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Seven New Sesquiterpenes from Cultures of the Basidiomycete *Conocybe siliginea*†

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Seven new tremulane-type sesquiterpenes (**1**—**7**) have been isolated from cultures of the basidiomycete *Conocybe siliginea*. Their structures and relative configurations were elucidated by extensive spectroscopic data (HSQC, HMBC, ^{1}H-^{1}H COSY, ROESY) and MS analysis.

Keywords *Conocybe siliginea*, tremulane sesquiterpenes, basidiomycete

Introduction

The genus *Conocybe* belongs to the order Agaricales and family Bolbitiaceae. Previous investigations of the genus *Conocybe* have reported the isolation of hallucinogenic or toxic compounds, such as psilocybin,[1,2] psilocin,[2] and *a*-amanitin,[3] that interfere with the normal action of brain serotonin.[4-6] Our previous investigation on the cultures of this fungus resulted in isolation of twelve tremulane-type sesquiterpenes[7] and three aliphatic diketones.[7,8] The tremulanes constitute a class of unusual sesquiterpenes that were isolated from cultures of *Phellinus tremulae*[9] and *Phellinus igniarius*.[10] Some of these compounds were found to possess vascular-relaxing activity and 11β-hydroxysteroid dehydrogenase inhibitory activity.[8,10] In order to search for more novel and potentially bioactive secondary metabolites, we changed the condition and enlarged the fermentation scale of the fungus. In this paper, we describe the isolation and structural elucidation of seven new tremulane-type sesquiterpenes (**1**—**7**) (Figure 1) from cultures of *C. siliginea*.

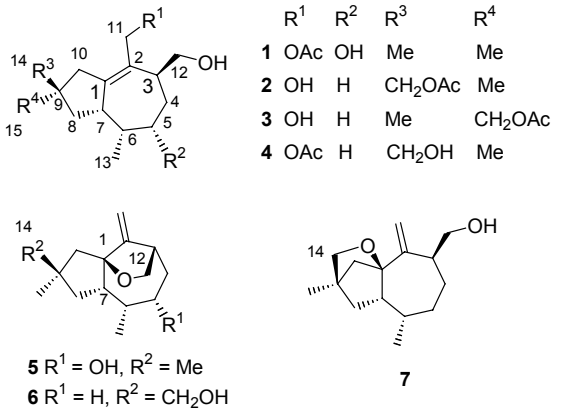

Figure 1 Structures of compounds **1**—**7**.

Results and Discussion

An EtOAc extract of the cultures of *C. siliginea* was separated by silica gel, Sephadex LH-20, and RP-18 to give seven new sesquiterpenoids **1**—**7**.

Compound **1** was obtained as a colorless oil. Its molecular formula $C_{17}H_{28}O_4$ with four degrees of unsaturation was established by the HRESIMS at *m/z* 319.1886 $[M+Na]^+$ (calcd for 319.1885). The IR spectrum revealed the hydroxy and carbonyl groups by the absorption bands at 3431 and 1738 cm^{-1}, respectively. The ^{1}H NMR and ^{13}C NMR data (Tables 1 and 3, respectively) revealed the existence of four methyls, five methylenes (two oxygenated), four methines (one oxygenated), and four quaternary carbons including an sp^2 quaternary carbon, and two olefinic carbons. The ^{1}H-^{1}H COSY spectrum showed correlations from H-3 to H_2-12, H-5 to H_2-4 and H-6, H_3-13 to H-6, and H-7 to H-8 (Figure 2). These data were closely related to those of conocenol B,[7] except for an additional acetoxy group [δ_H 2.05 (3H, s); δ_C 21.0 (q) and 171.1 (s)] in **1**. Compound **1** could be readily identified as the 11-*O*-acetyl-conocenol B by the downfield chemical shift of H-11 at δ_H 4.56 (d, J=11.6 Hz, 1H) and 4.47 (d, J=11.6 Hz, 1H), as well as the HMBC correlation from H-11 to δ_C 171.1 (s, $CH_3\mathbf{C}O_2$) (Figure 2). Further analyses of HMBC data suggested

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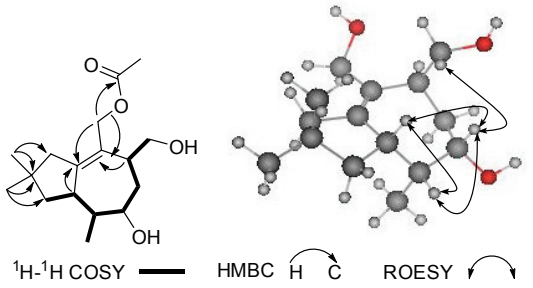

