Sesquiterpenes and Aliphatic Diketones from Cultures of the Basidiomycete *Conocybe siliginea*

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Five new tremulane-type sesquiterpenes, 11,12-dihydroxy-1-tremulen-5-one (**1**), 11,12-epoxy-12β-hydroxy-1-tremulen-5-one **(2)**, 5α,12-dihydroxy-1-tremulen-11-yl 2(*S*)-pyroglutamate (**3**), 2α,11-dihydroxy-1(10)-tremulen-5,12-olide (**4**), and 10β,11-dihydroxy-5,6-*seco*-1,6(13)-tremuladien-5,12-olide (**5**), as well as three new aliphatic diketones, 2,3-dihydroxydodecane-4,7-dione (**9** and **10**) and 1-hydroxydecane-2,5-dione (**11**), together with three known sesquiterpene analogues, tremulenediol A (**6**), conocenol B (**7**), and conocenolide A (**8**), were isolated from cultures of the basidiomycete *Conocybe siliginea*.

The genus *Conocybe* belongs to the order Agaricales and family Bolbitiaceae and comprises more than 240 species widely distributed throughout the world. Previous investigations of basidiomycetes in 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 in a manner similar to that of LSD (lysergic acid diethylamide).[4–6] Our previous investigations of this fungus have reported a series of tremulane-type sesquiterpenes.[7] The tremulanes constitute a class of unusual sesquiterpenes that were first isolated in 1993 from the aspen tree rotting fungus *Phellinus tremulae*.[8] Thus far, only 16 tremulane-type compounds have been reported. In this paper, we report the isolation and structure elucidation of five new tremulane-type sesquiterpenes (**1**−**5**) and three new aliphatic diketones (**9**−**11**) from a scale-up culture of the basidiomycete *Conocybe siliginea*.

Results and Discussion

The fungus was fermented in shakers (150 rpm) with modified PDA (potato-dextrose agar) medium. After culturing for 30 days at 25 °C, the whole culture broth (30 L) was extracted three times with EtOAc. The crude EtOAc extract (9.8 g) was subjected to repeated column chromatography to give pure **1** (2.6 mg), **2** (14.4 mg), **3** (5.6 mg), **4** (3.5 mg), **5** (5.4 mg), **9** (3.5 mg), **10** (4.6 mg), and **11** (1.0 mg).

Compound **1** was obtained as a colorless oil; $C_{15}H_{24}O_3$ by positive HRESIMS (found $[M + Na]^+$ 275.1621, calcd for 275.1623). The IR spectrum showed absorptions at 3439 and 1689 cm^{-1}, revealing the presence of OH and carbonyl groups. The ^1H NMR spectrum (Table 1) exhibited signals indicating two tertiary methyls (δ 1.10, 0.89), a secondary methyl (δ 1.01), and two oxymethylenes. The ^{13}C and DEPT NMR spectra (Table 2) displayed 15 carbons, including a ketone carbonyl group (δ 215.2), three quaternary carbons (two olefinic carbons at δ 145.3 and 131.5 and a sp^3 quaternary carbon resonance at δ 37.9), three methines, five methylenes (two oxygenated ones at δ 64.9 and 62.8), and three methyls (δ 11.0, 28.4, 26.6). The data suggested that **1** was a tremulane-type sesquiterpenoid similar to tremulenediol A (**6**).[8] The differences were that the ^{13}C NMR signals for C-4, C-5, and C-6 and ^1H NMR signals for H-4 and H-6 in **1** were shifted to lower field compared to those of **6**. The differences were caused by a ketone carbonyl group at C-5 in **1** being replaced by a methylene in **6**. This assignment was confirmed by HMBC correlations from H-3, H-4, H-6, H-7, and H-13 to C-5. On biogenetic considerations, the relative configurations at C-3, C-6, and C-7 of **1** with a tremulene skeleton were proposed to be the same as in **6**. This was supported by the ROESY experiment, which showed key correlations of H-6 with H-7 and of H-3 with H_3-13. Thus, compound **1** was elucidated as 11,12-dihydroxy-1-tremulen-5-one.

