Five Unique Compounds: Xyloketals from Mangrove Fungus *Xylaria* sp. from the South China Sea Coast

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Five unique metabolites, xyloketals A (**1**), B (**2**), C (**3**), D (**4**), and E **(5),** and the known **6** were isolated from mangrove fungus *Xylaria* sp. (no. 2508), obtained from the South China Sea. The structures of these compounds were elucidated by spectroscopic and X-ray diffraction experiments. Xyloketal A is a ketal compound with a C_3 symmetry and xyloketals B−E are its analogues. It was found that xytoketal C slowly rearranged to xytoketal B in DMSO-d_6 solution at room temperature. Xyloketal A exhibited the activity of inhibiting acetylcholine esterase.

Introduction

A large variety of new bioactive compounds have recently been isolated from different sources of organisms. A group that has yielded rich new bioactive compounds are the marine fungi,[1,2] especially the mangrove fungi. It was reported that most described marine fungi could be found from mangroves. Recently, we have embarked on a study of the metabolites of marine fungi including those from mangroves from the South China Sea, and this has yielded a number of interesting compounds.[3,4]

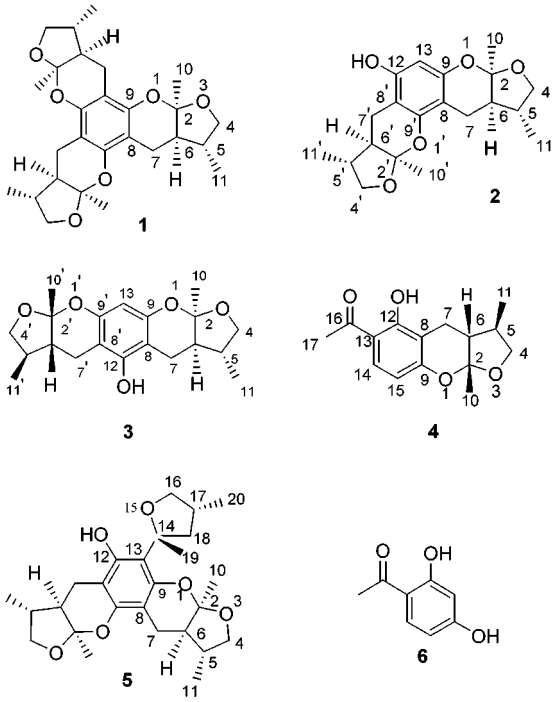
The mangrove fungus strain no. 2508, which was collected from seeds of an angiosperm tree and identified as *Xylaria* species (Ascomycota), was found to produce rich secondary metabolites. Xyloketals A (**1**), B (**2**), C (**3**), D (**4**), and E (**5**) were isolated from the fermentation broth of this fungus. The xyloketals represent a series of novel ketal compounds having a close biogenetic relationship. In the primary bioassay, xyloketal A inhibited acetylcholine esterase at 1.5×10^{-6} mol/L ($p < 0.01$).

Results and Discussion

The ethyl acetate extract of a fermentation broth of the fungus was repeatedly chromatographed on silica gel using a gradient elution from petroleum to ethyl acetate. Compound **1** was obtained from the fraction eluted with 8% ethyl acetate/petroleum ether as colorless block crystals, mp 164−166 °C. The NMR spectra of **1** were quite simple (Table 1).

There were merely nine signals (two CH_3, two CH_2, two CH, and three C). The elemental composition was determined as $C_9H_{12}O_2$ by the elemental analysis. However, the FABMS showed the molecular ion peak at 457 (M + 1), which is three times the mass of $C_9H_{12}O_2$. Thus, the molecule was composed of the same three partial structures in the same chemical environment. The COSY spectrum revealed a contiguous sequence from H-4 to H-7. The correlation between H-11 and H-5 located CH_3-11 at C-5. In the HMBC spectrum, the correlations between C-2 and H-4, H-7, H-10 and the correlations between C-8 and H-7, H-6 and between C-9 and H-7, respectively, established the partial structure in fragment **A** (Figure 1).