Figure 2 Key 2D NMR correlations of **1**.

that the other parts of **1** were the same to those of conocenol B.[7] In the ROESY spectrum, the observed ROESY correlations of H-5 with H-7 and H-12, and H-7 with H-6 suggested that compound **1** possessed the same relative configuration with that of conocenol B (Figure 2).[7] Therefore, compound **1** was elucidated as 11-*O*-acetyl-5*β*,11,12-trihydroxy-1-tremulene, as shown.

Compound **2** possessed a molecular formula $C_{17}H_{28}O_4$ as assigned by the HRESIMS at *m/z* 297.2069 $[M+H]^+$ (calcd for 297.2065). The IR spectrum displayed absorption bands at 3440 and 1738 cm^{-1}, ascribable for hydroxy and carbonyl groups, respectively. Comparison of NMR data with those of conocenol A (Tables 1 and 3) suggested that compound **2** exhibited similarities with those of conocenol A,[7] except for an additional acetoxy group [δ_H 2.02 (s, 3H); δ_C 21.2 (q) and 171.7 (s)] in **2**. The downfield chemical shifts of H-14 [δ_H 3.99 (d, J=10.6 Hz, 1H, H-14a) and 3.58 (d, J=10.6 Hz, 1H, H-14b)], as well as the HMBC correlation from H-14 to δ_C 171.7 (s, $CH_3\mathbf{C}O_2$) suggested that the acetoxy group was substituted at C-14. The ROESY spectrum displayed the same patterns to those of conocenol A,[7] implying the same relative configuration of them. Thus, compound **2** was established as 14-*O*-acetyl-11,12,14-trihydroxy-1-tremulene.

Compound **3** was isolated as a colorless oil. HRESIMS revealed the molecular formula $C_{17}H_{28}O_4$, the same to that of **2**. Besides, the NMR data were very closely related to those of **2**. According to the analysis of HSQC and HMBC data, compound **3** could be identified to have the same planar structure to that of **2**. However, the ROESY data revealed the different stereo-configuration between them. Biogenetically, H-7 was *β* oriented. Thus, the observed ROESY correlation of H-7 with H-14 indicated that the Me-14 was also *β* oriented. Detailed analysis of 2D NMR data finally established compound **3** to be 15-*O*-acetyl-11,12,15-trihydroxy-1-tremulene.

Compound **4** possessed a molecular formula $C_{17}H_{28}O_4$ as assigned by the HRESIMS at *m/z* 319.1883 $[M+Na]^+$ (calcd for 319.1885). The IR spectrum displayed absorption bands at 3445 and 1721 cm^{-1}, ascribable for hydroxy and carbonyl groups, respectively. Comparison of NMR data with those of conocenol A (Tables 1 and 3) suggested that compound **4** exhibited similarities with those of conocenol A,[7] except for an additional acetoxy group [δ_C 21.2 (q) and 171.3 (s)] in **4**. The downfield chemical shifts of H-11 [δ_C 68.4 (t)], as well as the HMBC correlation from H-11 to δ_C 171.3 (s, $CH_3\mathbf{C}O_2$) suggested that the acetoxy group was substituted at C-11. Detailed analysis of other 2D NMR (HSQC, HMBC, ^{1}H-^{1}H COSY) data suggested that the other parts of

Table 1 ^{1}H NMR spectroscopic data of **1**—**4** in $CDCl_3$ (δ, J in Hz)