Compound **2** was obtained as a colorless oil with a molecular formula of $C_{15}H_{22}O_3$ assigned by positive HRESIMS (found $[M + H]^+$ 251.1646, calcd for 251.1647). The ^1H and ^{13}C NMR spectra of **2** (Tables 1 and 2) showed features similar to those of **1**, suggesting that they were analogues. The key difference was a hemiacetal group (δ_H 5.36, δ_C 99.1) in **2** rather than an oxymethylene in **1**. The HMBC spectrum of **2** displayed correlations from H-4 to C-12 and from H-12 to C-2, C-3, C-4, and C-11, and the $^1H-^1H$ COSY spectrum showed correlations from H-3 to H-12, which suggested that the hemiacetal group was located at C-12. From a biogenetic point of view, **1** seemed to be the precursor of **2**, suggesting the relative configuration at C-3 in **2** was the same as that in **1** and that H-3 was α-oriented. The α-orientation of H-12 was deduced from the ROESY cross-peak between H-12 and H-3α, which was further supported by a 4.6 Hz coupling constant between H-3 and H-12. Hence, compound **2** was determined as 11,12-epoxy-12β-hydroxy-1-tremulen-5-one.

Compound **3** was a colorless oil and gave a molecular formula of $C_{20}H_{31}NO_5$ by HRESIMS. Comparison of ^1H and ^{13}C NMR data (Tables 1 and 2) of **3** with those of conocenol B (**7**)[7] revealed that **3** was an ester of **7** at C-11, since the HMBC spectrum showed a correlation from H_2-11 (δ 4.67, 4.59) to an ester carbonyl carbon (δ 172.0, C-16). Further analysis of the NMR data for the C_5 moiety led to the conclusion that it was 2(*S*)-pyroglutamate, which was in good agreement with ^1H and ^{13}C NMR data in the literature.[9,10] The relative configurations at C-5, C-6, and C-7 in **3** were proposed to be the same as conocenol B (**7**). Therefore, compound **3** was assigned as 5α,12-dihydroxy-1-tremulen-11-yl 2(*S*)-pyroglutamate.

Compound **4** had the molecular formula $C_{15}H_{22}O_4$ as determined by HRESIMS, which required 5 degrees of unsaturation in the molecule. Careful analysis of NMR spectral data (Tables 1 and 2) indicated that **4** was also a tremulane-type sesquiterpene. The ^{13}C NMR data at 139.6 (s, C-1) and 144.4 (d, C-10) and the HMBC correlations of H-3, H-6, H-8, and H-10 with C-1, H-8, H-14, and H-15 with C-10, and H-10 with C-1, C-2, C-7, C-8, and C-9 revealed the presence of a trisubstituted double bond located at C-1/C-10. Furthermore, an oxygenated quaternary carbon (δ 77.9) assigned as C-2 was supported by the HMBC correlations from H-3, H-4, and H-10 to C-2. Additionally, the HMBC correlations

