Pergamon

PII: S0031-9422(97)01109-6

Phytochemistry, Vol. 48, No. 3, pp. 519–524, 1998

Printed in Great Britain
0031-9422/98 $19.00+0.00

EREMOPHILANE SESQUITERPENES FROM *CACALIA ROBOROWSKII*

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(*Received in revised form* 23 *September* 1997)

Key Word Index—*Cacalia roborowskii*; Compositae; eremophilane sesquiterpenes.

Abstract—Nine new eremophilane sesquiterpenes were isolated from the methanol extract of the roots of *Cacalia roborowskii*. They were identified as 8β,10β-dihydroxy-6β-methoxyleremophilenolide, 3β-acetoxyl-8β,10β-dihydroxy-6β-methoxyeremophilenolide, 3β-angeloyloxy-8β,10β-dihydroxy-6β-methoxyeremophilenolide, 3β-(2-methylbutyryloxy)-8β,10β-dihydroxy-6β-methoxyeremophilenolide and 8β-hydroxy-6β-methoxyeremophil-7(11),9-dien-8,12-olide, 8-oxo-eremophila-6,9-dien-12-oic acid, 3β-acetoxyl-8-oxo-eremophila-6,9-dien-12-oic acid, 3β-angeloxyl-8-oxo-eremphila-6,9-dien-12-oic acid and 3β-(2-methylbutyryloxyl)-8-oxo-eremophila-6,9-dien-12-oic acid, respectively, based on 1D and 2D NMR experiments.

INTRODUCTION

The genus *Cacalia* belongs to the tribe Senecioneae with more than 60 species occurring in China [1], of which ca 26 have long been used as Chinese traditional folk herbs [2]. Several species of genus *cacalia* have been investigated due to their antioxidant, antiradical and anti-histamine activities [3]. The presence of pyrrolizidine alkaloids and sesquiterpenes in many species of the tribe Senencioneae is well documented [4–9]. In a continuation of our study of bioactive compounds from the *Cacalia* genus, we report our results on the isolation and structural elucidation of new sesquiterpenes from the methanol extract of the roots of *Cacalia roborowskii* (Maxim) Ling, a perennial herb distributed in the Gansu, Qinghai and Sichuan provinces of China.

RESULTS AND DISCUSSION

The root extract yielded nine new eremophilane derivatives **1–9.** The IR spectra of compounds **1–5** displayed the typical unsaturated γ-lactone bond bands at 1770 and 1795 cm^{-1}. The ^1H and ^{13}C NMR spectra were similar to those of eremophilenolides isolated from *Hertia cheirifolia* [9, 10]. The molecular formula of compound **1** was assigned as $C_{16}H_{24}O_5$ by its ^1H and ^{13}C NMR, DEPT and mass spectrum. In the ^1H NMR spectrum the downfield shifted signal for H-8 was missing indicating that C-8 was substituted. This was supported by two doublets at δ 2.45 (*d*, *J* = 14.5 Hz) and 2.17 (*d*, *J* = 14.5 Hz) attributable to H-9a and H-9b, respectively. The long range coupling of C-6 with methoxyl group protons and H-14 in the HMBC spectrum of **1** located the methoxyl group at C-6. The missing long range coupling between H-13 and H-6 showed that the hydroxyl group at C-8 was β-oriented. The NOESY cross-peak observed between H-4 and H-9 implied a *cis* eremophilane. The methoxyl group at C-6 was β-equatorial as shown by the NOE cross-peak between H-6 and H-15 observed in the NOESY experiment [4, 10]. Therefore, **1** was 8β,10β-dihydroxy-6β-methoxy-eremophilenolide.

