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Limonoids from *Cedrela sinensis*

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Abstract

Five limonoids were isolated from the leaves of *Cedrela sinensis* (Meliaceae) and their structures were determined to be 11β-hydroxy-7α-obacunyl acetate, 11-oxo-7α-obacunyl acetate, 11-oxo-7α-obacunol, 11β-hydroxycneorin G, and 11-oxocneorin G, by 2D NMR spectroscopic experiments, X-ray crystallographic analysis, and chemical methods.

Keywords: *Cedrela sinensis*; Meliaceae; Limonoids; X-ray analysis

1. Introduction

Cedrela sinensis Juss. (Meliaceae) is a tall tree growing in China and Korea, and in these countries, its leaves have been used for treatment of enteritis, dysentery, and itching. Some biological effects of this plant, such as the scavenging effects on peroxynitrite (Kang et al., 2003), and inhibitory effects on human immunodeficiency virus (HIV) type 1 protease (Park et al., 2000), have been reported. As regards its phytochemical investigation, isolation of limonoids, phytol derivatives, flavonoids, and phenolic compounds were previously reported (Luo et al., 2000; Park et al., 1996). In the present study, we isolated five new limonoids from the leaves of *C. sinensis* and determined their structures to be 11β-hydroxy-7α-obacunyl acetate (**1**), 11-oxo-7α-obacunyl acetate (**2**), 11-oxo-7α-obacunol (**3**), 11β-hydroxycneorin G (**4**), and 11-oxocneorin G (**5**), mainly by spectroscopic studies. Limonoids have been found in the plants of the families Meliaceae, Rutaceae, Simaroubaceae, and Cneoraceae, and many of these tetranortriterpenoids are reportedly bioactive against insects.

2. Results and discussion

HP-20 column chromatography and subsequent activated charcoal column chromatography of a MeOH extract of the leaves of *C. sinensis*, and further purification of the chromatographic fractions by preparative HPLC afforded five new tetranortriterpenoids **1**–**5**, which were all limonoids.

Limonoid **1** (11β-hydroxy-7α-obacunyl acetate) was isolated as colorless prisms. Its molecular formula was determined to be $C_{28}H_{34}O_9$ by the $[M + H]^+$ ion peak at *m/z* 515.2286 (calcd for $C_{28}H_{35}O_9$, 515.2281) in the HRESIMS. Its NMR spectra generally resembled those of 7α-obacunyl acetate (Straka et al., 1976; Bennett and Hasegawa, 1982), suggesting that **1** had a limonoid skeleton. The ^{1}H NMR spectrum of **1** displayed signals due to five tertiary methyl groups (δ 1.15, 1.31, 1.34, 1.46, and 1.65), two olefinic protons (δ 5.92 and 6.72, both *d*, $J = 12.8$ Hz), an acetate methyl group (δ 2.11, *s*),

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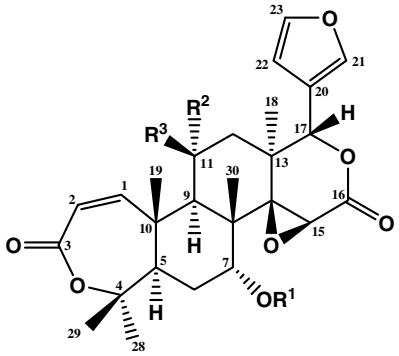


11β-Hydroxy-7α-obacunyl acetate (**1**)

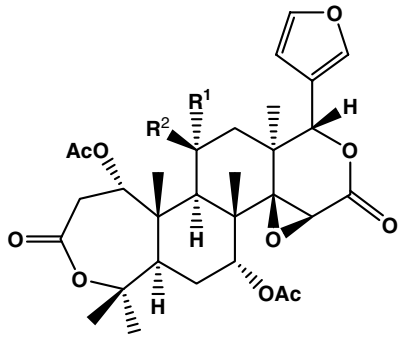
R^1 = Ac, R^2 = H, R^3 = OH

11-Oxo-7α-obacunyl acetate (**2**)

R^1 = Ac, R^2 = R^3 = O

11-Oxo-7α-obacunol (**3**)

R^1 = H, R^2 = R^3 = O



11β-Hydroxycneorin G (**4**)

R^1 = H, R^2 = OH

11-Oxocneorin G (**5**)