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Chart 1

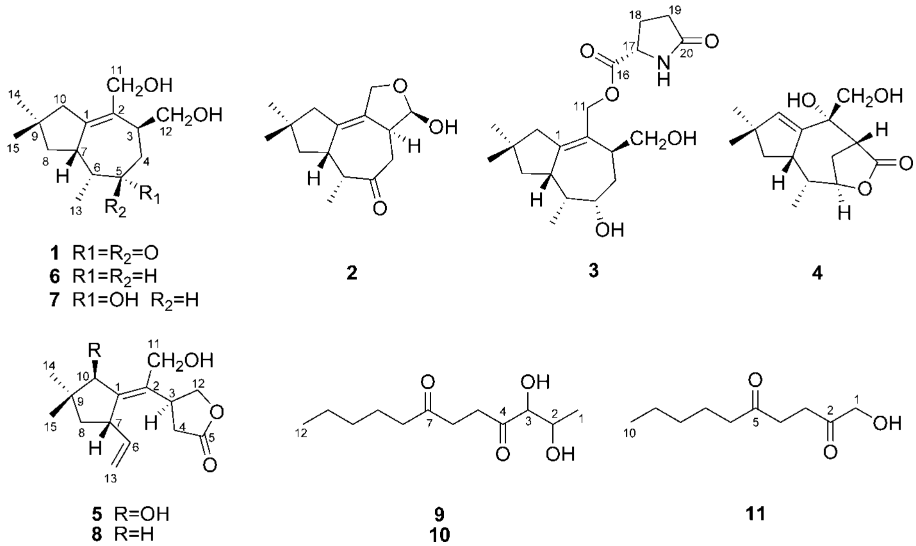

Table 1. ^{1}H NMR Data of Compounds **1−5** in $CDCl_3$ at 400 MHz

no.	1	2	3	4	5
3	2.77 (m)	2.90 (m)	2.51 (m)	2.89 (m)	3.84 (m)
4	2.79 (m)	3.10 (dd, 13.7, 13.7)	1.93 (m)	2.33 (m)	2.63 (d, 9.3)
	2.57 (m)	2.52 (m)	1.65 (td, 12.3, 2.5)	2.26 (m)	
5			4.04 (br d, 11.9)	4.68 (m)	
6	2.47 (m)	2.57 (dd, 7.3, 2.2)	1.90 (m)	2.20 (m)	5.78 (m)
7	3.05 (m)	3.48 (m)	2.85 (br t, 9.0)	3.00 (m)	3.33 (m)
8	1.57 (ddd,11.0,11.0,1.8)	1.47 (d, 10.0)	1.57 (td, 11.5, 1.8)	1.90 (dd,14.2,10.8)	1.71 (m)
	1.46 (dd, 11.0, 11.0)		1.45 (t, 11.5)	1.61 (m)	
10	2.37 (dd, 15.3, 1.8)	2.11 (d, 16.6)	2.26 (dd, 15.3, 1.8)	5.82 (s)	4.15 (s)
	2.04 (d, 15.3)	1.98 (br d, 16.6)	1.97 (d, 15.3)		
11	4.25 (d, 11.4)	4.49 (d, 12.7)	4.67 (d, 11.7)	3.80 (d, 12.2)	4.43 (d, 11.5)
	3.89 (d, 11.4)	4.31 (d, 12.7)	4.59 (d, 11.7)	3.28 (d, 12.2)	4.12 (d, 11.5)
12	3.59 (dd, 10.5, 5.5)	5.36 (d, 4.6)	3.71 (t, 10.7)		4.34 (dd, 8.8, 8.8)
	3.49 (dd, 10.5, 8.1)		3.57 (dd, 10.7, 6.0)		4.04 (dd,17.6, 8.8)
13	1.01 (d, 7.0)	1.13 (d, 7.6)	0.75 (d, 6.7)	0.92 (d, 7.3)	5.03 (d, 18.7) 5.00 (d, 11.0)
14	1.10 (s)	1.11 (s)	1.08 (s)	1.04 (s)	1.08 (s)
15	0.89 (s)	1.03 (s)	0.84 (s)	1.14 (s)	0.83 (s)
17			4.26 (dd, 8.6, 4.5)		
18			2.46 (m)		
			2.23 (m)		
19			2.37 (m)		

