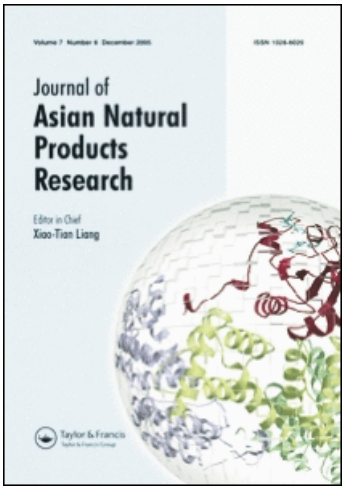

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Note

NEOPALLAVICININ FROM THE TAIWANESE LIVERWORT *PALLAVICINIA SUBCILIATA*

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Neopallavicinin (**2**), a diastereomer of pallavicinin (**1**), was identified from the Taiwanese liverwort *Pallavicinia subciliata*. The structure of neopallavicinin was deduced by spectroscopic analysis. Three chemotypes may be classified for the species *Pallavicinia subciliata*.

Keywords: Pallavicinia subciliata; Pallaviciniaceae; Neopallavicinin; Pallavicinin; *Jensenia spinosa*; Chemotaxonomy

INTRODUCTION

Previously we reported a novel rearranged 7,8-secolabdanoid, pallavicinin (**1**), from the Taiwanese liverwort *Pallavicinia subciliata* (Aust.) Steph. [1] collected at Tatung Shan, Taipei Hsien. In our continuous investigation, a diastereomer of pallavicinin was recently isolated from the same species collected at a different location. In this paper, the structural elucidation of neopallavicinin (**2**) and the chemotaxonomy of this species are discussed.

RESULTS AND DISCUSSION

The GC–MS of the crude oil of *P. subciliata* collected near Wufonchi Waterfalls revealed two large peaks with fairly long retention times. Both

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TABLE I ^{1}H and ^{13}C NMR data of neopallavicinin (**2**)

Atom No.	$\delta^{1}H$ (*J*, Hz)	$\delta^{13}C$
1a(pro-R)	1.76 (*dd*, *J* 12.9, 4.5)	42.1
1b(pro-S)	2.31 (*d*, *J* 12.9)	
2	2.72 (*d*, *J* 4.5)	60.0
3	—	214.4
4		45.1
5	2.26 (*d*, *J* 10.2)	49.2
6	5.69 (*dt*, *J* 17.3, 10.2)	135.6
7a	5.02 (*dd*, *J* 17.3, 1.8)	117.1
7b	5.04 (*dd*, *J* 10.2, 1.8)	
8	—	95.7
9	2.27 (*d*, *J* 8.7)	65.2
10	—	46.1
11	5.18 (*dd*, *J* 8.7, 7.1)	81.3
12	5.26 (*br d*, *J* 7.1)	77.8
13		127.4
14	7.10 (*qd*, *J* 7.2, 1.9)	145.8
15	1.98 (*d*, *J* 7.2)	16.2
16	—	170.4
17	1.42 (*s*)	25.4
18	0.83 (*s*)	25.3
19	1.04 (*s*)	27.4
20	1.21 (*s*)	25.6

peaks displayed very similar mass fragments with the same molecular ions of *m/z* 330 and base peaks at *m/z* 83. The component of the earlier GC peak was eluted first upon chromatography on Sephadex and silica gel. Its ^{1}H NMR proved to be identical with that of the known pallavicinin (**1**) isolated previously from the same species collected at a different location [1]. The compound corresponding to the later GC peak was obtained from a more polar fraction. Although its ^{1}H NMR (Table I) appeared very similar to that of pallavicinin (**1**), but many of the signals were slightly shifted. Obviously this compound was a stereoisomer of pallavicinin (**1**). The proton and carbon assignments at each atom (Table I) were achieved by ^{13}C-DEPT, ^{1}H-^{1}H COSY, ^{13}C-^{1}H COSY and long range ^{13}C–^{1}H COSY. The stereochemistry was deduced from the NOESY spectrum as shown in Fig. 1. The key correlation which supported a *cis*-relationship between H_9 and H_{11} was unambiguously observed, whereas such a cross peak was not shown in the NOESY spectrum of pallavicinin (**1**) [1]. The *endo*-form of the lactone ring could also explain the downfield shift of H_5 at δ 2.26 (δ 1.78 for pallavicinin (**1**) [1]) by the inductive electron withdrawal of the sp^3-oxygen atom in close vicinity [2] (Fig. 1). Hence this new compound was confirmed to be a diastereomer of pallavicinin (**1**) with stereochemistry differing at C_{11} and C_{12}, and thus named neopallavicinin (**2**).