The ^1H and ^{13}C NMR (Tables 2 and 3) and IR spectra of **2** were very close to those of **1** except for the presence of an acetoxyl and the downfield shifted H-3 agreed. The molecular formula, $C_{18}H_{26}O_7$, was deduced from its MS and NMR spectra. The long range coupling between the C-3 signal and the H-15 signal observed in the HMBC experiment, as well as the correlation between H-3 and H-4 observed in the ^1H–^1H COSY spectrum (Table 2) suggested that the acetoxyl group was at C-3. Its equatorial and β-orientation was indicated by fluctuations and confirmed by a cross placed between H-3 and H-4 in the NOESY spectrum. Compound **2** was, therefore, assigned as

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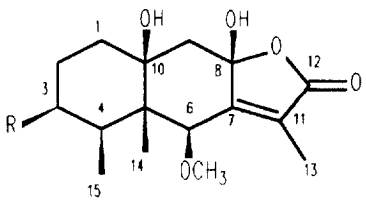
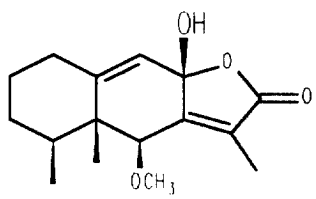


1 R = H

2 R = OAc

3 R = OAng

4 R = OMebut



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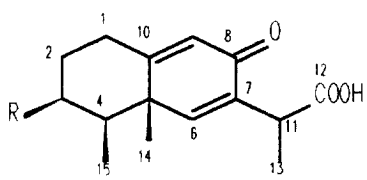

6 R = H

7 R = OAc

8 R = OAng

9 R = OMebut

3β-acetoxyl-8β,10β-dihydroxy-6β-methoxyeremophilenolide.

Compound **3** displayed similar spectral data (Tables 2 and 3) to those of **1** and **2** except for the presence of an angeloyloxy group in **3** instead of the acetate in **2**. The stereochemistry was deduced from this NOESY experiment. Thus, compound **3** was 3β-angeloyoxyl-8β,10β-dihydroxy-6β-methoxyeremophilenolide.

The spectral data of **4** was very close to those of **2** and **3**. The localization of a 2-methylbutyryl at C-3 was again deduced from the ^{1}H–^{1}H COSY and HMBC experiments. Hence, compound **4** was 3β-(2-methyl butyryloxyl)-8β,10β-dihydroxy-6β-methoxyeremophilenolide.

The molecular formula of compound **5**, $C_{16}H_{22}O_4$ was deduced from the MS. The ^{1}H and ^{13}C NMR and DEPT data resembled those of **1–4** and 8β-hydroxyeremophil-7(11),9-dien-8,12-olide [11]. In the ^{13}C NMR spectrum the oxygen-bearing quaternary carbon (δ_C 75 in **1–4**) was missing in agreement with the absence of free alcohol (3450 cm^{-1}) in the IR spectrum. An olefin proton signal at δ_H 5.64 (*d*, J = 1.6) assigned to H-9 was observed in the ^{1}H NMR spectrum. In the HMBC experiment the long range correlation between H-9 and C-5 and C-7, and between H-14 and C-10 suggested a Δ^8 double-bond. The localization of the methoxyl group at C-6 was deduced from the long range correlation between C-6 and the 6-OCH$_3$ protons and H-14 protons obscured in the HMBC spectrum. The stereochemistry was deduced from a NOESY experiment. Compound **5** was, therefore, 8β-hydroxy-6β-methoxyeremophil-7(11),9-dien-8,12-olide.

The IR spectra of compounds **6–9** showed the characteristic α,β,α′,β′-unsaturated ketone bonds peaks at 1664, 1632 and 1619 cm^{-1} [12, 13].

Compound **6** was obtained as colorless gum. Its spectral data were similar to those of 8-oxo-eremophila-6,9-diene derivatives reported in the literature [12–15]. A comparison of the ^{1}H NMR spectral data with those of the corresponding 1β-hydroxy derivative [12] indicated that the C-1 position was not substituted. The HMQC, HMBC and NOESY experiments supported the structure of **6** as 8-oxo-eremphila-6,9-dien-12-oic acid.

The spectra of **7–9** were similar to those of **6**. The H-3 signal was shifted downfield and additional ester signals appeared for acetate (**7**), angelate (**8**) or methylbutyrate (**9**), respectively. The stereochemistry was deduced from NOESY experiments.

EXPERIMENTAL

General

OR: $CHCl_3$; IR: KBr; ^{1}H and ^{13}C NMR and 2D NMR; $CHCl_3$ with TMS as int. standard; FAB-MS: VQ Quattro mass spectrometer.