Table 2. ^{13}C NMR Data of Compounds **1−5** in $CDCl_3$ at 100 MHz

no.	1	2	3	4	5
1	145.3 s	134.4 s	148.4 s	139.6 s	150.4 s
2	131.5 s	128.2 s	126.2 s	77.9 s	136.0 s
3	43.3 d	43.7 d	41.6 d	46.5 d	37.0 d
4	40.8 t	41.5 t	28.9 t	25.8 t	32.4 t
5	215.2 s	215.6 s	71.6 d	83.6 d	177.1 s
6	49.7 d	48.8 d	38.9 d	39.0 d	142.6 d
7	41.5 d	41.0 d	42.8 d	43.2 d	44.7 d
8	43.8 t	44.6 t	44.9 t	41.5 t	44.6 t
9	37.9 s	37.1 s	37.5 s	44.2 s	41.5 s
10	48.0 t	46.9 t	48.1 t	144.4 d	80.7 d
11	64.9 t	69.0 t	68.9 t	70.1 t	59.7 t
12	62.8 t	99.1 t	61.1 t	178.5 s	70.8 t
13	11.0 q	12.5 q	5.7 q	11.8 q	114.0 d
14	28.4 q	29.2 q	28.3 q	32.6 q	26.0 q
15	26.6 q	27.7 q	26.8 q	28.0 q	21.9 q
16			172.0 s		
17			56.0 d		
18			24.9 t		
19			29.3 t		
20			179.0 s		

from H-5, H-3, and H-4 to a carbonyl group (δ 178.5, C-12) and from H-3, H-4, and H-13 to C-5, as well as the downfield chemical shift of H-5 at δ 4.68 suggested that a five-membered lactone was formed at C-5 and C-12. The α-orientation of the 2-OH group and H-5 and β-orientation of H-3 were apparent from the ROESY correlations of H-11 with H-7β, H-5 with H_3-13α, and H-3 with H-6β. Consequently, compound **4** was determined to be 2α,11-dihydroxy-1(10)-tremulen-5,12-olide.

Compound **5** had the molecular formula $C_{15}H_{22}O_4$ as established by HRESIMS (found $[M + Na]^+$ 289.1407, calcd for 289.1415). The IR spectrum indicated the presence of OH (3422 cm^{-1}) and carbonyl groups (1773 cm^{-1}). Detailed comparison of ^{1}H and ^{13}C NMR data of **5** (Tables 1 and 2) with those of conocenolide A (**8**)[7] showed that **5** and **8** were similar in structure. The only difference was in the NMR signals due to an OH group substituted at C-10, including the absence of a methylene with the appearance of an oxymethine (δ_H 4.15, δ_C 80.7) in **5**. This was confirmed by the HMBC spectrum, which showed correlations of H-7, H-8, H-14, and H-15 with C-10 and of H-10 with C-2, C-7, C-8, and C-14. The relative configuration of H-3α and H-7β was based on the assumption that **5** had the same configuration as **8** at C-3 and C-7. The OH group at C-10 was β-oriented, as deduced from ROESY cross-peaks of H_3-15 with H-7β and of H-10 with H_3-15β. Hence, compound **5** was determined to be 10β,11-dihydroxy-5,6-seco-1,6(13)-tremuladien-5,12-olide.

Table 3. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR Data of Compounds **9**−**11** in $CDCl_3$

	9		10		11	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1	1.20 (d, 6.4)	18.2 q	1.36 (d, 6.4)	19.7 q	4.33 (d, 4.4)	68.2 t
2	4.01 (m)	69.4 d	4.30 (br s)	68.2 d		208.5 s[a]
3	4.22 (t, 4.4)	80.5 d	4.09 (d, 3.9)	80.4 d	2.63 (t, 6.0)	29.7 t
4		210.2 s		210.0 s	2.82 (t, 6.0)	36.0 t
5	2.89 (m) 2.64 (m)	33.4 t	2.71 (m)	31.8 t		209.0 s[a]
6	2.91 (m) 2.76 (m)	36.3 t	2.86 (m)	36.4 t	2.45 (t, 7.7)	42.6 t
7		210.3 s		210.4 s	1.56 (m)	23.5 t
8	2.46 (t, 7.6)	42.5 t	2.45 (t, 7.5)	42.5 t	1.25 (m)	31.3 t
9	1.57 (m)	23.5 t	1.56 (m)	23.5 t	1.25 (m)	22.4 t
10	1.25 (m)	31.3 t	1.24 (m)	31.3 t	0.89 (t, 7.1)	13.9 q
11	1.30 (m)	22.4 t	1.31 (m)	22.4 t		
12	0.88 (t, 7.2)	13.9 q	0.88 (t, 7.0)	13.9 q		

[a] Signals were absent in ^{13}C NMR spectra, and assignments were based on HMBC spectra.