R^1 = R^2 = O

Fig. 1. Structures of limonoids from *Cedrela sinensis*.

two oxymethine protons (δ 4.49 and 4.62), and a β-substituted furan ring (δ 6.34, 7.41 and 7.42, 1H each). The ^{13}C NMR spectrum indicated the presence of six methyls, two methylenes, 11 methines, and nine quaternary carbons, three of which at δ 167.1, 167.2, and 169.9 were assigned to ester carbonyl carbons. In the HMBC spectrum, the cross-signal between δ_C 169.9 and δ_H 4.49 (H-7) demonstrated that the acetoxy group was attached to C-7, and the correlations of the C-1 resonance at δ 151.4 to the proton signals of H-2 and H_3-19, and the carbonyl C-3 resonance at δ 167.2 to the proton signals of H-2 and H_3-28 (a four-bond correlation) suggested that the A-ring of **1** was an α,β-unsaturated lactone group (Fig. 2). The cross-signals between H-15/C-14, H-15/C-16, H-17/C-13, and H17/C-20 in the HMBC spectrum suggested the presence of a δ-lactone group with a 14,15-epoxide in D-ring of **1**. As regards the relative stereochemistry of **1**, NOESY correlations detected between H-5/H-9, H-5/H_3-28, H-9/H-11, H_3-18/H-11, H_3-18/H-15, H_3-18/H-21, H_3-18/H-22, H_3-19/H_3-29, H_3-19/H_3-30, and H_3-30/H-7 showed that H-5, OAc-7, H-9, Me-18, and Me-28 were of α-orientation, whereas OH-11, 14,15-epoxide, H-17, Me-19, Me-29, and Me-30 were of β-orientation, as in 7α-obacunyl acetate (Fig. 3). Accordingly, the structure of **1** was determined to be 11β-hydroxy-7α-obacunyl acetate as shown in Fig. 1.

Limonoid **2** (11-oxo-7α-obacunyl acetate) was obtained as colorless prisms. The molecular formula, $C_{28}H_{32}O_9$, was determined by the HRESIMS (*m*/*z* 513.2153 $[M + H]^+$, calcd for $C_{28}H_{33}O_9$, 513.2125).

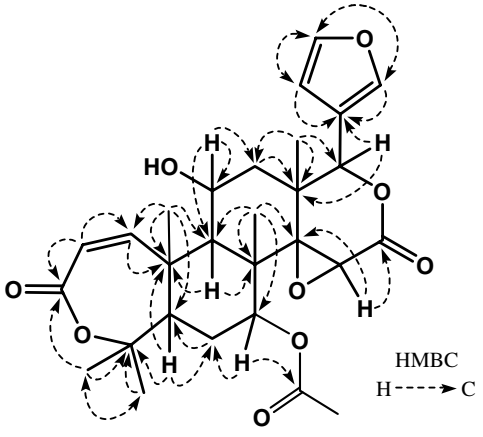


Fig. 2. Selected HMBC correlations for **1**.

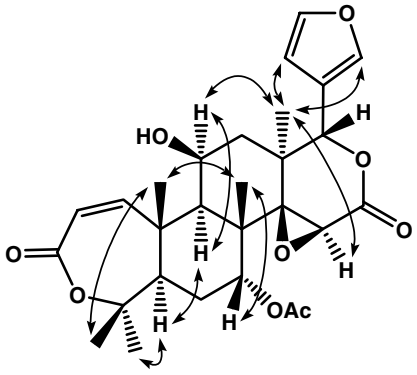


Fig. 3. Selected NOE correlations for **1**.

