

Article

## Four Eremophil-9-en-8-one Derivatives from *Cremanthodium stenactinium* Samples Collected in China

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**Abstract:** Two samples of *Cremanthodium stenactinium* (Asteraceae) were collected in Sichuan Province, China. From the ethyl acetate extracts of the roots, three new eremophilane-type sesquiterpenoids and one new trinoreremophilane compound were isolated, together with other known eremophilanes. Their structures were determined based on the spectroscopic data. This is the first report of isolation of eremophilane-type compounds from the genus *Cremanthodium*.

**Keywords:** Asteraceae; *Cremanthodium stenactinium*; eremophilanes; sesquiterpenes

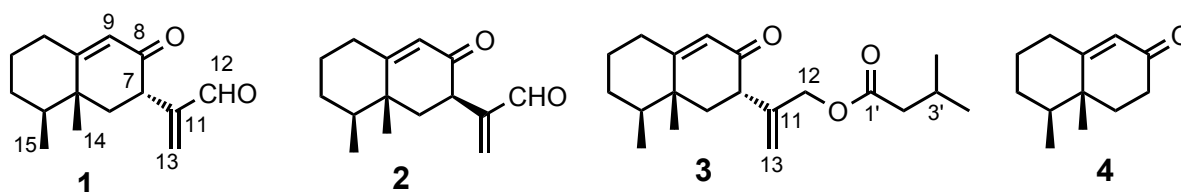
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### 1. Introduction

Plant species belonging to the genus *Cremanthodium* (Asteraceae) are known to grow in high mountain areas and to be very small in size [1,2]. To date there are few reports about these species, presumably due to the difficulty of collection and the scarcity of suitably sized samples. Bisabolane- and oplopane-type sesquiterpenoids and aromatic compounds were isolated from *Cremanthodium ellisii*

[3-7], bisabolane-type and steroids from *C. discoideum* [8,9], triterpenoids from *C. potaninii* [10], and some hydrocarbons from *C. pleurocaule* [11]. However, there are no reports about the phytochemicals of *C. stenactinium*. We have been investigating both inter- and intra-specific diversity of *Ligularia* [12-18]. In 2009, we had an opportunity to collect two samples of *C. stenactinium* at different locations in Sichuan Province of China. From the EtOAc extracts of the root we have now isolated four new compounds, three eremophilanes **1–3** and trinoreremophilane **4** (Figure 1), and their structures have been determined based on the spectroscopic data.

**Figure 1.** New compounds isolated in this work.



## 2. Results and Discussion

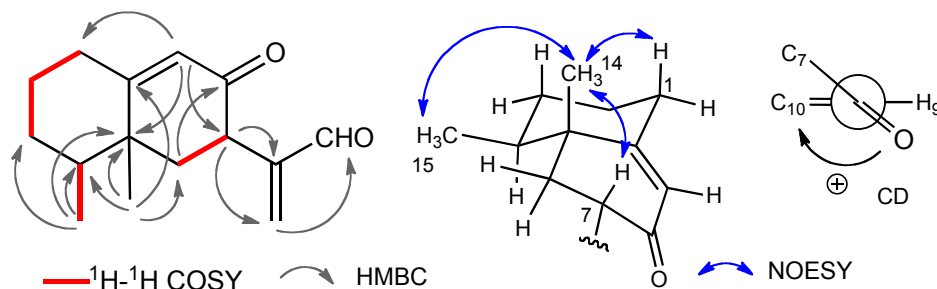
The molecular formula of compound **1** was determined to be  $C_{15}H_{20}O_2$  by HRMS. The IR spectrum exhibited a conjugated carbonyl group absorption at  $1,695\text{ cm}^{-1}$ . The  $^{13}\text{C}$ -NMR and HSQC spectra indicated the presence of two methyl, five methylene, four methine, and four quaternary carbon signals. The  $^1\text{H}$ -NMR spectrum exhibited the presence of a trisubstituted olefin and an exomethylene, as well as an aldehyde (Table 1).