Compound **9** had the molecular formula $C_{12}H_{22}O_4$ as determined by positive HRESIMS (found $[M + Na]^+$ 253.1413, calcd for 253.1415), indicating 2 degrees of unsaturation. Since the ^{13}C NMR spectra of **9** (Table 3) showed two ketone carbonyl carbon signals (δ 210.2, 210.3) accounting for 2 degrees of unsaturation, **9** was acyclic. The ^{13}C and DEPT NMR spectra showed 12 carbon signals, including two methyls, six methylenes, two oxymethines, and two quaternary carbonyl carbons. The HMBC correlations observed between the secondary methyl signal at δ_H 1.20 (d, J = 6.4 Hz, H-1) and two oxymethines (C-2, C-3), the oxymethine signal at δ_H 4.22 and a carbonyl carbon (δ 210.2, C-4), two methylene protons (H-5, H-6), and two ketone carbonyl carbons signal at 210.2 (C-4) and 210.3 (C-7) implied the presence of a CH_3-CH(OH)CH(OH)$COCH_2CH_2CO$ moiety. The above assignment, combined with the molecular formula led to the final structure determination of **9** as 2,3-dihydroxydodacane-4,7-dione.

Compound **10** gave the same molecular formula ($C_{12}H_{22}O_4$) as **9** by positive HRESIMS (found $[M + Na]^+$ 253.1415, calcd for 253.1415). Comparison of NMR (^{1}H and ^{13}C NMR, DEPT, HMBC, HSQC) and IR data of **10** with those of compound **9** suggested that both compounds shared the same planar structure. Considering the differences of **9** and **10** in optical rotations (see data below) and behavior on TLC, they were determined as being a pair of stereoisomers. Unfortunately, determination of their stereochemistry proved difficult due to the limited amounts of compounds **9** and **10** and since 1,2-diols should be treated as one stereocluster.[11] It is not conclusive to apply derivatization with chiral auxiliary reagents to determine the absolute configuration of **9** and **10** using procedures such as the Mosher method.[12]

Compound **11** had the molecular formula $C_{10}H_{18}O_3$ as determined by HRESIMS (found $[M + Na]^+$ 209.1140, calcd for 209.1153), indicating 2 degrees of unsaturation. Since the ^{13}C NMR spectra of **11** (Table 3) showed two ketone carbonyl carbon signals (δ 208.5, 209.0) accounting for 2 degrees of unsaturation, **11** was acyclic with a free OH group. The ^{13}C and DEPT NMR spectra showed 10 carbon signals, including one methyl, seven methylenes, and two quaternary carbonyl carbons. Compound **11** was isolated as a minor constituent during the separation of **9** and **10**, and its structure determination followed a course similar to that of **9**. Accordingly, compound **11** was determined to be 1-hydroxydecane-2,5-dione.

The structures of the known compounds isolated were identified as tremulenediol A (**6**),[8] conocenol B (**7**),[7] and conocenolide A (**8**)[7] by comparison of their spectroscopic data with literature values.

Experimental Section

General Experimental Procedures. Optical rotations were measured on a Horiba SEPA-300 polarimeter. IR spectra were obtained on a Tensor 27 with KBr pellets. NMR spectra were recorded on Bruker AV-400 and Bruker DRX-500 spectrometers in $CDCl_3$ solvent (δ_H 7.26 ppm, δ_C 77.0 ppm). EIMS were recorded with a VG Autospec-3000 spectrometer. ESIMS and HRESIMS were recorded with an API QSTAR Pulsar 1 spectrometer. Silica gel (200−300 mesh, Qingdao Marine Chemical Inc., China), RP-18 gel (40−75 μm, Fuji Silysia Chemical Ltd., Japan), and Sephadex LH-20 (Amersham Biosciences, Sweden) were used for column chromatography. Fractions were monitored by TLC, and spots were visualized by heating silica gel plates sprayed with 10% H_2SO_4 in ethanol.