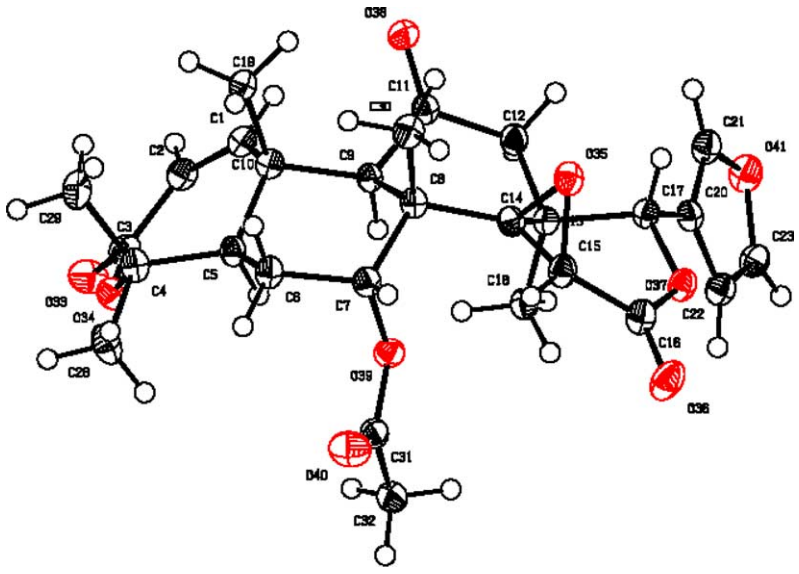


Fig. 4. ORTEP representation of **2** as determined by single-crystal X-ray analysis.

The ^{1}H and ^{13}C NMR spectra of **2** were quite similar to those of **1**, demonstrating that **1** and **2** had the same basic structure. The differences observed between them were that the C-11 signal of **2** was at δ 205.2, implying that it was a carbonyl carbon, whereas the corresponding C-11 signal of **1** was at δ 65.6, which was a hydroxyl methine carbon. TPAP oxidation (Ley et al., 1994) of **1** afforded an oxidation product, which was shown to be identical to natural **2** by analysis of the spectral data. Thus, **2** was determined to be 11-oxo-7α-obacunyl acetate. This structure was also confirmed by X-ray analysis (Fig. 4).

Limonoid **3** (11-oxo-7α-obacunol) was obtained as colorless prisms. From the $[M + H]^+$ ion peak at *m/z* 471.2063 (calcd for $C_{26}H_{31}O_8$, 471.2019), its molecular formula was determined to be $C_{26}H_{30}O_8$. The ^{1}H and ^{13}C NMR spectra of **3** showed its close resemblance to **2**, implying that they were of the same basic structure. The differences noted between the NMR spectra of **2** and **3** were that **3** had no signals due to an acetyl group and that the C-7 signal of **3** (δ 69.4) was in a higher field than the corresponding C-7 signal of **2** (δ 72.3), demonstrating that **3** had no acetyl group at C-7. These facts revealed that **3** was deacetyl **2** or 11-oxo-7α-obacunol, which was determined by X-ray analysis (Fig. 5).

Limonoid **4** (11β-hydroxycneorin G) was obtained as colorless prisms. Its molecular formula was determined to be $C_{30}H_{38}O_{11}$ by the $[M + H]^+$ ion peak at *m/z* 575.2513 (calcd for $C_{30}H_{39}O_{11}$, 575.2492) in the HRESIMS. The NMR spectra of **4** were generally similar to those of **1**, implying that **4** was also a limonoid of the same series. Comparison of their NMR

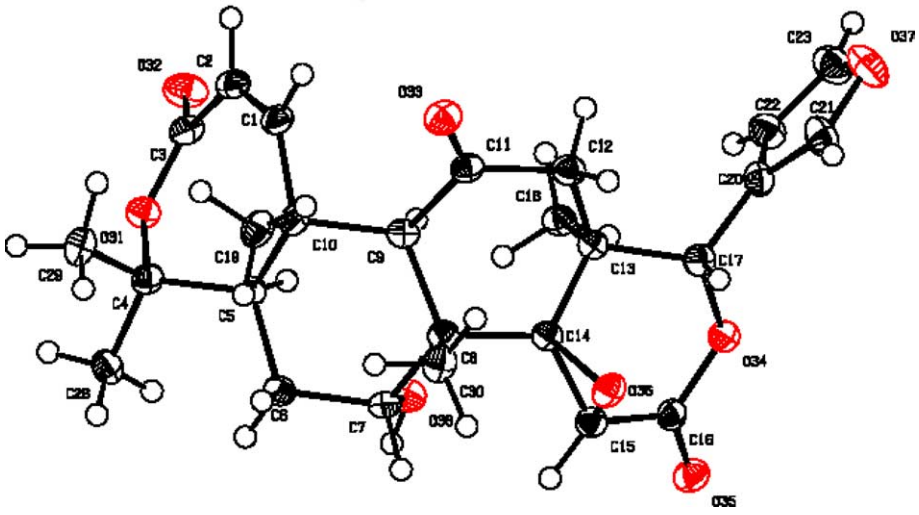


Fig. 5. ORTEP representation of **3** as determined by single-crystal X-ray analysis.