Three fragments A assembled to give the intact molecule **1**. The structure of **1** was finally confirmed by X-ray diffraction analysis that showed the relative configurations of **1** to be 2*R**,5*R**,6*R**. Compound **1** is a chiral



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[||] Institute of Chemistry CRC.

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Table 1. NMR Data of 1 ($CDCl_3$ TMS)

no.	^{13}C	^1H	$^1H-^1H$ COSY	HMBC	ROESY
2	107.4 (C)			H-4, 7, 10	
4	74.0 (CH_2)	(a) 3.53	(a) H-4b, 5	H-5	(a) H-4b, 5
		(b) 4.17	(b) H-4a, 5		(b) H-4a, 5
5	35.5 (CH)	2.14 (ddd, J = 6.5, 8.5, 8.5 Hz)	H-4, 6, 11	H-6, 11	H-4, 6, 11
6	47.6 (CH)	1.89 (dd, J = 6.5, 11.0 Hz)	H-5, 7	H-7, 11	H-5, 7, 10, 11
7	18.9 (CH_2)	(a) 2.64 (dd, J = 6.5, 18.0 Hz)	(a) H-6, 7b		(a) H-6, 7b, 11,
		(b) 2.85 (d, J = 18.0 Hz)	(b) H-6, 7a		(b) H-6, 7a, 10
8	98.9 (C)			H-6, 7	
9	149.8 (C)			H-7	
10	22.9 (CH_3)	1.50 (s)			H-6, 7a
11	16.1 (CH_3)	1.05 (d, J = 6.5 Hz)	H-5		H-5, 6, 7b

Table 2. NMR Data of 2 ($CDCl_3$ TMS)

no.	^{13}C	^1H	$^1H-^1H$ COSY[a]	HMBC[a]	ROESY[a]
2	107.4 (C)			H-4, 6, 7, 10	
2′	107.7 (C)			H-4′, 6′, 7′, 10′	
4	74.0 (CH_2)	(a) 3.50 (dd, 8.5, 17.0 Hz)	(a) H-4b, 5	H-5, 11	
		(b) 4.17 (dd, 7.5, 17.0 Hz)	(b) H-4a, 5		
4′	74.0 (CH_2)	(a) 3.55 (dd, 8.5, 17.0 Hz)	(a) H-4′b, 5′	H-5′, 11′	
		(b) 4.10 (dd, 6.5, 17.0 Hz)	(b) H-4′a, 5′		
5	35.5 (CH)	2.13 (m)	H-4, 6,11	H-6, 7, 11	H-6
5′	35.3 (CH)	2.14 (m)	H-4′, 6′, 11′	H-6′, 7′, 11′	H-6′
6	47.8 (CH)	1.88 (ddd, 1.0, 4.0, 6.5 Hz)	H-5, 7	H-4, 10, 11	H-5, 11
6′	47.5 (CH)	1.91 (ddd, 1.0, 4.5, 7.0 Hz)	H-5′, 7′	H-4′, 10′, 11′	H-5′, 11′
7	18.6 (CH_2)	(a) 2.62 (dd, 6.5, 17.0 Hz)	H-6, 7b	H-5, 6	
		(b) 2.80 (d, 17.0 Hz)	H-6, 7a		
7′	18.4 (CH_2)	(a) 2.82 (d, 16.0 Hz)	H-6′, 7′b	H-5′, 6′	
		(b) 2.69 (dd, 7.0, 16.0 Hz)	H-6′, 7′a		
8	99.4 (C)			H-6, 7, 13	
8′	98.5 (C)			H-6′, 7′, 13	
9	152.0 (C)			H-7, 13	
9′	152.1 (C)			H-7′, 13′	
10	22.8 (CH_3)	1.50 (s)		H-6	
10′	23.1 (CH_3)	1.52 (s)		H-6′	
11	15.9 (CH_2)	1.05 (d, 7.0 Hz)	H-5	H-4, 6	H-6
11′	16.1 (CH_2)	1.07 (d, 7.0 Hz)	H-5′	H-4′, 6′	H-6′
12	153.2 (C)			H-7′, 13, OH	
13	95.9 (CH)	6.13 (s)			
14	OH	6.14 (s)			

[a] The signals symbolized with and without a prime were not resolvable.