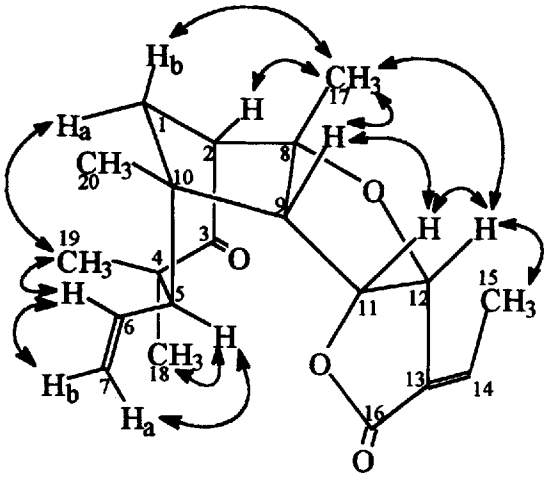

FIGURE 1 Key NOE's observed for noepallavacinin (**2**).

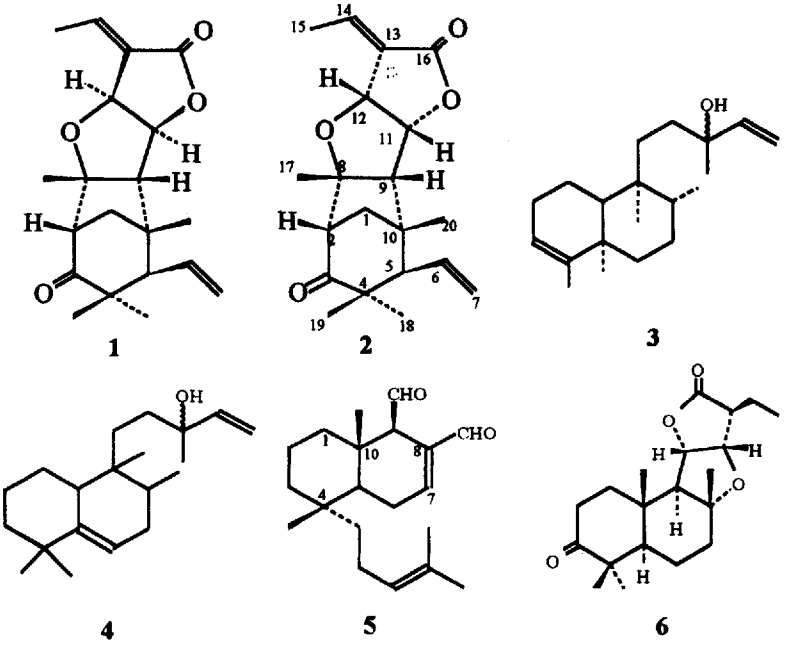

TABLE II Chemotypes of *P. subciliata* based on the diterpene skeleton

Locality	*Chemotype*	*Labdane*	*Clerodane*
TP	I	+	–
TT	I	+ + +	
SL	I	+	–
AL	I	+	–
FS	II	–	+ + +
WFC	III	+ + +	+
YM	III	+	+ + +
NR	III	+	+

TP: Taiping Shan, Ilan Hsien; TT: Tatung Shan, Taipei Hsien; SL: Shanlinchi, Nantou Hsien; AL: Ali Shan, Chiayi Hsien; FS: Fu Shan, Ilan Hsien; WFC: Wufonchi, Ilan Hsien; YM: Yangming Shan, Taipei City and NR: Kasuga mountain, Nara City, Japan.

We have checked several specimens of *P. subciliata* collected from different localities on their major chemical constituents [3], and found that three chemotypes may be classified for this species on the basis of diterpene skeleton. (Table II) Chemotype I biosynthesizes the rearranged 7,8-secolabdanoid – pallavicinin (**1**) or neopallavicinin (**2**) or both. Chemotype II produces a clerodane alcohol – (-)-cleroda-3,14-dien-13-ol (**3**) instead, no labdane-type diterpenoids could be detected. Chemotype III biosynthesizes both labdane- and clerodane-type compounds (**1**–**3**) as their distinct constituents.