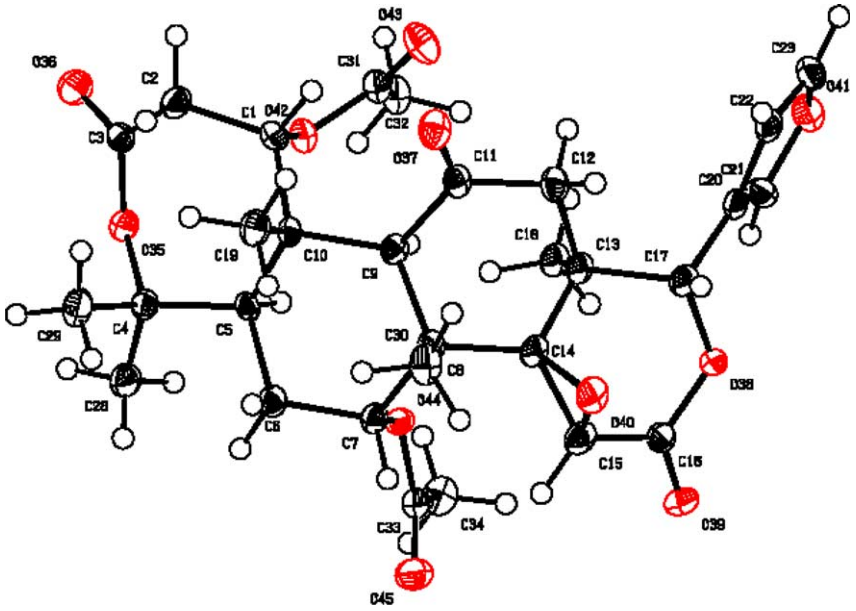


Fig. 6. ORTEP representation of **5** as determined by single-crystal X-ray analysis.

spectra, however, showed that the C-1 (δ 151.4) and C-2 (δ 118.5) signals in **1** were upfield shifted considerably in **4** (C-1 at δ 71.8 and C-2 at δ 34.9) showing that the C1–C2 olefinic bond in **1** was saturated in **4** to be acetoxy methine C-1 and methylene C-2, respectively. The NOESY spectrum of **4** showed correlations between H-1, H_3-19, and H_3-29, in addition to those observed in **1**, demonstrating that the acetate at C-1 was of α-orientation. Thus, the structure of **4** was determined to be 11β-hydroxycneorin G.

Limonoid **5** (11-oxocneorin G) was isolated as colorless prisms. Its molecular formula of $C_{30}H_{36}O_{11}$ was determined by the HRESIMS ion peak at *m/z* 573.2363 $[M + H]^+$ (calcd for $C_{30}H_{37}O_{11}$, 573.2336). The NMR spectra of **5** were generally very similar to those of **4**, suggesting that they had the same basic structure. The difference observed between **4** and **5** was analogous to that observed between **1** and **2**. Thus, **5** had a carbonyl group at C-11, as demonstrated by the 2D NMR spectroscopic studies, whereas **4** had a hydroxyl methine at C-11. The TPAP oxidation product of **4** was shown to be identical to natural **5** by comparison of the spectral data, demonstrating that **5** was 11-oxocneorin G (**5**). The structure was also confirmed by the X-ray analysis (Fig. 6).

From a cheomotaxonomic view point, the new limonoids **1**–**5** isolated from this plant source are structurally related to obacunol from Meliaceous (Adesida and Taylor, 1972) and Rutaceous (Bennett and Hasegawa, 1982) plants as well as cneorin G from a Cneoraceous plant (Mondon and Epe, 1976); however they have the distinguishing feature of an oxygen functionality at C-11.