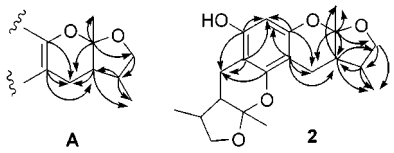

Figure 1. Correlation of HMBC of **2** and **a**.

molecule with C_3 of symmetry, $[\alpha]_D = -4.88°$. The three furan rings have cis configuration (Figure 2). Compound **2** was isolated from the fraction eluted with 50% ethyl acetate/petroleum ether. It was a colorless gelatinous solid, mp 84−86 °C. Most of the NMR spectral data of **2** were similar to **1**, but the signals appeared in pairs, and there were a phenolic hydroxyl proton (δ_H 6.14) and an aromatic CH (δ_H 6.13, δ_C 95.9) in the NMR spectra of **2**. The FABMS of **2** showed a molecular ion peak at *m*/*z* 347 (M + 1) that was 110 mass less than that of **1**. This number is equal to losing an "arm" from **1** and adding a hydroxyl group. The structure of **2** was determined by comparing its spectra, mainly 2D NMR, with those of **1**. In the HMBC spectrum, most correlation signals were similar to those of **1** (Table 2). The correlations between C-12 and H-7′ and between C-9 and H-13 could be used to assigned the position of the OH group. The coupling constants in the ^{1}HNMR spectrum of **2** are nearly identical to those of **1**, and the ROESY spectrum showed

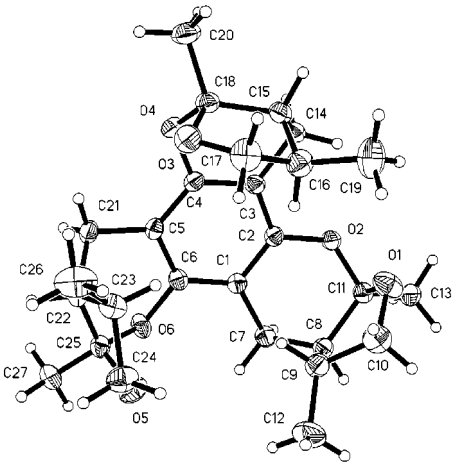

Figure 2. Molecular structure of **1**.

the correlation between H-6 and H-11, implying the same stereochemistry at C-2, C-5, and C-6.

The polarity of **3** was greater than that of **2**. Compound **3** was obtained as colorless needles, mp >260 °C. The molecular ion peak of **3** at 347 (M + 1) in the FABMS and the elemental composition $C_{20}H_{26}O_5$ determined by elemental analysis were identical to that of **2**. Compound **3** also carried a phenolic hydroxyl group (δ_H 8.39) and an aromatic CH (δ_H 5.65, δ_C 95.8). However, the NMR

Table 3. NMR Data of 3 ($CDCl_3$ TMS)

no.	^{13}C	^{1}H	$^{1}H-^{1}H$ COSY	HMBC	ROESY
2	106.6 (C)			H-4, 5, 7	
4	72.8 (CH_2)	(a) 3.36 (t, 8.0 Hz)	(a) H-4b, 5	H-11	(a) H-4b, 5
(b) 3.96 (t, 8.0 Hz)	(b) H-4a, 5	(b) H-4a, 5			
5	34.8 (CH)	1.89 (overlap)	H-4, 11	H-4, 6, 7, 11	H-4, 11
6	47.1 (C)	1.86 (overlap)	H-7	H4, 5, 7, 11,10	H-7, 11
7	18.6 (CH_2)	(a) 2.65 (dd, 6.0, 17.0 Hz)	(a) H-6, 7b		(a) H-6, 7b
(b) 2.76 (d, 17.0 Hz)	(b) H-6, 7a	(b) H-6, 7a			
8	99.2 (C)			H-6, 7, 13, OH	
9	151.9 (C)			H-7, 13	
10	22.8 (CH_3)	1.37 (s)			
11	15.4 (CH_3)	0.99 (d, 6.0 Hz)	H-5	H-4, 5	H-5, 6
12	153.0 (C)			OH	
13	95.8 (CH)	5.65 (s)			
OH	8.39 (s)				