Plant material

The roots of *C. roborowskii* (Maxim) Ling were collected in Linxia County, Gansu province, P.R. China in August 1993. The plant was identified by Dr J. Ma from the Department of Biology, Lanzhou University, where a voucher is deposited.

Extraction and isolation

The air dried and ground roots (750 g) of the plant were placed in a chromatography column (10 cm × 1 m) and eluted at room temp. with MeOH for 3 days. The MeOH was evaporated *in vacuo* until the vol. was reduced to 1 l, then cooled to −15° for 3 h. Filtration and evaporation afforded 120 g of residue, 80 g of

Table 1. ^1H and ^{13}C NMR chemical shift assignments and HMBC correlations of **1**

H	δ_H	C	δ_C	^1H–^{13}C long range correlation
1	1.63–1.71 *m*	1	34.5 *t*	
1′	1.39–1.43 *m*			
2	1.59–1.62 *m*	2	21.8 *t*	
2′	1.30–1.34 *m*			
3	1.36–1.38 *m*	3	29.6 *t*	H-15
4	1.21–1.25 *m*	4	33.5 *d*	H-14, H-15
		5	47.7 *s*	H-6β, H-9, H-14, H-15
6	4.39 *s*	6	80.6 *d*	OCH_3, H-14
		7	153.4 *s*	H-13, H-9
		8	103.7 *s*	H-9, H-9′, H-6β
9	2.45 *d* (14.5)	9	44.9 *t*	
9′	2.17 *d* (14.5)			
		10	75.1 *s*	H-6β, H-9, H-14
		11	129.4 *s*	H-13
		12	170.7 *s*	H-13
13	1.92 *s*	13	8.7 *q*	
14	1.17 *s*	14	11.0 *q*	
15	0.82 *d* (6.3)	15	16.4 *q*	
OCH_3	3.32 *s*	6-OCH_3	57.8 *q*	H-6β

Multiplicities were determined by DEPT.

which were chromatographed over silica gel H (600 g) using petrol–Et_2O (1:2) → Et_2O → Et_2O–EtOAc (8:2 to 1:1) as eluent. Based on the differences in composition exhibited by TLC, 25 crude fractions were obtained. Fraction 4 (700 mg) was subjected to CC on silica gel H (70 g), eluting with the mixture of petrol–Me_2CO containing amounts of Me_2CO to afford compounds **1** (20 mg), **2** (30 mg) and **3** (15 mg). Fraction 2 (300 mg) was chromatographied on silica gel H (30 g) and eluted with a hexane–EtOAc (7:3 → 1:1) gradient yielding **4** (20 mg), **5** (60 mg) and several fatty acids. Fraction 17 (2 g) was chromatographed on silica gel H with a mixture of EtOAc–Et_2O as eluent to yield four Frs: CR 17-1 (600 mg), CR 17-2 (200 mg), CR 17-3 (250 mg) and CR 17-4 (100 mg). Fraction CR 17-1 was purified by CC over silica gel H using the mixture of petrol–Me_2CO (4:2) or CH_2Cl_2–Et_2O–Me_2CO (4:1:0.5) as an eluent to give **6** (40 mg), **7** (20 mg), **8** (25 mg) and **9** (18 mg).

8β,10β-Dihydroxy-6β-methoxyeremophilenalide (**1**)

Amorphous solid, $C_{16}H_{24}O_5$, $[\alpha]_D$: +138.4° ($CHCl_3$, ca 1.1). FABMS (70 eV) *m/z* (rel. int.): 296 $[M]^+$(2), 278 $[M—H_2O]^+$ (8), 264 $[M—OCH_3\text{-}1]^-$ (42), 246 $[M—CH_3OH—H_2O]^+$(36), 222 (22), 213 (18), 204 (67), 154 (80), 134 (28), 121 (26), 97 (100), 91 (36), 83 (50), 67 (40); IR ν_{max} (KBr) cm^{-1}: 3433, 3258 (OH), 1770 (γ-lactone), 1319, 1161, 1081, 735; ^1H and ^{13}C NMR: Table 1.

