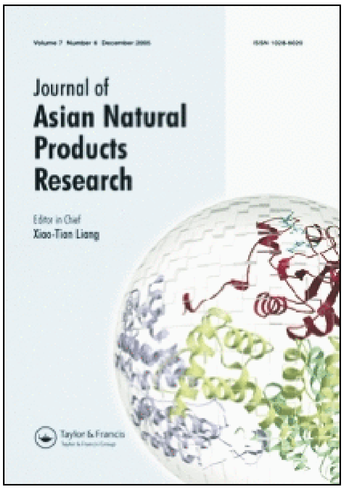

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Chia-Li Wu[a]; Tsuei-Lien Kao[a]
[a] Department of Chemistry, Tamkang University, Tamsui, Taiwan, ROC

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A NEW GYMNOMITRANE-TYPE SESQUITERPENOID FROM THE LIVERWORT *CYLINDROCOLEA RECURVIFOLIA*

CHIA-LI WU* and TSUEI-LIEN KAO

Department of Chemistry, Tamkang University, Tamsui 251, Taiwan, ROC

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A novel gymnomitrane-type alcohol was identified from the liverwort *Cylindrocolea recurvifolia*. The structure of this new compound was confirmed by X-ray analysis. This is the first report on the chemical constituents of this genus.

Keywords: *Cylindrocolea recurvifolia*; Cephaloziellaceae; Liverwort; Gymnomitr-3(15)-en-5α-ol

INTRODUCTION

Many liverwort species have been studied chemically and found to contain terpenoids and lipophilic aromatics as their major secondary metabolites [1]. However, the genus of *Cylindrocolea* has never been investigated previously. Therefore, we carried out the present study as we collected the liverwort species *Cylindrocolea recurvifolia* from the natural reserve area Yuenyang Lake of Taiwan. It was found that the two most abundant components of this liverwort were gymnomitrane-type sesquiterpenes. One of them was β-barbatene (**1**), the other one was a previously unreported alcohol (**2**).

RESULTS AND DISCUSSION

Both the compounds **1** and **2** were recognized to be gymnomitrane-type sesquiterpenes on the basis of their GC-MS fragment patterns. Compound **1** was confirmed to be the common liverwort component β-barbatene by comparison of its GC-MS data [2] and ^{1}H NMR data [3] with those of authentic sample. Gymnomitrane-type sesquiterpenoids always show two major C_7 and C_8 fragments in their mass spectra (Table I) with the cleavage indicated in Fig. 1. The mass spectrum of compound **2** revealed a molecular ion $[M]^+$ 220 ($C_{15}H_{24}O$) and major

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*Corresponding author. Tel.: +886-2-2623-0821. Fax: +886-2-2620-9924. E-mail: clwu@mail.tku.edu.tw

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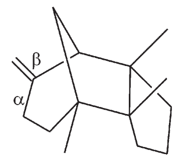
TABLE I Major MS fragments of gymnomitrane-type sesquiterpenoids

Cpd	*[M]$^+$*	*Major MS fragments*		*Ref.*
		C_7 m/z (%)	*C_8 m/z (%)*	
1α	204	96 (50)	108 (80), 93 (100) (108-CH_3)	[2]
1β	204	96 (90), 95 (65)	108 (80), 93 (100)	[2]
2	220	96 (40), 95 (100), 94 (50)	124 (35) ($C_8H_{12}O$)	The present study
4	220	96 (66)	123 (100), 106 (36) (124-H_2O)	[4]
6	202	–	106 (95), 91 (100) (106-CH_3)	[2]
7	220	95 (100)	124 (52), 106 (39)	[5]
8	218	110 (100) ($C_7H_{10}O$)	93 (57) (108-CH_3)	[6]

fragments at *m*/*z* 94, 95, 96 (C_7) and 124 (C_8). Compound **2** was isolated from the 10% EtOAc/*n*-hexane eluate of the hydrodistilled oil from column chromatography on silica gel. The ^{1}H NMR (Table II) displayed signals of three tertiary methyl groups at δ_H 0.91, 1.00, and 1.03 (all s), one oxygen-bearing methine at δ_H 3.65 (dd, $J = 10.8$, 8.1 Hz, 1 H), and two exomethylenes at δ_H 4.62 and 4.65 (both t, $J = 1.5$ Hz, 1H each). The ^{13}C-DEPT NMR (Table II) confirmed three methyl groups, six methylenes, two methines, and four quaternary carbons. The spectral data above were indeed consistent with a secondary alcohol of gymnomitrane skeleton. Three known gymnomitrane secondary alcohols **3**, **4**, **5** have been reported [4,7,8]. But none of their spectral data agreed with those of compound **2**. The subsequent HMQC and HMBC experiments (Table II) indicated that the alcohol functional group should be placed at C-5. Although the NOESY correlations (Fig. 2) suggested an