Table 4. NMR Data of 4 ($CDCl_3$ TMS)

no.	^{13}C	^{1}H	COSY	HMBC	ROESY
2	108.3 (C)			H-4, 7, 10	
4	74.3 (CH_2)	(a) 3.57 (t, 8.0 Hz)	(a) H-4b, 5	H-11	(a) H-4b
		(b) 4.20 (t, 8.0 Hz)	(b) H-4a, 5		(b) H-4a
5	35.1 (CH)	2.15 (m)	H-4, 6, 11	H-4, 6, 7, 11	H-4
6	47.0 (CH)	1.98 (ddd, 1.0, 6.5, 11.0 Hz)	H-5, 7	H-4, 7, 10, 11	H-7b, 11
7	18.0 (CH_2)	(a) 2.72 (dd, 6.5, 18.0 Hz)	(a) H-6, 7b		(a) H-7b
		(b) 2.97 (d, 18.0 Hz)	(b) H-6, 7a		(b) H-6, 7a
8	106.2 (C)			H-6, 7, 15, OH	
9	159.5 (C)			H-7, 14	
10	22.7 (CH_3)	1.53 (s)			
11	15.8 (CH_3)	1.07 (d, 7.0 Hz)	H-5		H-6, 7b
12	162.9 (C)			H-7, 14, OH	
13	113.2 (C)			H-15, 17, OH	
14	130.0 (CH)	7.51 (d, 9.0 Hz)	H-15		H-15
15	108.8 (CH)	6.36 (d, 9.0 Hz)	H-14		H-14
16	202.6 (C)			H-14, 17	
17	26.1 (CH_3)	2.54 (s)			
18	OH	13.09 (s)			

spectra of **3** are more similar to those of **1** than **2** and did not inhibit pairs of peaks. This suggested symmetry in the molecule. The COSY, ROESY, and HMBC spectra proved the structure of **3** (see Table 3). The correlations between the OH and C-12, C-8, respectively, located the OH at C-12. According to the optical rotation of **3** (α = 52.4°) and an X-ray experiment**,** the stereochemistry of the chiral centers could be assigned.

The polarity of **4** was the lowest of the five compounds. It was isolated as colorless blocks, mp 111−113 °C. In the NMR spectrum of **4** (Table 4), there are similar signals as found in **1**, additional signals due to an acetyl group, a hydroxyl group, and two vicinal aromatic CH groups. Compound **4** had the molecular formula $C_{15}H_{18}O_4$ as determined by FABMS and elemental analysis. These data suggested that **4** was also an analogue of **1** losing two "arms". The downfield signal of the OH at δ 13.09 indicated that it was located on the ortho position to the acetyl group. In the HMBC spectrum of **4**, the correlations between C-8 and both H-6 and the OH defined the position of two substitutents on the benzene ring.

Compound **5** was eluted following **1**, mp 170−172 °C. Its structure was elucidated by comparing the spectra with those of the other xyloketals. The structures of **3**−**5** were further confirmed by X-ray single-crystal structure analysis. (Figure 3 and Supporting Information).

The absolute configuration of xyloketals A (**1**) and D (**4**) at the stereogenic centers 2, 5, and 6 can either be *all-S* or *all-R*, since their relative configurations are known from X-ray analysis. Both polycyclic compounds have rather rigid structures and thus a limited number of stable conformations. Therefore, they are suitable substrates for quantum mechanical calculations of their CD spectra as employed previously by us in the palmarumycin[6] or preussomerin series.[7] Comparison with experimental data then leads to matching and mismatching curves, allowing the assignment of the absolute configuration.