No.	**1**[a]	**2**[b]	**3**[a]	**4**[a]
3	2.75—2.51 m	2.51—2.47 m	2.55—2.50 m	2.49—2.43 m
4a	1.91—1.87 m	1.76—1.73 m	1.83—1.78 m	1.77—1.72 m
4b	1.70 td (12.8, 3.6)	1.55—1.51 m	1.62—1.56 m	1.71—1.65 m
5a	4.00 dt (12.2, 3.5)	1.75—1.71 m	1.79 t (9.8)	1.90—1.85 m
5b		1.55—1.52 m	1.62—1.58 m	1.62—1.56 m
6	1.92—1.88 m	1.71—1.68 m	1.79—1.75 m	1.76—1.71 m
7	2.88 t (9.4)	3.03 t (9.4)	3.13 t (9.7)	3.05 t (9.6)
8a	1.57 td (12.0, 2.0)	1.67—1.63 m	1.52—1.49 m	1.72—1.66 m
8b	1.46 dd (12.0, 12.0)	1.32 dd (13.0, 10.8)		1.35 dd (13.0, 10.4)
10a	2.27 dd (15.2, 1.7)	2.38 dd (15.6, 2.3)	2.30 dd (15.2, 1.6)	2.72 dd (15.6, 1.8)
10b	2.00 br d (15.2)	1.82 br d (15.6)	2.04 br d (15.2)	1.86 br d (15.6)
11a	4.56 d (11.6)	4.14 d (11.2)	4.21 d (11.0)	4.77 d (11.6)
11b	4.47 d (11.6)	3.69 d (11.2)	3.81 d (11.0)	4.29 d (11.6)
12a	3.71—3.67 m	3.95 t (10.0)	3.97 t (9.7)	3.77 dd (10.2, 7.0)
12b		3.51 dd (10.0, 4.8)	3.59 dd (9.7, 4.6)	3.70 dd (10.2, 7.0)
13	0.77 d (6.8)	0.76 d (6.8)	0.81 d (6.8)	0.83 d (7.0)
14a	0.84 s	3.99 d (10.6)	0.92 s	3.26 d (11.0)
14b		3.58 d (10.6)		3.23 d (11.0)
15a	1.08 s	1.04 s	3.94 br s	1.08 s
15b				
OAc	2.05 s	2.02 s	2.07 s	2.05 s

[a] Measured at 400 MHz, [b] measured at 600 MHz.

4 were the same to those of conocenol A. The ROESY spectrum also displayed the same patterns to those of conocenol A, implying the same relative configuration of them. Therefore, compound **4** was established as 11-*O*-acetyl-11,12,14-trihydorxy-1-tremulene.

Compound **5** possessed a molecular formula $C_{15}H_{24}O_2$ as assigned by the HRESIMS at *m/z* 259.1674 $[M+Na]^+$. The IR spectrum showed the presence of hydroxy (3428 cm^{-1}) and carbonyl (1631 cm^{-1}) groups. The NMR data (Tables 2 and 3) indicated the presence of two tertiary and one secondary methyls, five methylenes (one oxygenated and one sp^2), four methines and three quaternary carbons (one oxygenated and one sp^2). The ^{1}H-^{1}H COSY spectrum revealed the fragment as shown in Figure 3. The comparison of these data with those of tremulene sesquiterpenoids isolated from the same source suggested that compound **5** was also a sesquiterpenoid with a tremulene skeleton.[7-10] In the HMBC spectrum, a key correlation from δ_H 3.75 (br s, 2H, H-12) to δ_C 91.6 (s, C-1) suggested the existence of an 1,12-epoxy moiety (Figure 3). Besides, a terminal double bond located between C-2 and C-11 was established by two olefinic protons at δ_H 5.04 and 4.88 (each 1H, br s, H-11) and their HMBC correlations to δ_C 91.6 (s, C-1), 154.8 (s, C-2), and 43.0 (d, C-3) (Figure 3). In the ROESY spectrum, the correlations of H-5 with H-7 and H-12, and H-7 with H-6 suggested that H-5, H-6, H-7, and the 1,12-epoxy were β oriented (Figure 3). Further analysis of 2D NMR data (HSQC, HMBC, ^{1}H-^{1}H COSY, ROESY) revealed that the other parts of **5** were the same to those of conocenol B. Thus, compound **5** was established to be 1β,12-epoxy-5α-hydroxy-3(11)-tremulene.

Table 2 ^{1}H NMR spectroscopic data of **5**—**7** in $CDCl_3$ (δ, J in Hz)

