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NOVEL SKELETAL DITERPENOIDS FROM THE JAPANESE LIVERWORT *PALLAVICINIA SUBCILIATA*

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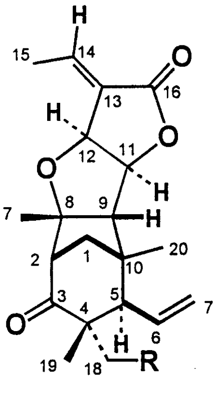
The diethyl ether extract of *Pallavicinia subciliata* yielded unique skeletal diterpenoids in addition to the previously known compound. The structures of six new diterpenoids have been established by 2D NMR and/or X-ray crystallographic analysis. They are shown to be a modified labdane-type diterpenoid.

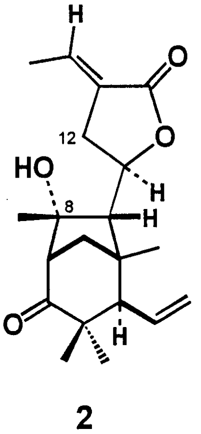
KEY WORDS liverwort; Metzgeriales; *Pallavicinia subciliata*; diterpenoids; chemosystematics

Phytochemical study of bryophytes has been performed from the chemosystematic point of view in our laboratory. Classification of liverworts is very difficult and study of their chemical constituents is necessary. Since the liverworts occasionally produce their own peculiar constituents,1) the viewpoint of natural product chemistry of liverworts is of considerable interest.

Pallavicinia subciliata (Aust.) Steph, which belongs to the Metzgeriales, is widely distributed in Japan and grows on wet rocks. The diethyl ether extract of *P. subciliata* yielded unique skeletal diterpenoids **1-6** in addition to the previously known compound 7.2) The structures of the new diterpenoids have been established by 600-MHz 2D NMR and/or X-ray crystallographic analysis. Here we report on the isolation and structure determination of the six new diterpenoids.



1 R=OH
7 R=H



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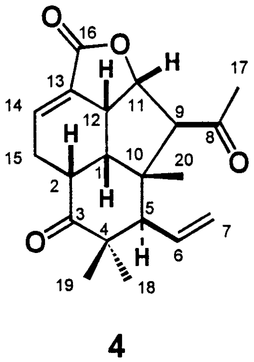

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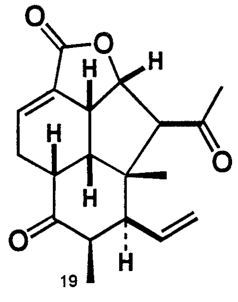

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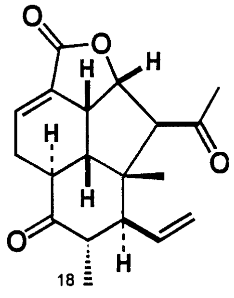

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P. subciliata (#96052, dry weight 317.5 g) was collected in Tsushima, Nagasaki, in May 1996. The diethyl ether extract was chromatographed on silica gel and then on Sephadex LH-20 to give a mixture, including compounds **1-7**. Further purification of the mixture by preparative HPLC on silica gel afforded **1-7** (**1**, 0.12 %; **2**, 1.04 %; **3**, 0.38 %; **4**, 0.56 %; **5**, 0.30 %; **6**, 0.07 %; 7, 0.16 % in yield of the extract), respectively. Compound 7 was identified as a known compound by means of its spectral data.2) The structures of **1**, mp 246°, $[\alpha]_D$-15.3° ($CHCl_3$, *c* 0.97) and **3**, mp 191°, $[\alpha]_D$-223.0° ($CHCl_3$, *c* 1.30) were established by X-ray crystallographic analysis of crystals3) obtained from ethyl acetate solution, respectively. The structures of **2**, $[\alpha]_D$+2.9° ($CHCl_3$, *c* 3.32) **4**, $[\alpha]_D$-34.2°($CHCl_3$, *c* 4.73) **5**, $[\alpha]_D$-29.6° ($CHCl_3$, *c* 2.43), and **6**

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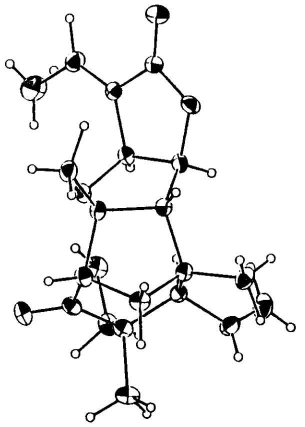
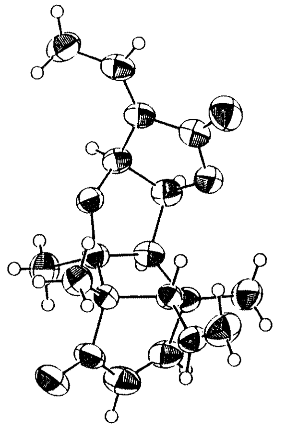
$[\alpha]_D$-145.7°($CHCl_3$, *c* 0.61) were established by comparing their spectral data with those of **1**, **3**, and 7.

