	2.8	H-6/H-8	7	53.6 (CH)	H-7	
8	5.43 *d*	2.8	H-7	8	76.2 (CH)	H-8	
9	5.73 *s*			9	70.1 (CH)	H-9	
10				10	54.4 (C)		
11a	4.96 *d*	13	H-11b	11	66.0 (CH_2)	H-11	
11b	4.76 *d*	13	H-11a				
12	1.57 *s*			12	29.7 (CH_3)	H-12	
13				13	83.4 (C)		
14	1.68 *s*			14	25.5 (CH_3)	H-14	
15	1.46 *s*			15	24.8 (CH_3)	H-15	
Fu							
2′	8.19 *s*		H-4′/H-5′	2′	148.9 (CH)	H-2′	
3′				3′	118.6 (C)		
4′	6.83 *s*		H-2′/H-5′	4′	109.8 (CH)	H-4′	
5′	7.44 *s*		H-2′/H-4′	5′	143.9 (CH)	H-5′	
6′				6′	160.5 (C)		H-9
8′	7.99 *s*		H-10′/H-11	8′	148.7 (CH)	H-8′	
9′				9′	118.4 (C)		
10′	6.72 *s*		H-8′/H-11′	10′	109.8 (CH)	H-10′	
11′	7.41 *s*		H-8′/H-10′	11′	143.9 (CH)	H-11′	
12′				12′	161.4 (C)		H-8
Bu							
16	1.12 *d*	7	H-18	16	18.4 (CH_3)	H-16	
17	1.05 *d*	7	H-18	17	18.4 (CH_3)	H-17	
18	2.56 *m*		H-17/H-17	18	34.0 (CH)	H-18	
19				19	176.7 (C)		H-11/H-16, 17, 18
Ac							
20	2.17 *s*				21.4 (CH_3)	H-20	
21	2.12 *s*				21.1 (CH_3)	H-21	
22	1.66 *s*				20.5 (CH_3)	H-22	
					169.7 (C)		H-1/H-2/H-6 and
					169.7 (C)		H-20, 21, 22
					169.7 (C)		

*Assignments in the same vertical column may be reversed.

C-9. The long range coupling of the carbonyl signals at δ169.4, 169.5 and 170.2 with the proton signals at δ5.36 (H-2), 5.44 (H-1), 4.76 and 4.71 (H-11a,b) and the acetyl methyl signals at δ2.06, 1.53 and 2.32 indicated the presence of acetyl groups on C-2, C-1 and C-11. The last carbonyl carbon at δ175.9 was correlated with the proton signals at δ5.60 (H-8), 0.87 (H-16), 0.99 (H-17) and 2.32 (H-18). Thus, this isobutyryl group had to be situated on C-8. It left only one oxygenated sp^3-carbon atom (C-6), which must bear a hydroxyl group. Therefore, the structure was established as **4**.

Compounds bearing these ester groups and having H-1_{ax}, H-2_{eq}, H-6_{ax}, H-8_{eq} and H-9_{eq} stereochemistry have not been reported earlier. Some related sesquiterpenes [14–17] have been reported from the Celastraceae. However, compounds **1–4** are different from the formerly isolated compounds both in substitution pattern and stereochemistry.

EXPERIMENTAL

Celastrus augulatus Maxim. was collected in Kunming. A voucher specimen is deposited in the Herbarium of Kunming Institute of Botany, Academia Sinica.

General. 1D NMR: 400 MHz (^1H) and 125 MHz (^{13}C); 2D NMR: 500 MHz (^1H) and 125 MHz (^{13}C). MS: Finnigan MAT 90.