**Table 1.** NMR data for compounds **1** and **2** (500 MHz for  $^1\text{H}$  and 125 MHz for  $^{13}\text{C}$  in  $C_6D_6$ ).

position	$^{13}\text{C}$ (ppm)	$^1\text{H}$ (ppm)	
	<b>1</b>	<b>1</b>	<b>2</b>
1	32.7	1.72–1.81 (2H, m)	1.60–1.68 (m)
2	26.4	-	1.91 (td, $J = 12.2, 5.2$ Hz)
		1.02–1.08 (m)	0.94–1.01 (m)
3	30.4	1.37–1.42 (m)	1.43–1.50 (m)
		0.98–1.05 (m)	0.98–1.06 (m)
4	43.5	1.08–1.13 (m)	1.09–1.15 (m)
		1.00–1.05 (m)	1.50–1.55 (m)
5	39.7	-	-
6	41.9	1.67 (dd, $J = 13.0, 5.6$ Hz)	1.62 (t, $J = 13.7$ Hz)
		1.71 (dd, $J = 13.4, 13.0$ Hz)	1.73 (dd, $J = 13.7, 4.6$ Hz)
7	42.8	3.60 (dd, $J = 13.4, 5.6$ Hz)	3.64 (dd, $J = 13.7, 4.6$ Hz)
8	195.5	-	-
9	124.3	5.76 (d, $J = 1.7$ Hz)	5.80 (d, $J = 1.3$ Hz)
10	168.0	-	-
11	149.3	-	-
12	192.8	9.34 (s)	9.31 (s)
13	134.4	5.52 (s)	5.52 (s)
		5.80 (s)	5.88 (s)
14	15.5	0.71 (s)	0.63 (s)
15	15.1	0.54 (d, $J = 6.4$ Hz)	0.60 (d, $J = 6.9$ Hz)

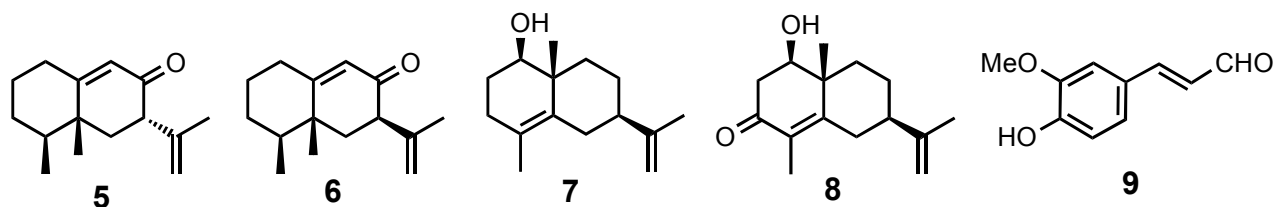
The HMBC spectrum of compound **1** showed correlations between H-15 and C-3, C-4, and C-5, between H-14 and C-4, C-5, C-6, and C-10, between H-7 and C-11 and C-13, and between H-9 and C-1, C-5, and C-7 (Figure 2).  $^1\text{H}$ - $^1\text{H}$  COSY correlations as shown in Figure 2 were also detected.