No.	**5**[a]	**6**[b]	**7**[b]
3	2.86—2.84 m	2.89—2.87 m	2.76—2.72 m
4a	1.88—1.86 m	1.85—1.81 m	1.78—1.76 m
4b	1.81—1.77 m	1.65—1.60 m	1.26—1.24 m
5a	4.32—4.29 m	1.55—1.51 m	1.63—1.59 m
5b			1.50 dd (12.4, 6.0)
6	2.13—2.08 m	2.09 dd (14.0, 7.0)	1.72—1.69 m
7	2.55—2.50 m	2.41—2.34 m	2.39 t (9.4)
8a	1.43 t (12.4)	1.44 t (13.6)	1.67 t (2.6)
8b	1.35 ddd (12.4, 6.2, 2.0)	1.25 dd (12.0, 6.0)	1.38—1.33 m
10a	1.84 br d (14.8)	2.00 d (14.8)	1.71 br d (9.6)
10b	1.75 dd (14.8, 2.0)	1.66 d (13.4)	1.56 br d (9.6)
11a	5.04 s	4.97 s	5.11 s
11b	4.88 s	4.93 s	5.31 s
12a	3.75 br s	3.84 t (7.0)	4.03 t (11.0)
12b		3.72 d (7.6)	3.52 t (11.0)
13	0.87 d (7.5)	0.88 d (7.4)	0.82 d (7.2)
14	1.13 s	3.47 s	3.56 s
15	1.09 s	1.16 s	1.18 s

[a] Measured at 600 MHz, [b] measured at 400 MHz.

Table 3 ^{13}C NMR spectroscopic data of **1**—**7** in $CDCl_3$ (δ)

No.	**1**[a]	**2**[c]	**3**[a]	**4**[b]	**5**[c]	**6**[a]	**7**[c]
1	148.3 s	143.3 s	143.6 s	148.4 s	91.6 s	91.4 s	90.9 s
2	126.5 s	133.2 s	133.2 s	127.4 s	154.8 s	155.5 s	148.9 s
3	42.4 d	45.7 d	45.3 d	44.7 d	43.0 d	44.6 d	48.9 d
4	29.6 t	22.6 t	22.4 t	21.0 t	36.2 t	28.6 t	29.7 t
5	71.9 d	32.7 t	32.5 t	31.8 t	70.8 d	28.8 t	31.7 t
6	39.1 d	31.8 d	31.6 d	31.7 d	39.8 d	31.0 d	34.5 d
7	42.6 d	45.9 d	44.9 d	46.2 d	51.3 d	51.5 d	50.6 d
8	44.9 t	41.2 t	40.5 t	40.8 t	43.5 t	37.2 t	41.1 t
9	37.4 s	41.6 s	40.5 s	42.6 s	35.4 s	40.4 s	43.2 s
10	48.2 t	43.3 t	43.2 t	42.9 t	52.5 t	47.2 t	46.8 t
11	68.1 t	65.9 t	65.4 t	68.4 t	106.4 t	105.9 t	112.5 t
12	62.1 t	63.1 t	63.1 t	61.7 t	69.4 t	70.0 t	63.4 t
13	5.6 q	11.6 q	11.5 q	11.5 q	7.9 q	15.1 q	13.8 q
14	26.7 q	69.9 t	22.4 q	69.3 t	29.5 q	72.0 t	77.5 t
15	28.3 q	23.9 q	72.1 t	23.3 q	30.4 q	25.1 q	16.9 q
CH_3CO_2	21.0 q	21.2 q	20.9 q	21.2 q			
CH_3CO_2	171.1 s	171.7 s	171.3 s	171.3 s			

[a] Measured at 100 MHz, [b] measured at 125 MHz, [c] measured at 150 MHz.

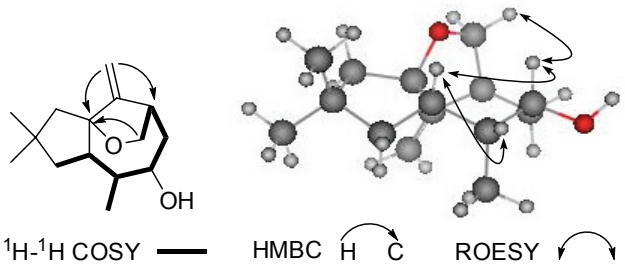

Figure 3 Key 2D NMR correlations of **5**.

Compound **6** had the same molecular formula to that of **5** as established by HRESIMS. Besides, the comparison of its NMR data with those of **5** indicated that compound **6** possessed the same backbone to that of **5**, while he HMBC and ^{1}H-^{1}H COSY spectra also revealed fragments for the evidence that compound **6** also contained a terminal double bond between C-2 and C-11, as well as an 1,12-epoxy moiety. However, the HMBC correlation from δ_H 3.47 (2H, s) to the sp^3 quaternary carbon at δ_C 40.4 (s, C-9) suggested that the hydroxy was substituted at C-14 or C-15 rather than C-5 in **5**. The ROESY spectrum displayed correlation of H-7 with the protons of the oxygenated methyl (δ_H 3.47), implying that the hydroxy was substituted at C-14. Therefore, compound **6** was established to be 1β,12-epoxy-14-hydroxy-2(11)-tremulene.