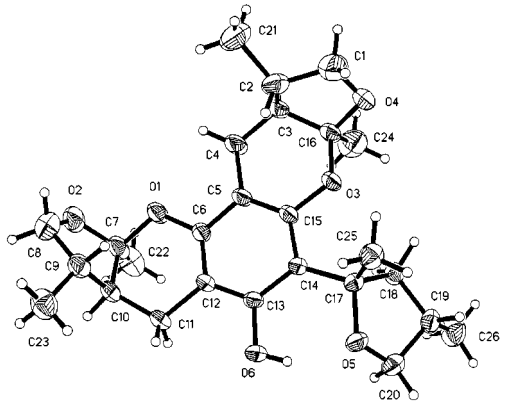

Figure 3. Molecular structure of **5**.

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(6) Bringmann, G.; Busemann, S.; Krohn, K.; Beckmann, K. *Tetrahedron* **1997**, *53*, 1655−1664.

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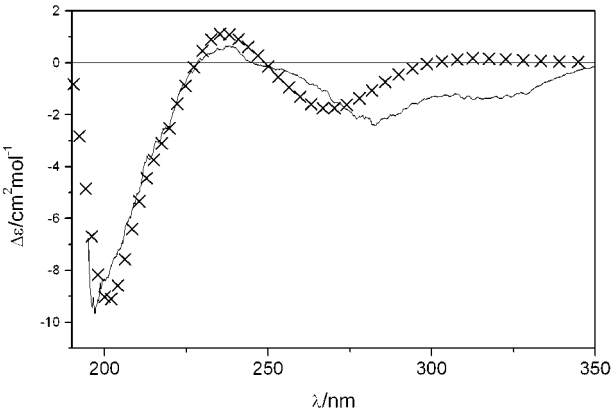

Figure 4. Experimental CD spectrum and calculated spectrum (dotted line) of xyloketal A (**1**).

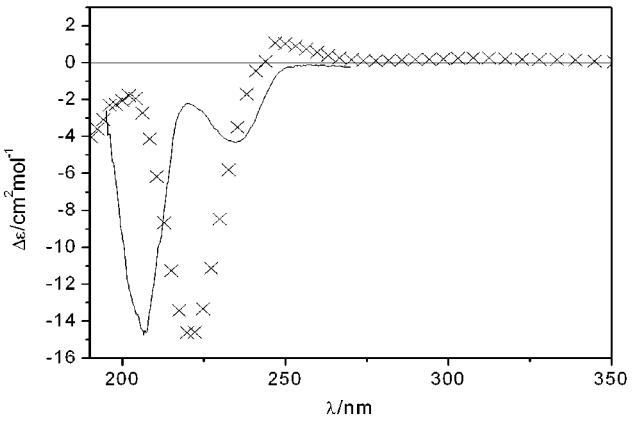

Figure 5. Experimental CD spectrum and calculated spectrum (dotted line) of xyloketal D (**4**).

The conformational analysis of the more simple xyloketal D (**4**), using the Spartan force field package,[8] shows that the five-membered ring is relatively rigid and only the six-membered ring shows some flexibility. The calculations showed the existence of only two major conformers from which the CD spectra were calculated employing the BDZDO/MCDPPD program package of Downing as modified by Fleischhauer.[9] The Boltzmann-weighted calculated CD spectrum was then compared with the experimental spectrum (dotted line). As shown in Figure 4, the experimental spectrum matches that of the calculated spectrum for the 2*R*,5*R*,6*R* configuration of xyloketal D (**4**).