**Figure 2.** Selected 2D correlations and the sign of the CD for compound **1**.



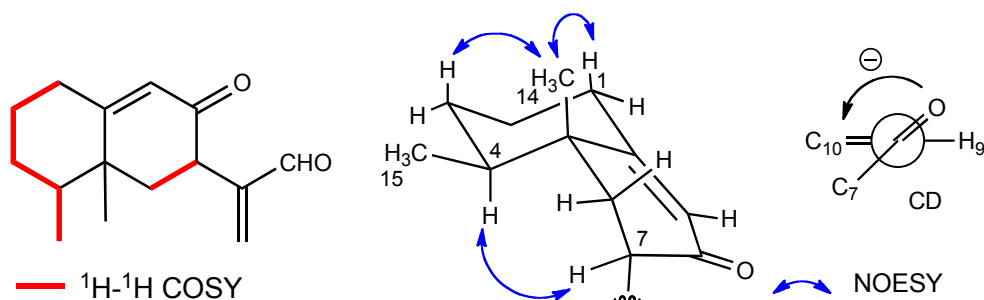
From these results the planar structure was determined to be 8-oxoeremophila-9,11(13)-dien-12-al. The stereochemistry was revealed by the NOESY spectrum. NOEs between H-14 and H-1 $\beta$ , H-15, and H-7 were observed, therefore, H-7 was established to be  $\beta$ -oriented. The CD spectrum of compound **1** showed the Cotton effect  $[\theta] +27000$  at 237 nm (EtOH) [19] which was similar to that of the known compound, 7*S*-eremophila-9,11-dien-8-one (**5**), also found in this extract (Figure 3). The structure of **1** was established to be 4*S*,5*R*,7*S*-8-oxoeremophila-9,11(13)-dien-12-al.

**Figure 3.** Known compounds isolated in this work.



The molecular formula of compound **2** was the same as that of compound **1**. The presence of a conjugated carbonyl group was also shown by the IR spectrum ( $1,693\text{ cm}^{-1}$ ). The  $^1\text{H}$ -NMR spectrum, which was very similar to that of compound **1**, exhibited the presence of an aldehyde, a trisubstituted olefin, an exomethylene, a singlet methyl, and a doublet methyl (Table 1).  $^1\text{H}$ - $^1\text{H}$  COSY correlations from H-1 through H-4 to H-15 was detected and the planar structure was determined to be as depicted in the formula (Figure 4).

**Figure 4.** Selected 2D correlations and the sign of the CD for compound **2**.



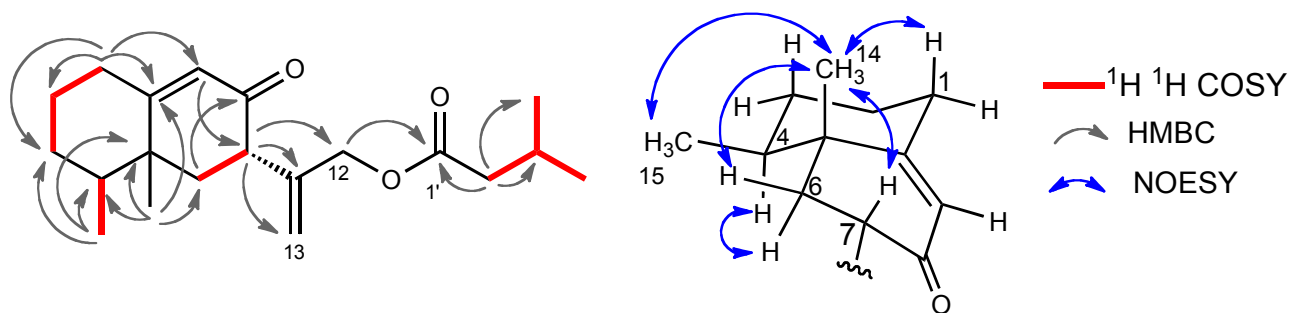
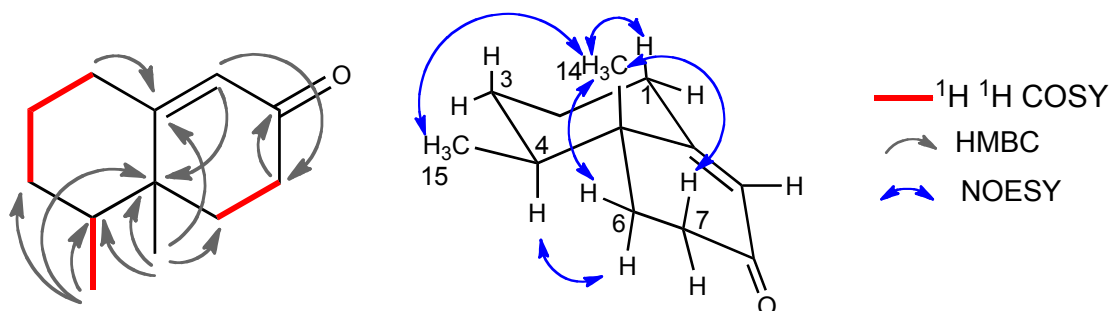
The stereochemistry was deduced by the NOEs between H-14 and H-1 $\beta$  and H-3 $\beta$  and between H-4 $\alpha$  and H-7 $\alpha$ . The CD spectrum showed the Cotton effect  $[\theta]$  -12000 at 225 nm (EtOH) which was similar to that of the known compound, 7*R*-eremophila-9,11-dien-8-one (**6**), also present in this extract (Figure 3). Therefore, compound **2** was established to be 4*S*,5*R*,7*R*-8-oxoeremophila-9,11(13)-dien-12-al.