The ^1H and ^{13}C NMR[4)] data of **2** and **4-6** are summarized in Table 1 and references. The gross structures of **2** and **4-6** were proved by extensive 2D NMR experiments involving the determination of ^1H-^1H COSY, NOESY, HSQC, and HMBC spectra. Compounds **2-7** were also isolated from *P. subciliata* (#95156) collected in Tokushima in July 1995. These carbon skeletons were formed by C_7-C_8 bond cleavage of labdane-type diterpenoids. The biosynthesis of **1-7** was of considerable interest. It can be presumed that the biosynthesis was performed by bond reconstruction of C_{15}-C_2 and C_{12}-C_1 (compounds **4-6**), and of C_8-C_2 or C_8-C_4 (compounds **1**, **2**, and **3**) after the cleavage.



ORTEP drawing of **1**



ORTEP drawing of **3**

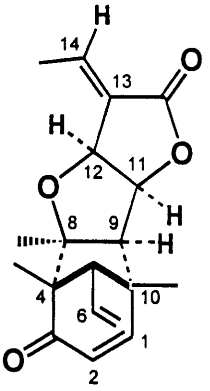


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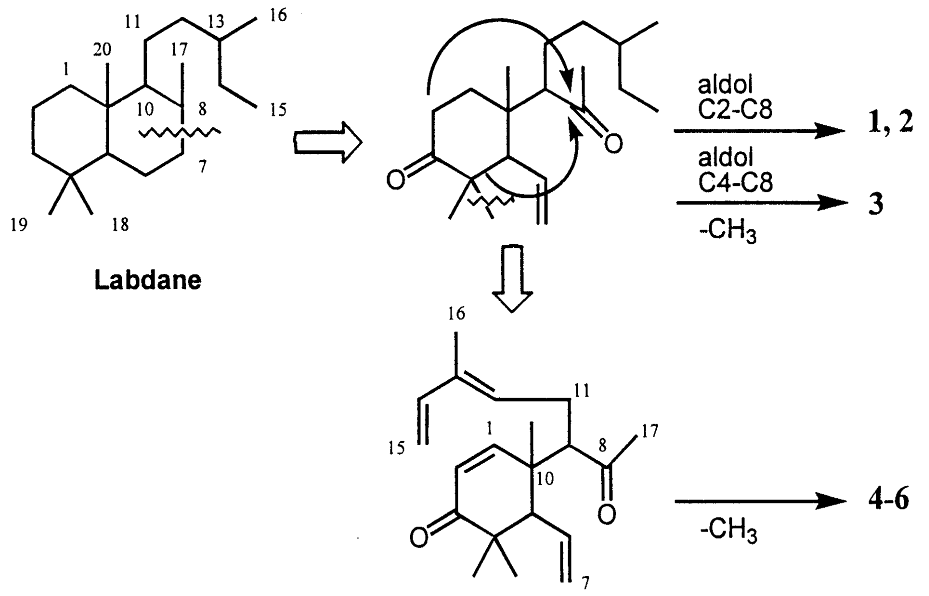
Table 1. 600-MHz ^1H NMR data for **2** and **4-6** in $CDCl_3$

