Pergamon

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ISOPLAGIOCHILIDE FROM THE LIVERWORT *PLAGIOCHILA ELEGANS*

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Key Word Index—*Plagiochila elegans*; Plagiochilaceae; liverwort; isoplagiochilide; plagiochiline C.

Abstract—A new 2,3-secoaromadendrane, isoplagiochilide, was isolated from the liverwort *Plagiochila elegans* along with the known sesquiterpenoid plagiochiline C. *P. elegans* is thus classified as chemotype I species.

INTRODUCTION

Plagiochilide (**1**) has previously been isolated from three liverwort species, *Plagiochila yokogurensis* [1], *P. asplenioides* [2] and *P. goyana* [3]. Recently, acetoxyisoplagiochilide (**2**) was found as an isolate from another species, *P. ovalifolia* [4]. In this paper we report one more related structure, isoplagiochilde (**3**), from a different *plagiochila* species, *P. elegans*, collected in the middle part of Taiwan [5]. The plants are robust and large, usually 5–8 mm wide and *ca.* 10 cm long. This species has been reported from the Himalayas, China and Taiwan [6], but its chemistry has never been investigated.

RESULTS AND DISCUSSION

Isoplagiochilide (**3**) appeared as the most abundant peak in the GC profile of the volatile oil. Its GC-mass spectrum showed a molecular ion of m/z 232 ($C_{15}H_{20}O_2$) and a base peak of m/z 69. The ^{1}H NMR spectrum (Table 1) displayed four singlet methyls (δ 0.99, 1.09, 1.62 and 2.35), one olefinic proton (δ 6.15 *bs*), and two protons on a cyclopropane ring (δ 0.57, $t, J = 9.3$ Hz; 0.56, *m*). The ^{13}C-DEPT NMR spectrum indicated four methyls, two methylenes, three methines, one trisubstituted (δ 115.7 and 133.0) and one tetrasubstituted (δ 122.2 and 160.1) double bond, in addition to one lactone carbonyl at δ 161.5. The identity of δ 160.1 for a double bond carbon was confirmed by the subsequent HMBC spectrum. The particular high-field shift of the lactone carbonyl (δ 161.5) also supported the conjugated nature of these two functional groups. These spectral characters clearly suggested structure **3** of 2,3-secoaromadendrane skeleton for this compound. Sesquiterpenoids of 2,3-secoaromadendrane skeleton have been shown to be the chemical marker of many *Plagiochila* species [7]

The ^{13}C NMR data of compounds **2** and **3** agreed well except that the assignments of C-1 (δ 160.01) and C-10 (δ 122.0) for compound **2** [4] were reversed compared with those of compound **3**. According to the conjugated nature of the double bond with the lactone ring, the correct chemical shift assignment should be as shown in Table 1 [8].

In addition to isoplagiochilide (**3**), plagiochiline C (**4**) [9, 10] was also isolated as the other major component. Plagiochiline C showed significant antiplatelet effects on arachidonate (100 μM) (95% and 45% inhibitions at 100 and 50 μg ml^{-1}, respectively) and collagen (10 μg ml^{-1}) (100% inhibition at 100 μg ml^{-1} level) induced aggregations of washed rabbit platelets. Conversely, isoplagiochilide (**3**) displayed fairly weak activities.

Plagiochila species have been classified into eight chemotypes [4]. *P. elegans* belongs to type I, the 2,3-secoaromadendrane type.

Table 1. ^{1}H and ^{13}C NMR data of isoplagiochilide (**3**) (in $CDCl_3$)

C	C-Type	$\delta_{^{13}C}$	$\delta_{^{1}H}$	J(Hz)
1	4°C	122.2	–	
2	4°C	161.5	–	
3	CH	133.0	6.15	br. s
4	4°C	115.7	–	
5	CH	37.0	2.96	d, J 9.0
6	CH	31.1	0.57	t, J 9.3
7	CH	20.7	0.56	m
8	CH_2	16.7	1.75	m
			1.83	m
9	CH_2	37.0	2.05	dt, J 13.6, 4.3
			2.35	m
10	4°C	160.0	–	
11	4°C	19.5	–	
12	CH_3	15.6	1.09	s
13	CH_3	28.8	0.99	s
14	CH_3	24.1	2.35	s
15	CH_3	15.5	1.62	s

Assignments were determined by consideration of data from ^{13}C–^{1}H COSY, ^{1}H–^{1}H COSY and HMBC as well.

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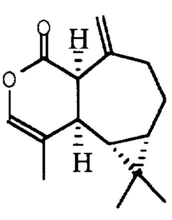

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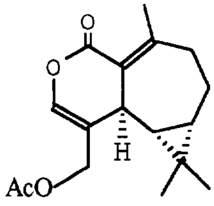

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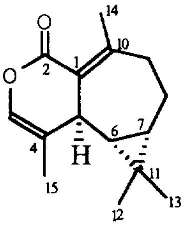

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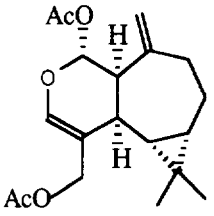

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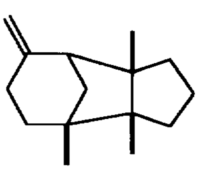

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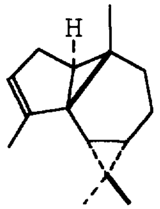

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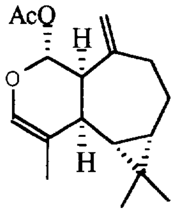

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EXPERIMENTAL

Methods. Solvents used for spectral measurements were: $CDCl_3$ (^1H and ^{13}C NMR, 300 MHz), 95% EtOH (UV), and $CHCl_3$ ($[\alpha]_D$ and IR). GC–MS: 70 eV, column, DBWAX, 30×0.25, 50–220°C (40 min), 5° min^{-1}.

Plant material. P. elegans Mitt. was collected in 1991 at Shanlin Chi, Nantow Hsien (1700 m) and identified by Dr K. Yamada (Ise-shi, Japan). The voucher specimens were deposited at the Department of Chemistry, Tamkang University, R.O.C.

Extraction and isolation. Air-dried and powdered whole plants (50 g) were extracted with EtOAc. The crude extract (0.7 g) was chromatographed on silica gel (70–230 mesh) using an *n*-hexane–EtOAc gradient. Fr. 4 (15% EtOAc–hexane) was rechromatographed on silica gel (230–400 mesh, 70% benzene–hexane) to yield isoplagiochilide (**3**) (16 mg). Fr. 5 (20% EtOAc–hexane) provided plagiochiline C (**4**) (29 mg) [9, 10]. A GC–MS examination of the crude oil indicated β-barbatene (**5**) as the second major peak with isoplagiochilide (**3**) among the volatile components. Other identified constituents were anastreptene (**6**), ethyl palmitate, plagiochiline H (**7**) [11], phytadienes, phytol and palmitic acid.

Isoplagiochilide (**3**). Oil; $[\alpha]_D + 55°$ (c 0.16); IR ν_{max} cm^{-1}: 3085, 1715, 1509. UVλ_{max} nm (logε): 260 (2.94). GC–MS m/z (rel. int.): 232 ($[M]^+$ (16), 203 (48), 164 (28), 161 (29), 149 (31), 135 (32), 121 (36), 91 (28), 69 (100), 41 (36). GC: R_t 43.59 min; TLC: R_f 0.6 (benzene–*n*-hexane, 9:1).

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