Compound **3** exhibited a quasi-molecular ion peak at  $m/z$  319 and the molecular formula was determined to be C<sub>20</sub>H<sub>30</sub>O<sub>3</sub> by HRMS. The <sup>1</sup>H-NMR spectrum indicated the presence of three doublet methyls, one singlet methyl, an exomethylene, a trisubstituted olefin, as well as two oxymethylene protons (Table 2).

**Table 2.** NMR data for compounds **3** and **4** (500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C; in C<sub>6</sub>D<sub>6</sub>).

position	<sup>13</sup> C (ppm)		<sup>1</sup> H (ppm)	
	<b>3</b>	<b>4</b>	<b>3</b>	<b>4</b>
1	32.6	33.1	1.74–1.83 (m)	1.76 (ddt, $J = 14.6, 4.2, 2.0$ Hz) 1.83 (ddd, $J = 14.6, 12.8, 5.2$ Hz)
2	26.5	26.7	1.03–1.09 (m) 1.38–1.43 (m)	1.03–1.09 (m) 1.39–1.44 (m)
3	30.4	30.5	1.00–1.05 (m) 1.10–1.15 (m)	0.99–1.06 (m) 1.12–1.15 (m)
4	43.6	43.1	1.00–1.05 (m)	0.96–1.02 (m)
5	39.6	38.8	-	-
6	41.7	35.7	1.72 (dd, $J = 12.9, 4.1$ Hz) 1.85 (dd, $J = 12.9, 4.1$ Hz)	1.27 (ddd, $J = 14.4, 13.4, 4.4$ Hz) 1.45 (ddd, $J = 13.4, 4.9, 3.5$ Hz)
7	47.5	34.3	3.12 (dd, $J = 14.7, 4.1$ Hz)	2.14 (ddd, $J = 16.6, 14.4, 4.9$ Hz) 2.25 (ddd, $J = 16.6, 4.4, 3.5$ Hz)
8	196.7	197.3	-	-
9	124.4	124.7	5.73 (s)	5.80 (s)
10	168.0	168.5	-	-
11	143.9	-	-	-
12	66.3	-	4.98 (s)	-
13	114.0	-	4.98 (s) 5.36 (s)	- -
14	15.4	15.6	0.69 (s)	0.61 (s)
15	15.1	15.2	0.57 (d, $J = 6.1$ Hz)	0.55 (d, $J = 6.4$ Hz)
1'	172.0	-	-	-
2'	43.4	-	2.07 (d, $J = 6.1$ Hz)	-
3'	25.8	-	2.05–2.15 (m)	-
4' 5'	22.5 (2C)	-	0.84 (d, $J = 6.4$ Hz)	-