Not surprisingly, the calculation of the xyloketal A (**1**) conformation showed a similar rigidity of the five-membered ring and some conformational flexibility of the six-membered rings. Since three six-membered rings are involved in **1**, the CD spectra of more conformations had to be calculated in this case. The agreement of the Boltzmann-weighted spectra with the experimental spectrum was not as perfect as for xyloketal D (**4**) (Figure 5). The strong negative Cotton effect resulting from the $^1B_{a,b}$ transition of the UV spectrum at 210 nm was shifted by 13 nm to lower wavelength. However, the similar shape of the curves and the same strong negative Cotton effect leaves no doubt that the absolute configuration of xyloketal A (**1**) is also 2*R*,5*R*,6*R* at the relevant stereogenic centers in the three heterocyclic parts of the C_3-symmetric molecule.

The known compound **6** was also isolated in relatively large amounts from the fungus. This may be useful for the deduction of the biogenesis of the xyloketals.

The analysis of the spectra of these xyloketals revealed some regularities; for example, in the FABMS of the compounds, they all showed strong M − $(98)_{1-2}$ peaks, which could be caused by the loss of one or two 1,4-dimethyl-4,5-dihydrofuran fragments via a retro hetero-Diels−Alder reaction. It was found that **3** slowly transformed to **2** in DMSO-d_6 over 3 months, which indicated that a rearrangement was occurring. Further studies are in progress.

Experimental Section

General Methods. NMR data were recorded on a Varian Inova 500NB NMR spectrometer, mass spectra on a VG-ZAB-HS mass spectrometer, IR spectra on a Bruker EQUINOX 55 spectrophotometer, UV spectra on a Shimadzu UV-2501PC spectrophotometer, optical rotations on a Horiba high-sensitivity polarimeter SEPA-300, elemental analyses on a Elementar Vario EL CHNS-O elemental analyzer, and X-ray data on a Bruker Smart 1000 CCD system diffractometer.

Fungal Strain. A strain of the fungus *Xylaria* sp. (no. 2508) was isolated from seeds of an angiosperm tree in Mai Po, Hong Kong, and was stored at the Department of Applied Chemistry, Zhongshan University, Guangzhou, China.

Culture Conditions. Starter cultures (from Professor E. B. G. Jones and Dr. L. L. P. Vrijmoed) were maintained on cornmeal seawater agar. Plugs of agar supporting mycelial growth were cut and transferred aseptically to a 250 mL Erlenmeyer flask containing 100 mL of liquid medium (glucose 10 g/L, peptone 2 g/L, yeast extract 1 g/L, NaCl 30 g/L). The flask was incubated at 30 °C on a rotary shaker for 5−7 days. The mycelium was aseptically transferred to a 300-L fermenter containing 170 L of GYT medium, incubated at 30 °C for 80 h.

Extraction and Separation of Metabolites. The cultures (170 L) were filtered through cheesecloth. The filtrate was concentrated to 3.5 L below 50 °C and extracted five times by shaking with an equal volume of ethyl acetate. The combined extracts were chromatographed on silica gel using a gradient elution from petroleum to ethyl acetate, to obtain **4** (30 mg), **1**(1.9 g), and **5** (50 mg) in turn from the 8% ethyl acetate/petroleum ether fraction. The known compound **6** (3.2 g) and then **2** (2.3 g) and **3** (23 mg) were eluted in turn from the 50% fraction.

Compound **1**: colorless blocks; mp 164−166 °C; $[\alpha]^{25}_D$ = −4.88° (*c* 0.205, $CHCl_3$); IR (KBr) cm^{-1} 2955, 2930, 2905, 2844, 1622, 1459, 1383, 1327, 1299, 1180, 1112, 1099, 1046, 1018, 931, 868, 699; UV λ_{max} ($CHCl_3$) 222 (ϵ 14 370), 224 (ϵ 14 300), 228 (ϵ 14 000), 272 (ϵ 1274); ^{1}H NMR, ^{13}C NMR, and 2D NMR, see Table 1; FABMS *m*/*z* 45 (M + 1), 456, 441, 397, 359, 315, 299, 259, 245, 217, 175, 163, 111, 83,55. Anal. Calcd for $C_{27}H_{36}O_6$: C, 71.05; H, 7.95. Found: C 71.13, H 7.74.