3β-Acetoxyl-8β,10β-dihydroxy-6β-methoxy eremophilenolide (**2**)

Gum, $C_{18}H_{26}O_7$, $[\alpha]_D$: +112.7° ($CHCl_3$ ca 0.2). FABMS (70 eV) *m/z* (rel. int.): 354 $[M]^+$(1), 336 $[M—H_2O]^+$(5), 322 $[M—CH_3OH]^+$ (4), 304 $[M—CH_3OH—H_2O]^+$ (20), 294 (10), 276 (10), 262 (20), 154 (100), 139 (22), 113 (12), 95 (70), 83 (30), 43 (50); IR ν_{max} (KBr) cm^{-1}: 3467, 3254 (OH), 1762 (γ-lactone), 1733 (CH_3CO—), 1256 (C—O), 1160, 1099, 737; ^1H and ^{13}C NMR: Tables 2 and 3.

3β-Angeloyloxy-8β,10β-dihydroxy-6β-methoxyeremophilenolide (**3**)

Gum, $C_{21}H_{30}O_7$, $[\alpha]_D$: +119.8° ($CHCl_3$, ca 4.3). FABMS (70 eV) *m/z*: 376 [M—H2O]$^-$ (4), 346 (45), 344 $[M—CH_3OH\text{-}H_2O]^+$ (48), 318 (7), 258 (18), 244 (30), 154 (90), 139 (20), 124 (20), 95 (60), 83 $[R—CO]^+$ (100), 55 $[RCO—CO]^+$ (60); IR ν_{max} (KBr) cm^{-1}: 3435, 3258, 1768, 1680, 1640, 1241; ^1H and ^{13}C NMR: Tables 2 and 3.

3β-(2-Methylbutyroyloxy)-8β,10β-dihydroxy-6β-methoxyeremophilenolide (**4**)

Gum, $C_{21}H_{32}O_7$, $[\alpha]_D$: +103.9° ($CHCl_3$, ca 0.9). FABMS (70 eV) *m/z* (rel. int.): 396 $[M]^+$ (0.5), 378 $[M—H_2O]^+$ (3), 364 $[M—CH_3OH]^+$ (5), 346 (10), 294 (5), 276 (10), 262 (15), 244 (20), 154 (80), 139 (25), 123 (21), 95 (60), 85 $[C_4H_9CO]^+$ (70), 83 (28), 57 $[C_4H_9CO—CO]^+$ (100); IR ν_{max} (KBr) cm^{-1}: 3467, 3254 (OH), 1764 (γ-lactone), 1736 (RCO—), 1250 (C—O), 1140, 1096, 737; ^1H and ^{13}C NMR: Tables 2 and 3.

8β-Hydroxy-6β-methoxyeremophil-7(11),9-dien-8,12-olide (**5**)

Gum, $C_{16}H_{22}O_4$, $[\alpha]_D$: + 41.5° ($CHCl_3$, ca 2.5). FABMS (70 eV) *m/z* (rel. int.): 278$[M]^+$ (4), 261 (21),

Table 2. ^{1}H NMR chemical shift assignments of compounds **2**–**5** in $CDCl_3$

H	2*	3†	4‡	5
1	1.54 *m*	1.65 *m*	1.68 *m*	2.15 *m*
	1.79 *m*	1.82 *m*	1.85 *m*	
2	1.36 *m*	1.34 *m*	1.37 *m*	1.68 *m*
	1.95 *m*	1.95 *m*	2.00 *m*	1.79 *m*
3	4.9 *dt* (3.0, 1.8)	4.99 *dt* (3.0, 1.8)	4.90 *dt* (1.8, 3.0)	1.40 *m*
4	1.34 *dq*	1.42 *dq*	1.40 *dq*	1.41 *dq*
6	4.24 *s*	4.24 *s*	4.21 *s*	4.18 q (1.3)
9	2.32 *d* (14.5)	2.34 *d*(14.5)	2.33 *d* (14.5)	5.64 *d* (1.6)
	2.22 *d* (14.5)	2.27 *d* (14.5)	2.24 *d* (14.5)	
13	1.93 *s*	1.93 *s*	1.93 *s*	1.98 *d* (1.5)
14	1.39 *s*	1.40 *s*	1.41 *s*	0.96 *s*
15	0.93 *d* (6.8)	0.94 *d* (6.8)	0.95 *d* (6.8)	1.06 *d* (6.8)
OCH_3	3.32 *s*	3.32 *s*	3.32 *s*	3.41 *s*