The presence of two carbonyl and two olefins was supported by the <sup>13</sup>C-NMR spectrum. Therefore, this molecule should be bicyclic, because the degree of unsaturation was six and the number of the double bonds was four. The HMBC spectrum showed the correlations between H-15 and C-3, C-4, and C-5, between H-14 and C-4, C-5, C-6, and C-10, between H-7 and C-11, C-12, and C-13, between H-12 and C-1', and other correlations shown in Figure 4. These observations indicate that this compound has an eremophilane skeleton and that 3-methylbutyryloxy group is substituted at C-12. The stereochemistry was determined by the correlations shown in Figure 4. The absolute configuration was also determined by the CD absorption of  $[\theta]$  +43000 (235 nm in EtOH), which was almost the same as that of compound **1**.

**Figure 4.** Selected 2D correlations for compound 3.**Figure 5.** Selected 2D correlations for compound 4.

The molecular formula of compound **4** was determined to be  $C_{12}H_{18}O$  by HRMS. The IR spectrum exhibited the absorption at  $1,680\text{ cm}^{-1}$  for a conjugated ketone, which was supported by the NMR signals ( $\delta_C$  197.3, 168.5, 124.7;  $\delta_H$  5.80) (Table 2). The  $^{13}C$ -NMR spectrum showed the presence of only 12 carbon signals, including two methyl, five methylene, two methine, and three quaternary carbons. The HMBC and  $^1H$ - $^1H$  COSY correlations (Figure 5) clearly indicated the trimeremophilane skeleton. The NOESY spectrum showed that both methyl groups were  $\beta$ -oriented, and the absolute configuration was determined by the CD absorption as depicted in the formula. Compound **4** was established to be  $4S,5R$ -trimeremophil-9-en-8-one. This compound has been known as a synthetic intermediate as a chiral compound ( $[\alpha]_D +185.6$  ( $CHCl_3$ )) [20], which also supported the absolute configuration of compound **4** (*vide supra*).

### 3. Experimental

#### General

Specific rotations and CD spectra were measured on a JASCO P-1030 and a JASCO J-725 auto recording polarimeter; IR spectra, on a Shimadzu FT/IR-8400S spectrophotometer;  $^1H$  and  $^{13}C$  NMR spectra (500 MHz and 125 MHz, respectively), on a Varian 500-MR spectrometer. Mass spectra, including high-resolution ones, were recorded on a JEOL JMS-700 MStation. A Chemcopak Nucleosil 50-5 column ( $4.6 \times 250\text{ mm}$ ) and a hexane-ethyl acetate solvent system were used for HPLC (JASCO pump system). Silica gel BW127ZH (100–270 mesh, Fuji Silysia) was used for column chromatography. Silica gel 60 F<sub>254</sub> plates (Merck) were used for TLC.

Sample 1 (200982) was collected in the boundary between Luhuo and Seda Counties, Sichuan (N  $31^\circ 42' 30.2''$ , E  $100^\circ 42' 31.6''$ ; altitude 3,700 m) and sample 2 (200938) in Litang County, Sichuan

(N: 30°13'32'', E:100°16'3.6''; altitude 4,400 m) in 2009 (voucher specimens No. 200982 and 200938, were deposited in the Herbarium of Kunming Institute of Botany). Both samples were identified by X. Gong, one of the authors.

Sample 1 (200982; dried weight 21.1 g) was extracted with EtOAc to give an extract (424 mg), which was separated by column chromatography (*n*-hexane-EtOAc gradient) followed by HPLC (Nucleosil 50-5, *n*-hexane-EtOAc) to afford **1** (0.6 mg), **2** (0.3 mg), a mixture of 7*S*- and 7*R*-eremophila-9,11-dien-8-one (**5** and **6**, 60 mg), and 4-hydroxy-3-methoxycinnamaldehyde (**9**, 0.2 mg).