Asakawa *et al.* had reported a rearranged labdadienol, pallavicinol (**4**), and sacculatal (**5**) from *P. levieri* [4]. The same group also identified a labdane lactone, symphyogynolide (**6**), closely related to pallavicinin (**1**), in *Symphyogyna braciliensis* from Venezuela [5]. We recently checked the oil of the same species from South Africa [6] by GC–MS, and identified symphogynolide (**6**) [5] as a minor component, in addition to a major isosymphogynolide with a molecular ion of $[M]^+$ 332, two mass units less than that of symphogynolide. All significant mass fragments of isosymphyogynolide were fairly similar to those of synphyogynolide [5]. Symphyogynoideae has been placed in the subfamily of Pallaviciniaceae by Grolle [7]. Spörke and Becker detected perrottetianal A, a double bond (Δ^8) positional isomer of **5**, in *S. brongniartii* of Panama as a major component [8]. Since the genus *Jensenia* is placed in the same subfamily of *Pallavicinia*, we obtained a South African sample of *Jensenia spinosa* (= *Pallavicinia stephanii*) from Perold [6] to check its major component by GC–MS. Clearly pallavicinin (**1**) was observed as a large peak in the crude oil. The above results support the close relationship of the two subfamilies of Pallaviciniaceae chemically, and indicate that diterpenoids of labdane-, clerodane-, and succulatane-types are the three main skeletons biosynthesized by the family of Pallaviciniaceae species.

EXPERIMENTAL SECTION

General Experimental Procedures

NMR spectra were measured in $CDCl_3$ on Bruker AM-300WB and DMX-500. All GC–MS (EI) spectra were taken at 70 eV. A DBWAX, 30 m × 0.25 mm (i.d.), fused silica capillary column was used for both GC and GC–MS. The column temperature was programmed from 50° to 220°C at 5°/min. For GC–MS analysis on the oil of *S. braciliensis*, a DB-5, 30 m × 0.25 mm (i.d.), capillary column was used instead, and the temperature was programmed from 150° to 220°C at 5°/min. IR spectra were measured as a film on KBr pellets, and the UV recorded in EtOH. Optical data were taken on Jasco DIP-360 in CH_2Cl_2.

Plant Materials

Plants of *P. subciliata* were collected at Wufonchi Waterfalls (600 m, alt.), Ilan Hsien, Taiwan. Specimens were identified by Dr. Kohsaku Yamada (Ise-shi, Japan) and deposited at the Department of Chemistry, Tamkang University.

Extraction and Isolation

The ground material of *P. subciliata* (12 g) was extracted with EtOAc. The crude oil (0.16 g) was first chromatographed on Sephadex LH-20 and eluted with $CHCl_3/CH_3OH$ (1 : 1). The third fraction was further chromatographed on silica gel (230–400 mesh) to afford pallavicinin (**1**) [1] (7.8 mg) in the 20% EtOAc/*n*-hexane eluate, and neopallavicinin (**2**) (4.6 mg) in the 40% eluate.

Pallavicinin (**1**) GC Rt 91.37 min; GC–MS *m/z* (rel. int.) 330 ([M^+], 5), 315 (5), 302 (12), 220 (45), 167 (68), 121 (75), 110 (62), 83 (100), 55 (68).

Neopallavicinin (**2**) oil; $[\alpha]_D^{25}$ −91.6 (c 0.23, CH_2Cl_2); UV (EtOH) λ_{max} nm (ε): 214 (7008); IR (film)$\nu_{max}^{cm^{-1}}$: 1759, 1710, 1639; GC Rt 97.26 min; GC–MS *m/z* (rel. int.) 330 ([M^+], 10), 315 (17), 220 (38), 167 (59), 121 (43), 107 (80), 83 (100), 55 (48); NMR data are shown in Table I.

Symphyogynolide (**6**) GC Rt 11.14 min (DB-5, 150° to 220°C at 5°/min); GC–MS *m/z* (rel. int.) 334 ([M^+], 26), 319 (43), 292 (12), 279 (45), 263 (55), . . . , 135 (90), 109 (90), 83 (74), 69 (74), 55 (100).

Isosymphygynolide GC Rt 12.87 min (DB-5, 150° to 220°C at 5°/min); GC–MS *m/z* (rel. int.) 332 ([M^+], 77), 317 (97), 290 (29), 277 (37), 261 (74), . . . , 135 (87), 109 (75), 107 (76), 81 (67), 69 (79), 55 (100).

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