* OAc: δ_H 2.08 ($COCH_3$).
† OAng: δ_H 6.09 (*q*, *J* = 7.3, 1H), 2.01 (*d*, *J* = 7.3 Hz, 3H), 1.85 (*s*, 3H).
‡ OMebut: δ_H 1.21 (*d*, *J* = 7.8 Hz, 3H), 0.85 (*t*, *J* = 6.9 Hz, 3H).

Table 3. ^{13}C NMR chemical shift assignments of compounds **2**–**5** in $CDCl_3$

C	2*	3†	4‡	5
1	27.4 *t*§	27.4 *t*	27.5 *t*	36.0 *t*
2	30.0 *t*	30.1 *t*	30.0 *t*	26.9 *t*
3	71.5 *d*	71.9 *d*	71.8 *d*	32.4 *t*
4	36.5 *d*	36.7 *d*	36.6 *d*	44.6 *d*
5	47.6 *s*	47.6 *s*	47.5 *s*	51.0 *s*
6	79.9 *d*	80.0 *d*	79.9 *d*	85.6 *d*
7	152.9 *s*	153.1 *s*	152.9 *s*	152.1 *s*
8	103.5 *s*	103.6 *s*	103.4 *s*	100.9 *s*
9	44.5 *t*	44.4 *t*	44.5 *t*	118.0 *d*
10	74.7 *s*	74.8 *s*	74.7 *s*	157.1 *s*
11	129.7 *s*	129.7 *s*	129.8 *s*	122.5 *s*
12	170.3 *s*	170.6 *s*	170.4 *s*	171.2 *s*
13	8.7 *q*	8.7 *q*	8.7 *q*	8.1 *q*
14	12.5 *q*	12.6 *q*	12.6 *q*	17.9 *q*
15	12.9 *q*	13.0 *q*	13.0 *q*	11.6 *q*
OCH_3	57.9 *q*	58.0 *q*	57.9 *q*	57.4 *q*

* OAc: δ_C 177.1 *s*, 21.3 *q*.
† OAng: δ_C 167.2 *s*, 127.4 *s*, 141.6 *d*, 20.89, 15.7 *q*.
‡ OMebut: δ_C 175.9 *s*, 41.8 *d*, 26.7 *t*, 11.6 *q*, 16.8 *q*.
§ Multiplicities were determined on the basis of DEPT spectra.

246 [M—CH_3OH]$^+$ (100), 231 [246—CH_3]$^+$ (30), 229 (40), 203 (80), 173 (40), 159 (40), 145 (45), 135 (70), 115 (35), 91 (66), 83 (50), 67(40). IR ν_{max} (KBr) cm^{-1}: 3254 (OH), 1765 (γ-lactone), 1680; ^{1}H and ^{13}C NMR: Tables 2 and 3.

8-*Oxo-eremophila*-6,9-*dien*-12-*oic acid* (**6**)

Gum, $C_{15}H_{20}O_3$, $[\alpha]_D$: −11.6° ($CHCl_3$, ca 2.9). FAB-MS *m/z* (rel. int): 249 [M + 1]$^+$(15), 233 [M—CH_3 + 1]$^+$(5), 231 [M—H_2O + 1]$^+$(10), 204 [M—CO_2]$^+$ (15), 203 [M—COOH]$^+$ (85), 175 (25), 149 (20), 147 (30), 133 (35), 91 (45), 69 (45), 57 (100), 55 (97); IR ν_{max} (KBr) cm^{-1}: 2600–3300 (*br*, bonded OH), 1710 (COOH), 1664, 1632, 1619 ($\alpha,\beta,\alpha',\beta'$-unsaturated ketone), 915, 732; ^{1}H and ^{13}C NMR: Table 4.