Compound **7** possessed the molecular formula $C_{15}H_{24}O_2$, identical to those of **5** and **6**, as revealed by the positive HRESIMS. Preliminary analysis of NMR data suggested that compound **7** possessed a tremulane-type skeleton and displayed the same patterns to those of **6**, including a terminal double bond, two oxygenated methylenes, and an oxygenated sp^3 quaternary carbon. Beyond three degrees of unsaturation occupied by the two skeleton rings and the double bond, the other one required an epoxy moiety in the structure. In the HMBC spectrum, the correlations from δ_H 3.56 (br s, 2H, H-14) to δ_C 90.9 (s, C-1) and 43.2 (s, C-9) suggested that an epoxy moiety existed between C-14 and C-1 in **7** rather than between C-12 and C-1 in **6**. The ROESY correlations between H-14 and H-7 suggested the epoxy moiety to be β oriented. Further analyses of 2D NMR (HSQC, HMBC, ^{1}H-^{1}H COSY, ROESY) data elucidated that the other parts of **7** were the same to those of **6**. Thus, compound **7** was established to be 1β,14-epoxy-12-hydroxy-2(11)-tremulene.

Experimental

General experimental procedures

Optical rotations were measured on a Horiba SEPA-300 polarimeter. IR spectra were recorded on a Bruker Tensor 27 spectrometer with KBr pellets. Both 1D and 2D NMR experiments were performed on a Bruker AM-400, DRX-500 or AVANCE III-600 spectrometer with tetramethylsilane (TMS) as the internal standard. Mass spectra (MS) were recorded on a VG Auto Spec-3000 or an APIQSTAR time-of-flight spectrometer. Column chromatography (CC) was performed on silica gel (200—300 mesh; Qingdao Marine Chemical Ltd., China), RP-18 gel (40—75 μm, Fuji Silysia Chemical Ltd., Japan), and Sephadex LH-20 (Amersham Biosciences, Sweden). TLC was carried out on silica gel GF_{254} plates (0.20—0.25 mm; Qingdao). Spots were visualized under UV light and by spraying with 10% H_2SO_4 in ethanol followed by heating.

Fungal material and cultivation condition

C. siliginea was isolated from the tissue culture of its fruiting bodies collected from a moist woodland (dominated by pines) of the Linglang county in Yunnan Province, People's Republic of China, in July 2003, and authenticated by Prof. Mu Zang, Kunming Institute of Botany, Chinese Academy of Sciences (CAS). A voucher specimen (KIB03071801) was deposited in the Herbarium of Kunming Institute of Botany, CAS. Culture PDA medium: glucose (5%), peptone from porcine meat (0.15%), yeast powder (0.5%), KH_2PO_4 (0.05%) and $MgSO_4$ (0.05%). Inoculums of *C. siliginea* were prepared in a 15 L-fermentor (Biostar, Shanghai Guo-Qiang, China) for 6 d under the following conditions: culture temperature 24 ℃, initial pH 6.0, agitation speed 250 r/min, inoculation volume 10% (by volume), and aeration rate 1.0 volume/culture volume/min. Then, the liquid seed was transferred into a 100 *L*-fermentation tank to be cultivated under the same conditions for 20 d to afford 80 L culture broth.

Extraction and isolation

The whole culture broth of *C. siliginea* (80 L) was filtered, and the filtrate was extracted four times with EtOAc. The organic layer was concentrated under reduced pressure to give an oily residue (40 g) that was subjected to column chromatography (CC) over silica gel (200—300 mesh) eluting with $CHCl_3$: MeOH (from 100 : 0 to 0 : 100) to afford fractions A—E. Fraction B was separated further by CC over RP-18, eluting with H_2O/MeOH (from 1 : 0 to 0 : 1) to give fractions B_1—B_4. Fraction B_2 was purified by CC over silica gel (petroleum ether : Me_2CO, 5 : 1) and then applied to Sephadex LH-20 (Me_2CO) to yield **1** (8.0 mg), **2** (2.2 mg), **3** (11.6 mg), and **4** (0.4 mg). Fraction B_3 was separated first by silica gel (petroleum ether : EtOAc, 6 : 1), then purified by Sephadex LH-20 (Me_2CO) to afford **5** (3.7 mg), **6** (10.6 mg), and **7** (1.7 mg).