Fungal Material and Cultivation Conditions. The fungus *C. siliginea* was collected from Linglang County, Yunnan Province, China, in July 2003, and identified by Prof. Mu Zang, Kunming Institute of Botany. The voucher specimen (KIB03071801) was deposited at the Herbarium of the Kunming Institute of Botany, CAS. Culture PDA medium: potato (peeled), 200 g, glucose, 20 g, KH_2PO_4, 3 g, $MgSO_4$, 1.5 g, citric acid, 0.1 g, and thiamin hydrochloride, 10 mg, in 1 L of deionized H_2O. The pH was adjusted to 6.5 before autoclaving, and the fermentation was carried out on a shaker at 25 °C and 150 rpm for 30 days.

Extraction and Isolation. The culture broth (30 L) was extracted three times with EtOAc. The EtOAc extracts were evaporated *in vacuo* to give a crude extract (9.8 g), which was subjected to silica gel CC (200−300 mesh, 4.5 × 50 cm) eluting with a $CHCl_3$−MeOH gradient (100:0−0:100) to produce fractions 1−8. Fraction 2 eluted with $CHCl_3$ was subjected to MPLC with a reversed-phased C_{18} column (MeOH−H_2O, 90:10, v/v), followed by Sephadex LH-20 ($CHCl_3$−MeOH, 1:1, v/v) and silica gel CC ($CHCl_3$−MeOH, 200:1, v/v) and gave compound **2** (14.4 mg). Fraction 3 eluted with $CHCl_3$−MeOH (98:2, v/v) was separated by reversed-phased C_{18} CC (MeOH−H_2O, 60:40−80:20) to afford fractions 3a and 3b. Fraction 3a was further purified by Sephadex LH-20 ($CHCl_3$−MeOH, 1:1, v/v) CC to give **6** (15.1 mg). Fraction 3b was repeatedly chromatographed on Sephadex LH-20 ($CHCl_3$−MeOH, 1:1, v/v) and silica gel CC eluting with chloroform−acetone (50:1−10:1) to yield **9** (3.5 mg), **10** (4.6 mg), and **11** (1.0 mg). Fraction 4 eluted by $CHCl_3$−MeOH (95:5, v/v) was further chromatographed over Sephadex LH-20 and silica gel CC eluting with petroleum ether−ethyl acetate (10:1−1:1, v/v) to give **1** (2.6 mg) and **5** (5.4 mg). Fraction 5 eluted by $CHCl_3$−MeOH (85:15, v/v) was purified over Sephadex LH-20 ($CHCl_3$−MeOH, 1:1, v/v), then by repeated silica gel CC with petroleum ether−acetone (10:1) to provide **4** (3.5 mg). After repeated silica gel and Sephadex LH-20 CC, **3** (5.6 mg) and **7** (34.0 mg) were obtained from fraction 6 eluted from $CHCl_3$−MeOH (90:10, v/v), respectively.

11,12-Dihydroxy-1-tremulen-5-one (1): colorless oil; $[\alpha]^{18}_D$ +41.4 (c 0.37, $CHCl_3$); IR (KBr) ν_{max} 3439, 2951, 2868, 1689, 1464, 1028 cm^{-1}; ^{1}H NMR, Table 1; ^{13}C NMR, Table 2; EIMS m/z 252 $[M]^+$ (1), 234 $[M - H_2O]^+$ (100), 203 (65), 175 (73), 161 (50), 119 (70); HRESIMS (positive) m/z 275.1621 $[M + Na]^+$ (calcd for $C_{15}H_{24}O_3Na$, 275.1623).

11,12-Epoxy-12β-hydroxy-1-tremulen-5-one (2): colorless oil; $[\alpha]^{19}_D$ −23.1 (c 0.39, $CHCl_3$); IR (KBr) ν_{max} 3427, 2932, 2867, 1699, 1464, 1011 cm^{-1}; ^{1}H NMR, Table 1; ^{13}C NMR, Table 2; EIMS m/z 250 $[M]^+$ (7), 232 $[M - H_2O]^+$ (10), 204 (100), 189 (25), 176 (23), 148 (97); HRESIMS (positive) m/z 251.1646 $[M + H]^+$ (calcd for $C_{15}H_{23}O_3$, 251.1647).