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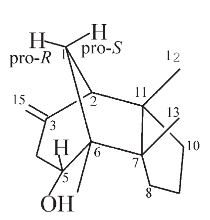

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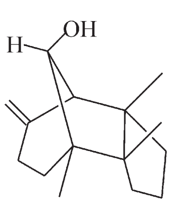

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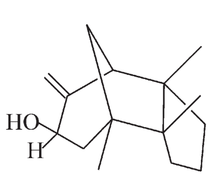

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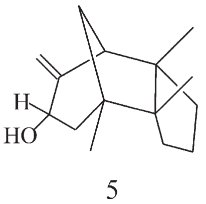

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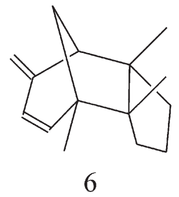

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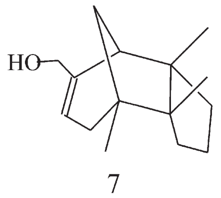

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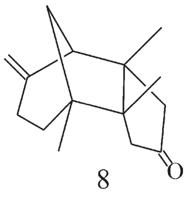

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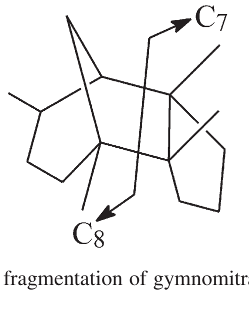

FIGURE 1 Typical MS fragmentation of gymnomitrane-type compounds.

TABLE II ^{1}H and ^{13}C NMR data of (−)-gymnomitr-3(15)-en-5α-ol (**2**)

Atom		*δ$_H$ (J, Hz)*	*δ$_C$*	*HMBC correlations (C #)*
1	CH$_2$(pro-*R*)	1.13 (d, 12.0)	45.9	7, 11
	CH$_2$(pro-*S*)	2.05 (dd, 12.0, 4.6)		2, 3, 6, 11, 14
2	CH	2.12 (d, 4.6)	55.3	1, 4, 7, 12
3	4°C	–	149.7	
4	CH$_2$ *α*	2.61 (br dd, 10.8, 8.1)	38.5	3, 5, 15
	CH$_2$ *β*	2.64 (tt, 10.8, 1.5)		
5	CH	3.65 (dd, 10.8, 8.1)	80.7	6, 7
6	4°C	–	47.8	
7	4°C	–	54.3	
8	CH$_2$ *α*	2.57 (br dd, 14.5, 10.5)	35.5	
	CH$_2$ *β*	1.07 (br dd, 14.5, 3.5)		14
9	CH$_2$	1.77 (m)	27.6	
10	CH$_2$	1.75 (m), 1.10*	36.8	12
11	4°C	–	55.5	
12	CH$_3$	1.03 (s)	27.3	2, 7, 10, 11
13	CH$_3$	0.91 (s)	24.1	6, 7, 8, 11
14	CH$_3$	1.00 (s)	21.4	1, 5, 6, 7
15	CH$_2$	4.62 (t, 1.5)	108.9	2, 4
		4.65 (t, 1.5)		2, 4

* Overlapped signal.

α-configuration of the alcohol at C-5, the coupling constants of this methine proton (dd, $J = 10.8$, 8.1 Hz) were not so clear. A final X-ray analysis of the crystal (Fig. 3) confirmed the relative configuration at C-5. Compound **2** was thus identified to be gymnomitr-3(15)-en-5α-ol.

Two other minor gymnomitrane hydrocarbons were also observed in the GC-MS examination of the oil. They were α-barbatene (**1**) [2] and gymnomitra-3(15),4-diene (**6**) [2]. The liverwort *C. recurvifolia* biosynthesized sesquiterpenes of gymnomitrane-type as its major skeleton. In the family of Cephaloziellaceae, the only other species which had been chemically studied was *Cephaloziella recurvifolia* [9]. The latter species produced sesquiterpenoids of aromadendrane-type as its major components.