	2	**4**	**5**	**6**
H-1	α, 1.58 (ddd, *J*=13, 4, 1 Hz) β, 2.20 (d, *J*=13 Hz)	2.99 (dd, *J*=11, 10 Hz)	2.95 (dd, *J*=11, 10 Hz)	2.17 (m)
H-2	2.59 (d, *J*=4 Hz)	3.32 (ddd, *J*=11, 4, 2 Hz)	3.07 (ddd, *J*=11, 4, 2 Hz)	2.20 (m)
H-4			2.61 (quin, *J*=7 Hz)	2.29 (m)
H-5	2.53 (brd, *J*=10 Hz)	2.67 (d, *J*=11 Hz)	2.64 (dd, *J*=10, 7 Hz)	2.43 (dd, *J*=10, 12 Hz)
H-6	5.77 (ddd, *J*=16, 10, 10 Hz)	5.87 (ddd, *J*=16, 10, 11 Hz)	5.74 (ddd, *J*=17, 10, 10 Hz)	5.55 (ddd, *J*=17, 10, 10 Hz)
H-7(*cis*)	5.09 (dd, *J*=10, 2 Hz)	5.27 (dd, *J*=10, 2 Hz)	5.32 (dd, *J*=10, 2 Hz)	5.16 (dd, *J*=10, 2 Hz)
H-7(*trans*)	5.04 (dd, *J*=16, 2 Hz)	5.15 (dd, *J*=16, 2 Hz)	5.20 (dd, *J*=16, 2 Hz)	5.05 (dd, *J*=17, 2 Hz)
H-9	1.71 (d, *J*=11 Hz)	2.39 (d, *J*=8 Hz)	2.47 (d, *J*=9 Hz)	2.96 (d, *J*=9 Hz)
H-11	4.73 (ddd, *J*=11, 7, 7 Hz)	5.15 (dd, *J*=8, 8 Hz)	5.39 (t, *J*=9 Hz)	5.22 (dd, *J*=10, 9 Hz)
H-12	α, 3.17 (dddd, *J*=18, 7, 3, 2 Hz) β, 2.63 (dddd, *J*=18, 7, 3, 2 Hz)	3.36 (dddd, *J*=10, 8, 3, 3 Hz)	3.38 (dddd, *J*=10, 9, 3, 3 Hz)	3.50 (m)
H-14	6.77 (qt, *J*=7, 3 Hz)	7.37 (ddd, *J*=8, 3, 3 Hz)	7.30 (ddd, *J*=8, 3, 3 Hz)	7.24 (ddd, *J*=8, 4, 4 Hz)
H-15	1.86 (dt, *J*=7, 2 Hz)	α, 2.74 (ddd, *J*=15, 8, 2 Hz) β, 1.91 (dddd, *J*=15, 4, 3, 3 Hz)	α, 3.02 (ddd, *J*=15, 8, 2 Hz) β, 1.77 (dddd, *J*=15, 4, 3, 3 Hz)	α, 2.78 (ddd, *J*=15, 8, 2 Hz) β, 1.84 (m)
H-17	1.51 (s)	2.25 (s)	2.26 (s)	2.26 (s)
H-18	1.08 (s)	1.07 (s)		1.01 (d, *J*=7 Hz)
H-19	1.10 (s)	0.98 (s)	1.04 (d, *J*=7 Hz)	
H-20	1.16 (s)	1.11 (s)	1.10 (s)	1.17 (s)



Possible biogenetic pathway of **1-6**

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3) Diffraction measurements were performed on a Mac Science MXC18 diffractometer using Cu K-alpha radiation (λ=1.54178 Å). The final R values of **1** and **3** were 0.045 and 0.054, respectively. Crystal data were as follows: Compound **1**: Orthorhombic, $P2_12_12_1$, a=7.978(2) Å, b=28.946(5) Å, c=7.735(2) Å, V=1786.4(6) Å^3, Z=4, D_{calc}=1.286, 1219 observed reflections. Compound **3**: Orthorhombic, $P22_12_1$, a=7.265(2) Å, b=8.167(4) Å, c=28.350(4) Å, V=1682.079956(1) Å^3, Z=4, D_{calc}=1.326, 1405 observed reflections. The CRYSTAN SIR92 program was used to solve the structures of **1** and **3**.

4) ^{13}C NMR data (150-MHz, in $CDCl_3$) for **2** and **4-6**.

2: 36.7(C-1), 63.1(C-2), 218.3(C-3), 45.0(C-4), 49.8(C-5), 136.2(C-6), 116.7(C-7), 79.1(C-8), 65.1(C-9), 46.1(C-10), 76.8(C-11), 32.1(C-12), 127.3(C-13), 135.2(C-14), 15.6(C-15), 170.5(C-16), 34.0(C-17), 26.2(C-18), 27.3(C-19), 27.8(C-20). **4**: 48.3(C-1), 44.1(C-2), 216.1(C-3), 44.9(C-4), 55.7(C-5), 136.4(C-6), 119.8(C-7), 207.0(C-8), 60.6(C-9), 47.2(C-10), 82.2(C-11), 40.3(C-12), 127.1(C-13), 141.3(C-14), 26.1(C-15), 168.6(C-16), 31.8(C-17), 28.7(C-18), 28.4(C-19), 23.7(C-20). **5**: 46.3 (C-1), 46.6(C-2), 212.5(C-3), 41.7(C-4), 50.1(C-5), 134.4(C-6), 121.6(C-7), 206.0(C-8), 60.3(C-9), 48.2(C-10), 81.7(C-11), 39.9(C-12), 127.8(C-13), 141.6(C-14), 25.1(C-15), 168.2(C-16), 31.8(C-17), 16.1(C-19), 24.7(C-20). **6**: 48.4(C-1), 48.2(C-2), 211.4(C-3), 44.0(C-4), 54.1(C-5), 135.6(C-6), 119.4(C-7), 207.0(C-8), 64.1(C-9), 51.4(C-10), 84.6(C-11), 40.4(C-12), 130.9(C-13), 141.0(C-14), 24.1(C-15), 168.6(C-16), 34.5(C-17), 14.1(C-18), 19.6(C-20).

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