Table 3. ^1H and ^{13}C NMR spectral data for compound **3** (in $CDCl_3$)

H	δ	J(Hz)	C	δ (DEPT)
1	5.52 *m*		1	70.7 (CH)*
2	5.52 *m*		2	68.1 (CH)*
3a	2.20 *m*		3	42.2 (CH_2)
3b	1.94 *m*			
4			4	70.0 (C)
5			5	91.4 (C)
6	6.31 *s*		6	75.7 (CH)*
7	2.45 *d*	2.9	7	53.6 (CH)
8	5.43 *d*	2.9	8	76.1 (CH)*
9	5.71 *s*		9	70.3 (CH)*
10			10	54.4 (C)
11a	4.93 *d*	12.6	11	65.2 (CH_2)
11b	4.77 *d*	12.6		
12	1.57 *s*		12	29.7 (CH_3)
13			13	83.4 (C)
14	1.65 *s*		14	25.6 (CH_3)
15	1.47 *s*		15	24.6 (CH_3)
Fu				
2′	8.20 *s*		2′	148.9 (CH)
3′			3′	118.9 (C)
4′	6.83 *d*	1.7	4′	110.0 (CH)
5′	7.44 *d*	1.7	5′	143.9 (CH)
6′			6′	160.6 (C)
8′	8.00 *s*		8′	148.8(CH)
9′			9′	118.2 (C)
10′	6.72 *d*	1.6	10′	109.8 (CH)
11′	7.41 *d*	1.6	11′	143.9 (CH)
12′			12′	160.6 (C)
MeBu				
16	1.10 *d*	7.0	16	16.6 (CH_3)
17	0.75 *t*	7.4	17	11.4 (CH_3)
18	1.38 *m*		18	26.5 (CH_3)
19	2.45 *m*		19	41.2 (CH)
20			20	176.5 (C)
Ac				
	2.11 *s*			21.4 (CH_3)
	2.03 *s*			21.1 (CH_3)
	1.64 *s*			20.6 (CH_3)

*Assignments in the same vertical column may be reversed.

Isolation of sesquiterpenes. The air-dried and powdered root-bark (2 kg) of *C. angulatus*, collected in Kunming, was extracted with Me_2CO at room temp. The Me_2CO exact (354 g) was extracted (×4) with $CHCl_3$. The $CHCl_3$ extract was partitioned against 2 l petrol–MeOH–H_2O (30:20:1). The aq. layer was concd *in vacuo* to give a yellow residue (70 g). The residue was dissolved in $CHCl_3$, passed through a column of neutral alumina, then concd to give 50 g of residue. 10 g of this residue was chromatographed on a silica gel column eluting with petrol–Et_2O (1:1), Et_2O and EtOAc. A subfr. of the petrol–Et_2O (1:1) eluant which was negative against Dragendorff's reagent, was subjected to HPLC (RP-18, MeOH–H_2O, 3:1, 1.0 ml min^{-1}, RI detector) and further purified by HPLC (diol, *n*-hexane–EtOAc, 3:1, 1.8 ml min^{-1}, RI detector) to afford compounds **1** (12 mg), **2** (9 mg), **3** (4 mg) and **4** (7 mg).

1β, 2β, 6α-*Triacetoxy*-4α-hydroxy-*hydroxy*-8β,11-*diisobutyryoxy*-9α-*furoyloxydihydro*-β-*agarofuran* (**1**). Amorphous; $[\alpha]_D$: −17° (*c* 0.45, $CHCl_3$); IR ν cm^{-1} (KBr): 3500 (*br*), 1730, 1380, 1230; EIMS (rel. int.): *m/z* 679 (1.8), 634 (5.4), 606 (10.2), 574 (6.2), 488 (7.9), 192 (49), 95 (100), 71 (34.6), 43 (74.6); ^1H and ^{13}C NMR: Table 1.

1β, 2β, 6α-*Triacetoxy*-4α-*hydroxy*-8β,9α-*difuroyloxy*-11-*isobutyryloxydihydro*-β-*agarofuran* (**2**). Amorphous; $[\alpha]_D$: −17° (*c* 0.38, $CHCl_3$); IR ν cm^{-1} (KBr): 3500 (*br*), 1730, 1380, 1230; EIMS *m/z*: 564, 546, 532, 461, 392, 305, 244, 192, 95; ^1H and ^{13}C NMR: Table 2.

