SUPPLEMENTARY MATERIAL

Cytotoxic tremulanes and 5,6-secotremulanes, four new sesquiterpenoids from a plant-associated fungus X1-2

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Abstract: Two new tremulanes and two new 5,6-secotremulanes, davotremulanes A-D **1-4**, along with four known compounds **5-8**, were isolated from the culture extract of X1-2, an unidentified plant-associated fungus, which was isolated from the endangered plant, *Davidia involucrate* Baill. in Shennongjia District. The structures of new compounds **1-4** were established on the basis of extensive spectroscopic analysis. Compounds **1-8** were evaluated for cytotoxic activity to four cancer cell lines, and compounds **1**, **2** and **5** displayed selectively moderate activities to A549 cell line with IC₅₀ at 15.3, 25.2, 35.2 $\mu\text{g/mL}$.

Keywords: Tremulanes; 5,6-secotremulanes; Plant-associated fungus; Secondary metabolites; Cytotoxic activity.

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Figure S1. The NMR spectrums of Davotremulanes A

COSY

HSQC

HMBC

Figure S2. The NMR spectrums of Davotremulanes B

¹H

¹³C

COSY

HSQC

HMBC

NOESY of D13-18-3

Figure S3. The NMR spectrums of Davotremulanes C and D

Current Data Parameters
NAME D13-18-b
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20111004
Time 21.17
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 114
DW 60.800 usec
DE 6.50 usec
TE 297.5 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 ¹H
P1 12.00 usec
PLW1 15.80000019 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300156 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

COSY

HSQC

NOESY

Figure S4. the HR- MS spectrums of Davotremulanes A

20120514-D-13-18-6_120508085017

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D-13-18-6

20120514-D-13-18-6_120508085017 #45-49 RT: 1.22-1.32 AV: 5 NL: 1.37E6
T: FTMS + p ESI Full ms [100.00-1000.00]

Figure S5. the HR- MS spectrums of Davotremulanes **B**

Figure S6. the HR- MS spectrums of Davotremulanes **C** and **D**

Figure S7. The CD spectrums of Davotremulanes A and B

the CD and the configuration analysis of Davotremulanes A

the CD and the configuration analysis of Davotremulanes B

Figure S8 the key HMBC correlations of compounds 1-4

Figure S9 the key NOESY correlations of compounds 1-4

Table S1: The NMR data of compounds **1-2** (400MHz for ^1H NMR and 100MHz for ^{13}C in CDCl_3)

NO	1		2	
	^{13}C	$^1\text{H}(J \text{ in Hz})$	^{13}C	$^1\text{H}(J \text{ in Hz})$
1	139.0(s)	-	37.7(d)	2.89 (dd, 10.0, 14.7, 1H)
2	125.2(s)	-	164.7(s)	-
3	37.4(d)	3.64(m,1H)	123.3(s)	-
4	30.1(t)	1.82(d,14.3,1H)	27.9(t)	2.75(dd,5.0,14.0,1H)
		2.06(m,1H)		2.54(dd,2.4,13.6,1H)
5	72.4(d)	4.06(t,4.0,1H)	71.6(d)	3.91(s, 1H)
6	38.3(d)	1.91(m,1H)	39.1(d)	2.17 (br s, 1H)
7	39.7(d)	3.37(m,1H)	40.8(d)	2.57 (m,1H)
8	39.2(t)	1.39(dd,11.0,13.0,1H)	39.5(t)	1.34 (t,8.0,1H)
		1.78(dd,8.0,11.0,1H)		1.69(t,5.0,8.0,1H)
9	43.8(s)	-	41.8(s)	-
10	41.4(t)	2.13(d,12.5,1H)	38.8(t)	1.63 (d,7.5,2H)
		1.85(m,1H)		
11	69.5(t)	4.74(dd,10.0,13.0, 2H)	70.6(t)	4.71 (d,14.4,1H)
				4.58 (d,14.8,1H)
12	180.1(s)	-	175.7(s)	-
13	11.5(q)	0.87(d,7.0,3H)	11.2(q)	1.01(d,7.0,1H)
14	23.5(q)	1.12(s,3H)	26.1(q)	1.05 (s,3H)
15	68.5(t)	3.28(dd,10.8,14.6,2H)	71.4(t)	3.41(s,2H)

Table S2. The NMR data of compounds 3-4 (400MHz for ^1H NMR and 100MHz for ^{13}C in CDCl_3)

NO	3		4	
	¹³ C	¹ H(<i>J</i> in Hz)	¹³ C	¹ H(<i>J</i> in Hz)
1	147.3(s)	-	142.1(s)	-
2	129.6(s)	-	124.1(s)	-
3	37.3(d)	3.81(m,1H)	35.6(d)	3.37(m,1H)
4	32.9(t)	2.57 (dd,1.2,9.4,1H)	32.1(t)	2.76(dd,4.4,16.0,1H) 2.57(dd,4.2,16.0,1H)
5	177.5(s)	-	173.1(s)	-
6	141.7(d)	5.72 (dd,8.1,10.0,1H)	139.6(d)	5.64(m,1H)
7	45.3(d)	3.42 (m, 1H)	45.7(d)	3.49(s,1H)
8	42.7(t)	1.74 (m,1H) 1.53 (m,1H)	43.0(t)	1.74(m,1H) 1.53(m,1H)
9	43.2 (C)	-	43.2(s)	-
10	41.0(t)	2.26 (dd,1.6,14.0,1H) 2.37 (d,14.0,1H)	41.1(t)	2.32(d,7.6,1H), 2.08(d, 7.8,1H)
11	60.3(t)	4.19 (d,12.01H) 4.27 (d,12.0,1H)	69.2(t)	4.82(d,14.0,1H), 4.72 (d,14.01H)
12	71.2(t)	4.26 (t,8.8,1H) 4.37 (t,8.8,1H)	63.5(t)	3.68(d,8.0,1H) 3.59(d,8.01H)
13	114.0(t)	5.01(t,3.8,6.2,1H) 5.04 (m, 1H)	114.9(t)	5.05(d,12.0,1H) 5.11(d,12.4, 1H)
14	22.7(q)	0.96 (s,3H)	22.8(q)	0.97(s,3H)
15	70.6(t)	3.49 (s,2H)	70.5(t)	3.50(s,2H)