5α,12-Dihydroxy-1-tremulen-11-yl 2(*S*)-pyroglutamate (3): colorless oil; $[\alpha]^{17}_D$ −23.1 (c 0.18, $CHCl_3$); IR (KBr) ν_{max} 3426, 2932, 2869, 1737, 1694, 1464, 1195, 1016 cm^{-1}; ^{1}H NMR, Table 1; ^{13}C NMR, Table 2; ESIMS (positive TOP) m/z 388 $[M + Na]^+$; HRESIMS (positive) m/z 388.2106 $[M + Na]^+$ (calcd for $C_{20}H_{31}NO_5Na$, 388.2099).

2α,11-Dihydroxy-1(10)-tremulen-5,12-olide (4): white, amorphous powder; $[\alpha]^{19}_D$ −32.0 (c 0.13, $CHCl_3$); IR (KBr) ν_{max} 3479, 2944, 1759, 1460, 1237, 1177, 1050 cm^{-1}; ^{1}H NMR, Table 1; ^{13}C NMR, Table 2; EIMS m/z 266 $[M]^+$ (1), 248 $[M - H_2O]^+$ (5), 236 (80), 217 (70), 163 (96), 121 (74), 95 (100); HRESIMS (positive) m/z 289.1408 $[M + Na]^+$ (calcd for $C_{15}H_{22}O_4Na$, 289.1415).

10β,11-Dihydroxy-5,6-seco-1,6(13)-tremuladien-5,12-olide (5): colorless oil; $[\alpha]^{18}_D$ −73.2 (c 0.31, $CHCl_3$); IR (KBr) ν_{max} 3422, 2954, 2869, 1773, 1636, 1467, 1180, 1014 cm^{-1}; ^{1}H NMR, Table 1; ^{13}C NMR, Table 2; EIMS m/z 266 $[M]^+$ (1), 248 $[M - H_2O]^+$ (20), 194 (100), 198 (50), 145 (65), 91 (75); HRESIMS (positive) m/z 289.1407 $[M + Na]^+$ (calcd for $C_{15}H_{22}O_4Na$, 289.1415).

2,3-Dihydroxydodacane-4,7-dione (9): colorless oil; $[\alpha]^{20}_D$ +23.2 (c 0.12, $CHCl_3$); IR (KBr) ν_{max} 3397, 2931, 1703, 1374, 1060 cm^{-1}; ^{1}H NMR, Table 3; ^{13}C NMR, Table 3; EIMS m/z 186 [M −

$CH_3CH(OH) + H]^+$ (1), 155 $[M - CH_3CH(OH)CH(OH)]^+$ (100); HRESIMS (positive) *m/z* 253.1413 $[M + Na]^+$ (calcd for $C_{12}H_{22}O_4Na$, 253.1415).

2,3-Dihydroxydodacane-4,7-dione (10): colorless oil; $[\alpha]^{17}_D$ −35.1 (*c* 0.19, $CHCl_3$); IR (KBr) ν_{max} 3424, 2931, 1710, 1402, 1057 cm^{-1}; ^1H NMR and ^{13}C NMR, Table 3; ESIMS (positive TOP) *m/z* 253 $[M + Na]^+$; HRESIMS (positive) *m/z* 253.1415 $[M + Na]^+$ (calcd for $C_{12}H_{22}O_4Na$, 253.1415).

1-Hydroxydecane-2,5-dione (11): colorless oil; ^1H NMR and ^{13}C NMR, Table 3; ESIMS (positive TOP) *m/z* 209 $[M + Na]^+$; HRESIMS (positive) *m/z* 209.1140 $[M + Na]^+$ (calcd for $C_{10}H_{18}O_3Na$, 209.1153).

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Supporting Information Available: MS and 1D and 2D NMR spectra of **1**−**5** and **9**−**11**. IR spectra of **1**−**5**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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