Compound **2**: colorless gelatinous solid; mp 84−86 °C;$[\alpha]^{25}_D$ = +8.2° (*c* 0.061, $CHCl_3$); IR (KBr) cm^{-1} 3356, 2962, 2935, 2891, 1622, 1508, 1454, 1342, 1190, 1117, 1069, 876, 818, 612; UV λ_{max} ($CHCl_3$) 215 (ϵ 68 790), 228 (ϵ 41 620), 274 (ϵ 9827); ^{1}H NMR, ^{13}C NMR, and 2D NMR, see Table 2; FABMS *m*/*z* 347 (M + 1), 346, 289, 249, 205, 189, 151, 111, 97, 83, 55. Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.36; H, 7.52. Found: C, 69.39; H, 7.35.

Compound **3**: colorless needles; mp > 260 °C; $[\alpha]^{25}_D$ = −52.4° (*c* 0.038, $CHCl_3$); IR (KBr) cm^{-1} 3357, 3056, 2982, 2953, 2905, 1627, 1595, 1491, 1450, 1381, 1337, 1223, 1191, 1113,1077, 987, 877, 810, 598, 569; UV λ_{max} ($CHCl_3$) 215 (ϵ 15 060), 227 (ϵ 9758), 275 (ϵ 1515); ^{1}H NMR, ^{13}C NMR, and 2D NMR, see

(8) Spartan SGI Version 5.1.3, Wavefunction Inc., Irvine.
(9) Downing, J. W. Program package BDZDO/MCDSPD, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO; modified by J. Fleischhauer, W. Schleker, B. Kramer; ported to LinuX by K.-P. Gulden.

Table 3; FABMS *m*/*z* 347 (M + 1), 346, 329, 289, 249, 205, 189, 176,149, 111, 89, 77, 57. Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.36; H, 7.52. Found: C, 68.81; H, 7.82.

Compound **4**: colorless blocks; mp 111−113 °C; $[\alpha]^{25}_D$ = −119.5° (*c* 0.113, $CHCl_3$); IR (KBr) cm^{-1} 3479, 3416, 3089, 3056, 2954, 2921, 2879, 1615, 1492, 1420, 1381, 1332, 1261, 1117, 1070, 1002, 854, 831, 804, 641, 609; UV λ_{max} ($CHCl_3$) 220 (ϵ 17 450), 228 (ϵ 10 720), 280 (ϵ 18 040), 307 (ϵ 8766); ^{1}H NMR, ^{13}C NMR, and 2D NMR, see Table 4; FABMS *m*/*z* 263 (M + 1), 247, 203, 177, 165, 147, 111, 97, 83, 55. Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.70; H, 6.87. Found: C, 68.80; H, 7.20.