1β, 2β, 6α-*Triacetoxy*-4α-*hydroxy*-8β,9α-*difuroyloxy*-11-(3-*methyl*)*isobutyryloxydihydro*-β-*agarofuran* (**3**). Amorphous; $[\alpha]_D$: 15° (*c* 0.18, $CHCl_3$); CIMS *m/z* (rel. int.): 733 $[M+1]^+$ (15.7), 732 (13.3), 672 (96.7), 620 (100), 612 (83.1), 578 (43.4), 560 (29.9), 500 (27.1), 192 (67.4), 95 (85), 57 (30.3); ^1H and ^{13}C NMR: Table 3.

1β, 2β, 11-*Triacetoxy*-4α,6α-*dihydroxy*-8α-*isobutyryloxy*-9β-*benzoyloxydihydro*-β-*agarofuran* (**4**). Amorphous; $[\alpha]_D$: −9° (*c* 0.23, $CHCl_3$); IR ν cm^{-1} (KBr): 3500 (*br*), 1730, 1380, 1280, 1230, 710; EIMS *m/z*: 619, 574, 546, 244, 202, 164, 105, 71, 43; ^1H and ^{13}C NMR: Table 4.

Table 4. ^1H and ^{13}C NMR spectral data for compound **4** (in $CDCl_3$)

H	δ	J(Hz)	^1H–H COSY correlation with	C	δ (DEPT)	^1H–^{13}C COSY correlation with	Significant COLOC correlation with
1	5.63 *d*	3.4	H-2	1	67.5 (CH)	H-1	
2	5.44 *q*	3.4	H-1/H-3	2	75.0 (CH)	H-2	
3	2.01 *m*		H-2	3	41.3 (CH_2)		H-3
4				4	72.2 (C)		
5				5	91.6 (C)		
6	5.20 *s*			6	76.7 (CH)	H-6	
7	2.57 *d*	3.1	H-8	7	53.8 (CH)	H-7	
8	5.60 *dd*	9.8, 3.1	H-7/H-9	8	73.5 (CH)	H-8	
9	6.04 *d*	9.8	H-8	9	75.5 (CH)	H-9	
10				10	53.8 (C)		
11a	4.76 *d*	12.7	H-11b	11	61.5 (CH_2)	H-11	

Continued overleaf

Table 4 *Continued*

H	δ	J(Hz)	^{1}H–H COSY correlation with	C	δ (DEPT)	^{1}H–^{13}C COSY correlation with	Significant COLOC correlation with
11b	4.71 *d*	12.7	H-11a				
12	1.70 *s*			12	30.1 (CH_3)	H-12	
13				13	84.6 (C)		
14	1.76 *s*			14	26.3 (CH_3)	H-14	
15	1.59 *s*			15	24.3 (CH_3)	H-15	
Bz							
1′				1′	129.5(C)		
2′, 6′	7.83 *bd*	7.8	H-3′, 4′, 5′	2′, 6′	129.5 (CH)	H-2′, 6′	
4′	7.53 *t*	7.2	H-2′, 3′ 5′ 6′	4′	133.4 (CH)	H-4′	
3′, 5′	7.39 *t*	7.8	H-2′, 4′, 6′	3′, 5′	128.7 (CH)	H-3′, 5′	
7′				7′	165.8 (C)		H-9/H-2′, 6′
iBu							
16	0.87 *d*	7	H-18	16	18.5 (CH_3)	H-16	
17	0.90 *d*	7	H-18	17	18.6 (CH_3)	H-17	
18	2.32 m		H-16/H-17	18	34.1 (CH)	H-18	
19				19	175.9 (C)		H-8/H-18/H-16, 17
Ac							
20	2.32 s			20	21.5 (CH_3)	H-20	
21				21	170.2 (C)		H-11a, b/H-20
22	2.06 *s*			21	21.0 (CH_3)	H-22	
23				23	169.4 (C)		H-1/H-22
24	1.53 *s*			24	20.5 (CH_3)	H-24	
25				25	169.5 (C)		H-2/H-24

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