A NOVEL SESQUITERPENOID FROM *Ecdysanthera rosea*

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A novel sesquiterpenoid was isolated from the whole plant of Ecdysanthera rosea *Hook. et Arn. Its structure was elucidated as tricyclo[5,3,1,$0^{2,4}$]-3-aldehyde-3,11-dimethyl-8-methanoic acid on the basis of spectral evidence (1D and 2D NMR) and was named ecdysanthblic acid.*

Key words: *Ecdysanthera rosea,* ecdysanthblic acid, sesquiterpenoid.

Ecdysanthera rosea Hook. et Arn. is distributed in Xishuangbanna, Yunnan province, P. R. China. It was a traditional herb for the Dai nationality [1] and has been used to treat garget and rheumatism; the chemical constituents of this plant have been reported; C_{21} steroids [2] and triterpenoid [3] were isolated. The present work describes the isolation and structural elucidation of a novel sesquiterpenoid (**1**) from this plant, designated as tricyclo[5,3,1,$0^{2,4}$]-3-aldehyde-3,11-dimethyl-8-methanoic acid. The plants were collected from Xishuangbanna, Yunnan province, P. R. China, in August 2005.

Compound **1** was obtained as a white powder; positive FABMS showed a molecular ion peak at m/z 251 $[M+H]^+$, and the HRESIMS of **1** gave an $[M+Na]^+$ peak at m/z 273.1466; combine with analysis of its NMR data, it possesses the molecular formula of $C_{15}H_{22}O_3$. The IR spectrum (KBr) showed the presence of carbonyl (2731, 2822, and 1701 cm^{-1}), carboxy (1729 cm^{-1}), and tricycle (2990 cm^{-1}). The ^{13}C NMR and DEPT exhibited 15 carbon signals for two methyls (δ_C 7.4 and 15.7), four methylenes, seven methines, and two quaternary carbons, including one carbonyl group (δ_C 203.0) and one carboxy group (δ_C 177.5). The methyl (δ_C 7.4) has a singlet signal (δ 1.17) in the ^1H NMR spectrum and an upfield shift in the ^{13}C NMR spectrum, suggesting that it is probably connected with a quaternary carbon and shielded by the carbonyl group, which means that C-13 (δ_C 7.4) and C-12 (δ_C 203.0) are both attached to C-3 (δ_C 35.0), as proved by the correlation of C-3 in the HMBC spectrum; H-2 (δ_H 1.37) correlated with H-1 (δ_H 1.20) and H-4 (δ_H 1.89) in the ^1H-^1H COSY spectrum, and both H-2 and H-4 correlated with C-3 in HMBC. This implies that C-2, C-3, and C-4 (δ_C 38.7) forms a three-carbon cycle. The correlation from H-5β to C-4 and C-6 in ^1H-^1H COSY confirmed that both C-4 and C-6 are attached to C-5. This partial structure is presented as A. The HMBC spectrum showed C-15 (δ_C 177.5) correlated with H-9α (δ_H 2.19) and H-9β (δ_H 1.95) besides H-8 (δ_H 2.95), but H-9α correlated with H-10α (δ_H 1.36) and H-8 in ^1H-^1H COSY, which proves that C-15 is attached to C-8 and not C-9. H-8 correlated with H-7 (δ_H 2.59) in ^1H-^1H COSY, showing that C-7 is also attached to C-8; a similar conclusion can be drawn that C-1 (δ_C 23.1) is attached to C-10 (δ_C 19.5) for the correlation from H-10α to H-1. Figure 1 (*b*) shows this partial structure. H-14 (δ_H 0.86) only correlated with H-11 in ^1H-^1H COSY and correlated with C-11 (δ_C 40.1) in HMBC, showing that C-14 is connected with C-11. In ^1H-^1H COSY, the H-11correlated with H-1 and H-7 very distinctly, and the correlation from H-11 to C-1 and C-7 in HMBC confirmed that both C-7 and C-1 are attached to C-11; considering the above structure (presented as B), a six-carbon cycle can be formed (presented C). H-7 correlated with H-6β (δ_H 1.57) in ^1H-^1H COSY, and the correlation from H-7 to C-6 in HMBC proved their connection. Other correlations in HMBC can be found in Table 1. The whole structure of compound **1** was identified as presented in Fig. 1.

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TABLE 1. NMR Spectral Data of Compound **1** in Pyridine (δ, ppm, J/Hz)