Sample 2 (200938; dried weight 42.1 g) was extracted with EtOAc to give an extract (1.3 g), which was separated by column chromatography (*n*-hexane-EtOAc gradient) followed by HPLC (Nucleosil 50-5, *n*-hexane-EtOAc) to afford **3** (2.4 mg), **4** (2.1 mg), eudesma-4,11-dien-1β-ol (**7**, 1.1 mg), 1β-hydroxyeudesma-4,11-dien-3-one (**8**, 1.4 mg), 4-hydroxy-3-methoxycinnamaldehyde (**9**, 0.2 mg), and vanillin (0.2 mg) (Scheme 2).

*4S,5R,7S-8-Oxoeremophila-9,11(13)-dien-12-al* (**1**):  $[\alpha]_D^{22} +99.5$  (*c* 0.12, EtOH); FT-IR (KBr) 1695, 1676  $\text{cm}^{-1}$ ; CD  $[\theta]$  (EtOH) -5323 (319 nm), +27023 (237 nm); MS (CI) *m/z* 232  $[\text{M}]^+$ , 150, 135 (base); HRMS (CI) Obs *m/z* 232.1456 (Calcd for  $\text{C}_{15}\text{H}_{20}\text{O}_2$  232.1463).

*4S,5R,7R-8-Oxoeremophila-9,11(13)-dien-12-al* (**2**):  $[\alpha]_D^{22} -72$  (*c* 0.01, EtOH); FT-IR (KBr) 1693, 1679  $\text{cm}^{-1}$ ; CD  $[\theta]$  (EtOH) +667 (328 nm), -12025 (225 nm); MS (CI) *m/z* 233  $[\text{M}+\text{H}]^+$  (base), 150, 135; HRMS (CI) Obs *m/z* 233.1540 (Calcd for  $\text{C}_{15}\text{H}_{21}\text{O}_2$  233.1541).

*4S,5R,7S-12-(3'-Methylbutyryloxy)eremophila-9,11(13)-dien-8-one* (**3**):  $[\alpha]_D^{21} +178$  (*c* 0.24, EtOH); FTIR (KBr) 1737, 1677  $\text{cm}^{-1}$ ; CD  $[\theta]$  (EtOH) -7240 (319 nm), +43635 (235 nm); MS (CI) *m/z* 319  $[\text{M}+\text{H}]^+$  (base), 217; HRMS (CI) Obs *m/z* 319.2275 (Calcd for  $\text{C}_{20}\text{H}_{31}\text{O}_3$  319.2273).

*4S,5R-Trinoreremophil-9-en-8-one* (**4**):  $[\alpha]_D^{22} +143$  (*c* 0.14, EtOH); FTIR (KBr) 1680  $\text{cm}^{-1}$ ; CD  $[\theta]$  (EtOH) -2768 (319 nm), +34310 (238 nm); MS (CI) *m/z* 179  $[\text{M}+\text{H}]^+$ , 89, 61 (base); HRMS (CI) Obs *m/z* 179.1422 (Calcd for  $\text{C}_{12}\text{H}_{19}\text{O}$  179.1436).

#### 4. Conclusions

Sample 1 afforded compounds **1** and **2**, and sample 2 compounds **3** and **4**. This is the first report of the isolation of eremophilane-type sesquiterpenoids from *Cremanthodium* spp. A trinoreremophilane compound, dendryphilellin A, has been isolated from the marine deuteromycete *Dendryphiella salina* [21], but there are only a few examples of simple trinoreremophilanes reported so far [22-25], which are biogenetically closely related with compounds **1**, **2**, **5**, or **6**. The present results show that eremophilane-type sesquiterpenoids are common compounds both in *Ligularia* and *Cremanthodium*, implying that the genus *Cremanthodium* is quite close to *Ligularia* or *Parasenecio* [1,2,26]. More samples are going to be investigated in the near future.

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*Sample Availability:* Samples of the compounds 1–9 are available from the authors.