3β-*Acetoxy*-8-*oxo-eremophila*-6,9-*dien*-12-*oic acid* (**7**)

Gum, $C_{17}H_{22}O_5$, $[\alpha]_D$: +28.6° ($CHCl_3$, ca 0.6). FAB-MS *m/z* (rel. int.): 247 [M—CH_3COOH + 1]$^+$ (15), 229 [M—CH_3COOH-H_2O + 1]$^+$ (25), 201 [M—CH_3COOH—COOH]$^+$ (55), 175 (10), 159 (15), 147 (20), 133 (30), 91 (35), 69 (40), 57 (78), 55 (90), 43 (100); IR ν_{max} (KBr) cm^{-1}: 2500–3400 (*br*, bonded OH). 1738 (CH_3CO), 1665, 1636, 1615 ($\alpha,\beta,\alpha',\beta'$-unsaturated ketone). 1710 (COOH), 1241 (C—O), 980, 915, 732; ^{1}H and ^{13}C NMR: Tables 5 and 6.

3β-*Angeloyloxy*-8-*oxo-eremophila*-6,9-*dien*-12-*oic acid* (**8**)

Oil, $C_{20}H_{26}O_5$, $[\alpha]_D$: +38.5° ($CHCl_3$, ca 1.2). EIMS (70 eV) *m/z* (rel. int.): 346 [M]$^+$ (1), 246 [M—angelic acid]$^+$ (50), 228 [246—H_2O]$^+$ (25), 202 [246—CO_2]$^+$ (80), 201 (60), 173 (32), 135 (36), 115 (50), 91 (74), 83 [C_4H_7CO]$^+$ (100), 77 (50), 55 (60); IR ν_{max}(KBr) cm^{-1}: 2500–3400 (*br*, bonded OH), 1720 (ester carbonyl), 1710 (COOH), 1665, 1634, 1620 ($\alpha,\beta,\alpha',\beta'$-unsaturated ketone), 1241 (C—O), 980, 915, 733; ^{1}H and ^{13}C NMR: Tables 5 and 6.

3β-(2-*methylbutyroyloxy*)-8-*oxo-eremophila*-6,9-*dien*-12-*oic acid* (**9**)

Oil, $C_{20}H_{28}O_5$, $[\alpha]_D$: +22.4° ($CHCl_3$, ca 4.6). EIMS (70 eV) *m/z* (rel. int.): 348 [M]$^+$ (0.5), 246 [M—2-methylbutyric acid]$^+$ (40), 228 [246[cg4]H_2O]$^+$ (58), 202 [246—CO_2]$^+$ (60), 200 (80), 187 (65), 173 (62), 162

Table 4. ^{1}H and ^{13}C NMR spectral data and HMBC correlations of compound **6** ($CDCl_3$, 400 MHz)

C	δ_C	δ_H	^{1}H–^{13}C long range correlations
1	32.9 *t*	2.43 *m*, 1.99 *m*	H-9
2	28.1 *t*	2.41 *m*, 1.57 *m*	H-1a, H-1b
3	30.2 *t*	1.50 *m*	H-15, H-1a, H-1b
4	38.9 *d*	1.40 *m*	H-14, H-15
5	44.3 *s*		H-6, H-9, H-1a, H-14, H-15
6	152.9 *d*	7.01 *s*	H-11, H-14
7	136.0 *s*		H-9, H-11, H-13
8	186.3 *s*		H-6, H-11,
9	123.6 *d*	6.15 *s*	H-1b, H-1a
10	170.3 *s*		H-6, H-1b, H-1a, H-14
11	41.8 *d*	3.78 *q* (7.0)	H-6, H-13
12	177.4 *s*		H-11, H-13
13	15.8 *q*	1.38 *d* (7.0)	H-11
14	17.2 *q*	1.15 *s*	H-6, H-4
15	16.4 *q*	1.08 *d* (6.0)	H-4

Table 5. ^{1}H NMR spectral data of compounds **7**–**9** ($CDCl_3$, 400 MHz)