C atom	δ_C	δ_H	HMBC	ROESY
1	23.1 (d)	1.20 (m)	C-4, C-11	14-H, 2-H, 10α-H, 8-H
2	22.6 (d)	1.37 (m)	C-1, C-3, C-11	1-H, 5α-H, 9α-H, 10α-H
3	35.0 (s)			
4	38.7 (d)	1.89 (m)	C-3, C-5, C-1, C-2, C-6	5β-H, 6β-H, 7-H
5	31.2 (t)	α : 1.66 (m)	C-4, C-2, C-6	6α-H, 9α-H, 8-H, 5β-H
		β : 2.09 (m)	C-4, C-6, C-2	5α-H, 7-H, 11-H
6	31.8 (t)	α : 1.27 (m)	C-5, C-7, C-11	14-H, 6β-H, 5α-H
		β : 1.57 (m)	C-5, C-7, C-11, C-4	6α-H, 11-H, 5β-H
7	44.8 (d)	2.59 (m)	C-8, C-11, C-5, C-6	11-H, 4-H, 5β-H, 6β-H
8	48.0 (d)	2.95 (m)	C-7, C-11, C-15, C-9	1-H, 10α-H, 5α-H, 9α-H
9	28.6 (t)	α : 2.19 (m)	C-8, C-7, C-10, C-1	10α-H, 9β-H, 8-H
		β : 1.95 (m)	C-8, C-7, C-1, C-10	14-H, 10β-H, 9α-H, 7-H
10	19.5 (t)	α : 1.36 (m)	C-1, C-2, C-9, C-11	1-H, 5α-H, 11-H, 8-H, 10β-H
		β : 1.72 (m)	C-8, C-11, C-9, C-1, C-2	10α-H, 5β-H, 9β-H
11	40.1 (d)	1.87 (m)	C-8, C-7, C-6, C-1, C-2	7-H, 6β-H, 10β-H
12	203.0 (d)	8.81 (s)	C-13, C-2, C-3	4-H, 11-H
13	7.4 (q)	1.17 (s)	C-2, C-3, C-4	2-H, 1-H
14	15.7 (q)	0.86 (d, J = 8 Hz)	C-1, C-11, C-7	1-H, 11-H
15	177.5 (s)			

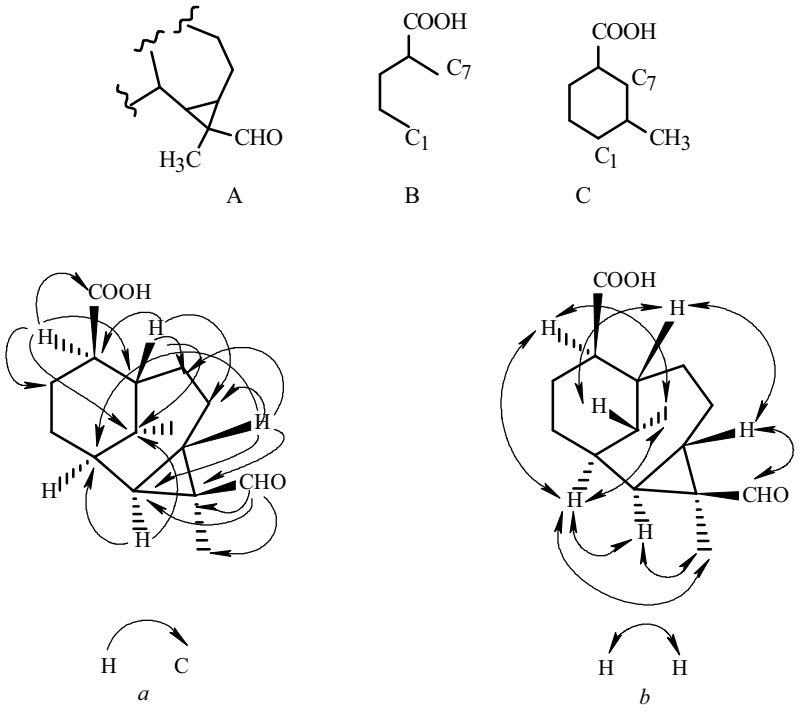

Fig. 1. Key HMBC (*a*) and Key ROESY (*b*) of compound **1**.

The relative stereochemistry at the chiral centers in compound **1** was supported by the ROESY spectrum. The NOE interaction from H-1 to H-2 and H-8 showed H-1, H-2, and H-8 at the same side. When we took the α configurations, C-13 and C-14 were at α positions too. The correlation from H-4 to H-11 and H-7 in the ROESY and no correlation from H-4 to H-1 and H-2, showed that H-4, H-7, and H-11 are at the β positions. The NOE interaction of H-2 with H-13 and H-1 with H-14 further confirmed the above assignment. There is more NOE interaction information in Table 1.

EXPERIMENTAL

General Experimental Producers. Melting point was obtained on a Koffler melting apparatus and was uncorrected. FABMS was recorded on a VG Auto spec-3000 spectrometer, and HR-ESIMS was measured with an API Qstar Pulsar instrument. All NMR experiments were obtained on a Bruker DRX-500 MHz NMR spectrometer at room temperature. IR spectra were obtained on a Bio-Rad FTS-135 spectrometer with KBr pellets.

Extraction and Isolation. The air-dried, milled whole plant of *Ecdysanthera rosea* Hook. et Arn. (7.5 kg) was extracted with 75% EtOH three times under reflux, and the residue (242 g) was obtained after removing the solvent in vacuum. The residue was subjected to silica gel chromatography, eluting with $CHCl_3$ and then $CHCl_3/CH_3OH$(10/1 to 0/1) to afford six major fractions. Fraction 3 was chromatographed on a reverse phase silica gel (RP-18) column eluted with CH_3OH/H_2O repeatedly to afford compound **1** (7.0 mg, 0.00093% dry weight).

Ecdysanthblic Acid. White powder, mp 249-252°, IR (KBr, ν_{max}, cm^{-1}) 2731, 2822, 1701, 1729, 2990; FAB^+MS *m/z* 251 $[M+H]^+$, 233, 205, 193; HRESIMS *m/z* 273.1466 $[M+Na]^+$ (Calcd for $C_{15}H_{22}O_3Na$, 273.1466); ^{13}C and ^1H NMR data see Table 1.

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