Compound **5**: colorless blocks; mp 170−172 °C; $[\alpha]^{25}_D$ = +5.35° (*c* 0.374, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.00 (d, J = 6.5 Hz, 3H), 1.04 (d, J = 6.5 Hz, 3H), 1.08 (d, J = 6.5 Hz, 3H), 1.48 (s), 1.50 (s, 3H), 1.53 (s, 3H), 1.78 (m, H), 1.84 (m, H), 1.90 (dd, J = 7, 12 Hz, H), 2.06 (m, H), 2.17 (m, H), 2.38 (m, H), 2.58 (dd, J = 17.0, 7.0 Hz, H), 2.64 (dd, J = 17.0, 7.0 Hz, H), 2.81 (d, J = 17.0 Hz, H), 2.83 (d, J = 17.0 Hz, H), 2.86 (dd, J = 6.0, 12.0 Hz, H), 3.38 (dd, J = 8.0, 10.5 Hz, H), 3.46 (J = 8.5 Hz, H), 3.54 (J = 8.5 Hz, H), 4.06 (dd, J = 7.0, 10.5 Hz, H), 4.08 (t, J = 8.5 Hz, H), 4.16 (t, J = 8.5 Hz, H), 10.81 (s, OH), ^{13}CNMR ($CDCl_3$) δ 15.5 (CH_3), 16.3 (CH_3), 16.2(CH_3), 19.1 (CH_2), 18.7 (CH_2), 22.5 (CH_3), 23.0 (CH_3), 28.4 (CH_3), 32.7 (CH), 35.4 (CH), 35.7 (CH), 47.0 (CH), 47.7 (CH), 49.3 (CH_2), 73.9 (CH_2), 74.0 (CH_2), 74.2 (CH_2), 89.1 (C), 98.2 (C), 98.8 (C), 107.3 (C), 107.5 (C), 110.8 (C), 148.3 (C), 150.2 (C), 152.0(C); FABMS 445 (M + 1), 444, 429, 385, 347, 331, 287, 249; UV λ_{max} ($CHCl_3$) 216 (ϵ 17 510), 226 (ϵ 11 390), 273 (ϵ 1450). Anal. Calcd for $C_{20}H_{26}O_5$: C, 70.27; H, 8.11. Found: C, 70.53; H, 8.42.

Compound **6**: colorless needles; mp 143−144.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.58 (s, 3H), 5.72 (s, OH), 6.40 (s, 1H), 6.41 (d, J = 8.5 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H) 12.69 (s, OH); ^{13}C NMR ($CDCl_3$) δ 26.2, 103.5, 107.7, 114.4, 133.1, 162.6, 165.1, 202.7.[5]

X-ray crystallographic data of 1: crystal system, space group monoclinic, $P2_1$; unit cell dimensions a = 10.0760(15) Å, α = 90°; b = 13.2084(19) Å, β = 116.725(2)°; c = 10.1571(15) Å, γ = 90°; volume = 1207.4(3) Å^3, Z = 2, D_{calcd} = 1.256 Mg/m^3, m = 0.087 mm^{-1}, F000 = 4492. All single-crystal data were collected using the hemisphere technique on a Bruker SMART 1000 CCD system diffractometer with graphite-monochromated Mo Kα radiation λ = 0.7l0 73 at 293(2) K. The structures were solved by direct methods using SHELXTLV5.0 (Siemens IndustriaI Automation lnc, Madison, WI) and refined using full-matrix least-squares difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were placed in idealized positions and refined as riding atoms with the relative isotropic parameters. Absorption corrections were applied with the Siemens area detector absorption program (SADABS). The final value of R was 0.0332, wR2 = 0.0903 [$I > 2\sigma(I)$].

X-ray Crystallography of 4. The conditions and methods of the experiment were the same as those used for compound **1**: crystal system, space group monoclinic, $P2_1$; unit cell dimensions a = 5.3820 (10) Å, α = 90°; b = 8.5550(10) Å, β = 93.64(2)°; c = 14.952(2) Å, γ = 90°; volume = 687.0(2) Å^3, Z = 2, D_{calcd} = 1.268 Mg/m^3, m = 0.091 mm^{-1}, F000 = 280. The final value of R was 0.0675, wR2 = 0.1310 [$I > 2\sigma(I)$].

X-ray Crystallography of 5. The conditions and methods of the experiment were the same as those used for compound **1**: crystal system, space group monoclinic, $P2_1$; unit cell dimensions a = 7.8868(12) Å, α = 90°; b = 10.2975(15) Å, β = 92.328(3)°; c = 15.237(2) Å, γ = 90°; volume = 1236.4(3) Å^3, Z = 2, D_{calcd} = 1.194 Mg /m^3, absorption coefficient m = 0.084 mm^{-1}, F(000) = 480, crystal size 0.35 × 0.13 × 0.11 mm; final R indices [$I > 2\sigma(I)$], R1 = 0.0465, wR2 = 0.118.

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Supporting Information Available: ^{1}HNMR of **3** and X-ray crystal structure data of **1**, **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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