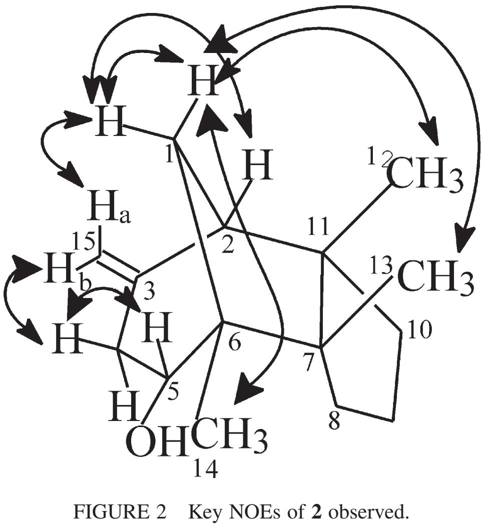

FIGURE 2 Key NOEs of **2** observed.

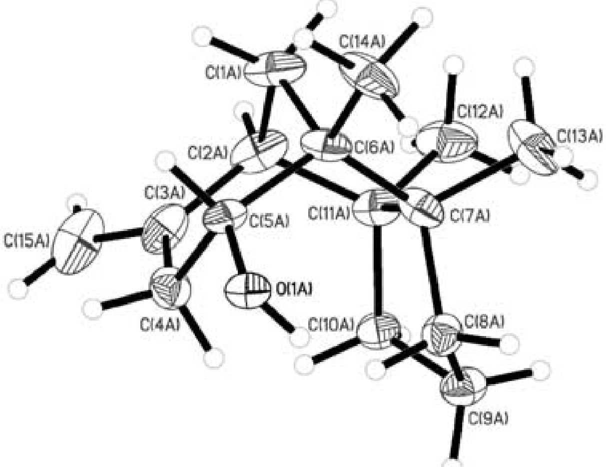

FIGURE 3 ORTEP drawing of compound **2**.

EXPERIMENTAL SECTION

General Experimental Procedures

Optical rotation was measured in $CHCl_3$. IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. ^1H and ^{13}C NMR were measured on Bruker AMWB-300, and AMX-500 using $CDCl_3$ as solvent. GC-MS measurements were performed with an HP 5890 gas chromatograph coupled to an HP GCD mass spectrometer (EI, 70 eV, column, DBWAX, 30×0.25, 50–220°C (5°C min^{-1}, 120 min in total).

Plant Material

C. recurvifolia (Steph.) Inoue was collected at the Yuenyang Lake (1700 m), Hsinchu Hsien, Taiwan in 1999. The specimen was identified by Dr K. Yamada (Ise-Shi, Japan) and deposited at the Department of Chemistry, Tamkang University.

Extraction and Isolation

The essential oil (~ 1 g) was obtained by distillation of the aqueous homogenates of the dried plants (100 g) using hexane as collection solvent. The GC-MS of this oil showed two distinct components in 25 and 35%, respectively. All other peaks were minute and smaller than 5% in area ratio. The hydrodistilled oil (~ 1 g) of *C. recurvifolia* was chromatographed on silica gel using EtOAc/*n*-hexane as gradient solvent. In the pure hexane fraction, β-barbatene (**1**) (20 mg) was obtained. In the 10% EtOAc/*n*-hexane eluate, compound **2** (30 mg) was furnished.

Gymnomitr-3(15)-en-5α-ol (**2**): colorless needles. $[\alpha]_D$ −11.7 (c 0.1, $CHCl_3$); IR (film) ν_{max} (KBr) cm^{-1} 3450, 1641; GC-MS(EI) *m/z* (rel. int.): 220 ($[M]^+$, 0.5), 124 (35), 96 (40), 95 (100), 94 (50); ^1H and ^{13}C NMR: Table II. Compound **2** afforded monoclinic crystals from pure hexane, cell parameters: $a = 7.179$, $b = 21.145$, $c = 13.341$ Å, space group $P2_1$, $Z = 6$. The diffraction intensities were collected on a NONIUS KappaCCD diffractometer using MoKα radiation. The structure was solved by direct methods and the final *R* value was 0.0772 for 6345 reflections.

Acknowledgements

Some of the NMR experiments were done by Miss S.-C. Lin, Department of Chemistry, Academia Sinica. X-ray analysis was performed by Mr G.-H. Lee at the Instrumentation Center of National Taiwan University. The present research was supported by the National Science Council of the Republic of China. We also thank Dr K. Yamada for the identification of the liverwort species.

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