11-*O*-Acetyl-5β,11,12-trihydroxy-1-tremulene (1) Colorless oil; $[\alpha]_D^{16}$ +57.7 (*c* 0.26, MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) data, see Tables 1 and 3, respectively; IR (KBr) ν_{max}: 3431, 2953, 2930, 1738, 1630, 1465, 1380, 1242, 1063, 1020 cm^{-1}; MS (ESI) *m/z* (%): 319 ([M+Na]$^+$, 100); HRMS (ESI) calcd for $C_{17}H_{28}O_4Na^+$ [M + Na]$^+$ 319.1885, found 319.1886.

14-*O*-Acetyl-11,12,14-trihydroxy-1-tremulene (2) Colorless oil; $[\alpha]_D^{18}$ +32.4 (*c* 0.22, MeOH); ^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHz) data, see Tables 1 and 3, respectively; IR (KBr) ν_{max}: 3440, 2958, 2927, 1738, 1630, 1461, 1387, 1246, 1033 cm^{-1}; MS (ESI) *m/z* (%): 319 ([M+Na]$^+$, 100); HRMS (ESI) calcd for calcd for $C_{17}H_{29}O_4^+$ [M + H]$^+$ 297.2065, found 297.2069.

15-*O*-Acetyl-11,12,15-trihydroxy-1-tremulene (3) Colorless oil; $[\alpha]_D^{15}$ +24.7 (*c* 0.22, MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) data, see Tables 1 and 3, respectively; IR (KBr) ν_{max}: 3422, 2954, 2932, 2871, 1739, 1630, 1465, 1384, 1246, 1031 cm^{-1}; MS (ESI) *m/z* (%): 319 ([M+Na]$^+$, 100); HRMS (ESI) calcd for $C_{17}H_{28}O_4Na^+$ [M + Na]$^+$ 319.1885, found 319.1883.

11-*O*-Acetyl-11,12,14-trihydorxy-1-tremulene (4) Colorless oil; $[\alpha]_D^{11}$ +101.1 (*c* 0.04, MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) data, see Tables 1 and 3, respectively; IR (KBr) ν_{max}: 3445, 2957, 2926, 1721, 1632, 1463, 1383, 1244, 1031 cm^{-1}; MS (ESI) *m/z* (%): 319 ([M+Na]$^+$, 100); HRMS (ESI) calcd for $C_{17}H_{28}O_4Na^+$ [M+Na]$^+$ 319.1885, found 319.1886.

1β,12-Epoxy-5α-hydroxy-3(11)-tremulene (5) Colorless oil; $[\alpha]_D^{19}$ −16.5 (*c* 0.37, MeOH); ^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHz)

data, see Tables 2 and 3, respectively; IR (KBr) ν_{max}: 3428, 3076, 2949, 1631, 1464, 1385, 1011, 973, 892 cm^{-1}; MS (ESI) *m/z* (%): 259 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{15}H_{24}O_2Na^+$ $[M+Na]^+$ 259.1673, found 259.1674.

1*β*,12-Epoxy-14-hydroxy-2(11)-tremulene (6) Colorless oil; $[\alpha]_D^{19}$ −36.14 (c 0.25, MeOH); ^1H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) data, see Tables 2 and 3, respectively; IR (KBr) ν_{max}: 3432, 3075, 2927, 2868, 1664, 1443, 1385, 1012, 987, 901 cm^{-1}; MS (ESI) *m/z* (%): 259 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{15}H_{24}O_2Na^+$ $[M+Na]^+$ 259.1673, found 259.1676.

1*β*,14-Epoxy-12-hydroxy-2(11)-tremulene (7) Colorless oil; $[\alpha]_D^{15}$ +22.46 (*c* 0.16, MeOH); ^1H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHz) data, see Tables 2 and 3, respectively; IR (KBr) ν_{max}: 3431, 2952, 1632, 1462, 1381, 1008, 986, 910 cm^{-1}; MS (ESI) *m/z* (%): 259 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{15}H_{24}O_2Na^+$ $[M+Na]^+$ 259.1673, found 259.1676.

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