H	**7***	**8**†	**9**‡
1	2.70 *m*	2.68 *m*	2.67 *m*
	2.33 *m*	2.33 *m*	2.32 *m*
2	2.21 *m*	2.20 *m*	2.13 *m*
	1.64 *m*	1.66 *m*	1.69 *m*
3	5.07 (2.7)	5.14 (2.8)	5.05 (2.8)
4	1.70 *m*	1.72 *m*	1.75 *m*
6	6.95 *s*	6.94 *s*	6.93 *s*
9	6.21 *s*	6.20 *s*	6.19 *s*
11	3.75 *q* (7.1)	3.74 *q*	3.74 *d* (7.1)
13	1.37 *d* (7.1)	1.37 *d* (6.8)	1.36 *d* (2.1)
14	1.34 *s*	1.36 *s*	1.34 *s*
15	1.17 *d* (7.0)	1.21 *d* (6.9)	1.19 *d* (7.0)

* OAc: δ_H 2.01.

† OAng: δ_H 6.13 (*q*, J = 7.3 Hz, CH), 2.05 (*d*, J = 7.3 Hz, CH_3), 1.97 (*s*, CH_3).

‡ OMebut: δ_H 0.94 (*t*, CH_3), 1.23 (*d*, CH_3), 2.00 (*m*, CH).

Table 6. ^{13}C NMR spectral data and HMBC correlations of compounds **2–4** ($CDCl_3$, 400 MHz)

C	2*	3†	4‡	^1H–^{13}C long range correlation
1	28.1 *t*§	28.2 *t*	28.0 *t*	H-9
2	32.7 *t*	32.7 *t*	32.7 *t*	H-1a, H-1b
3	73.0 *d*	72.3 *d*	72.6 *d*	H-15, H-1a, 1b
4	42.9 *d*	42.9 *d*	42.9 *d*	H-14, H-15
5	43.8 *s*	43.8 *s*	43.8 *s*	H-6, H-9, H-1a, H-14, H-15
6	151.7 *d*	151.8 *d*	151.7 *s*	H-11, H-14
7	135.6 *s*	135.7 *s*	135.7 *s*	H-9, H-11, H-13
8	185.8 *s*	185.9 *s*	185.9 *s*	H-6, H-11
9	124.2 *d*	124.1 *d*	124.2 *d*	H-1a, 1b
10	168.6 *s*	168.7 *s*	168.8 *s*	H-1a, 1b, H-6, H-14
11	38.9 *d*	38.9 *d*	38.8 *d*	H-6, H-13
12	177.0 *s*	177.1 *s*	177.1 *s*	H-11, H-13
13	15.8 *q*	15.7 *q*	15.7 *q*	H-11
14	20.1 *q*	20.2 *q*	20.2 *q*	H-4, H-6
15	12.4 *q*	12.5 *q*	12.5 *q*	H-4

* OAc: δ_C 170.3 *s* (CO), 21.2 *q* (CH_3).
† OAng: δ_C 167.2 *s* (CO), 127.5 *s* (C =), 139.2 *d* (CH), 20.9 *q* (CH_3), 15.8 *q* (CH_3).
‡ OMebut: δ_C 175.9 *s* (CO), 41.8 *d* (CH), 26.8 *t* (CH_2), 11.7 *q* (CH_3), 16.8 *q* (CH_3).
Multiplicities were determined on the DEPT spectra.

(55), 148 (45), 131 (20), 115 (20), 91 (30), 85 $[C_4H_9CO]^+$ (80), 77 (50), 68 (30), 57 $[C_4H_9CO—CO]^+$ (100), 55 (50); IR ν_{max} (KBr) cm^{-1}: 2500–3400 (*br*, bonded OH), 1734 (C_5H_9CO), 1710 (COOH), 1665, 1634, 1620 ($\alpha,\beta,\alpha',\beta'$-unsaturated ketone), 1240 (C—O), 980, 915, 732; ^1H and ^{13}C NMR: Tables 5 and 6.

Acknowlegments—The authors thank the Post Doctoral Administrational Committee of China for financial support (No. 9507).

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