3. Experimental

3.1. General

Optical rotations were measured on a JASCO DIP-360 digital polarimeter. UV spectra were taken on a Hitachi 557 spectrophotometer, IR spectra on a Perkin–Elmer 1710 spectrophotometer, NMR spectra on a Bruker DRX-500 spectrometer at 300 K, and mass spectra on a Micromass LCT spectrometer. Preparative HPLC was performed on a Shimadzu LC-6AD system equipped with a SPD-10A UV detector (at 205 nm) and a reversed-phase column, Wakosil-II 5C18HG prep (5 μm, 20 × 250 mm), by using a mixed solvent system of MeOH/H_2O or MeCN/H_2O, at a flow late of 10 ml/min. X-ray single crystal analysis was carried out on a Mac Science DIP diffractometer with Mo Kα radiation (λ = 0.71073 Å).

3.2. Plant material

Leaves of *C. sinensis* were collected in Jilin Province, China, in September 2000, and the botanical origin was identified by Professor Soo-Cheol Kim of the Agricultural College of Yanbian University. A voucher specimen (00CHI002) has been deposited in the herbarium of this university.

3.3. Extraction and isolation

Dried and powdered leaves of *C. sinensis* (10.3 kg) were extracted with hot MeOH (3 × 230 l). Following evaporation in vaccum, the MeOH extract (900 g) was placed on a column of HP-20 (3.0 kg) and fractionated

into five fractions, by eluting with H_2O, H_2O–MeOH (1:1), H_2O–MeOH (1:4), MeOH, and acetone (each 28 l). The H_2O–MeOH (1:4) fraction (150 g) was subjected to activated charcoal (400 g) cc eluting respectively with MeOH, $CHCl_3$/MeOH (1:9), and $CHCl_3$/MeOH (1:1), each 22 l. The $CHCl_3$/MeOH (1:9) fraction (14 g) was further subjected to reversed-phase HPLC eluting with MeOH/H_2O (50:50) to afford five fractions (frs.1–5). After removal of the solvent to dryness, frs. 1–5 were further subjected to reversed-phase HPLC using MeCN/H_2O (35:65), to give **5** (60.5 mg), **4** (34.3 mg), **1** (50.3 mg), **3** (30.8 mg), and **2** (122.7 mg), respectively.

*3.3.1. 11β-Hydroxy-7α-obacunyl acetate (**1**)*

Colorless prisms ($CHCl_3$–MeOH); m.p. 245–248 °C; $[\alpha]_D^{23} = +21.2°$ (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} nm (log ε): 209 (4.24); IR (film) ν_{max} cm^{-1} : 3460, 2987, 2952, 1739, 1682, 1632, 1504, 1457, 1373, 1328, 1279, 1232, 1165, 1125, 1053, 1026, 995, 922, 893, 876, 849, 805, 754; for ^1H and ^{13}C NMR spectra, see Tables 1 and 2; HRESIMS *m/z* 515.2286 ($[M + H]^+$, calcd for $C_{28}H_{35}O_9$, 515.2281).

*3.3.2. 11-Oxo-7α-obacunyl acetate (**2**)*

Colorless prisms ($CHCl_3$–MeOH); m.p. 280–283 °C; $[\alpha]_D^{23} = -52.2°$ (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} nm (log ε): 210 (4.20); IR (film) ν_{max} cm^{-1}: 2990, 1744, 1711, 1653, 1635, 1558, 1540, 1506, 1457, 1394, 1373, 1334, 1284, 1261, 1227, 1167, 1132, 1116, 1075, 1028, 989, 923, 876, 809, 754, 667; for ^1H and ^{13}C NMR spectra, see Tables 1 and 2; HRESIMS *m/z* 513.2153 ($[M + H]^+$, calcd for $C_{28}H_{33}O_9$, 513.2125).

*3.3.3. 11-Oxo-7α-obacunol (**3**)*

Colorless prisms ($CHCl_3$–MeOH); m.p. 243–245 °C; $[\alpha]_D^{23} = -25.8°$ (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} nm (log ε): 209 (4.17); IR (film) ν_{max} cm^{-1}: 2989, 1747, 1670, 1624, 1505, 1390, 1335, 1245, 1166, 1127, 1026, 913, 874, 823, 753; for ^1H and ^{13}C NMR spectra, see Tables 1 and 2; HRESIMS *m/z* 471.2063 ($[M + H]^+$, calcd for $C_{26}H_{31}O_8$, 471.2019).

*3.3.4. 11β-Hydroxycneorin G (**4**)*

Colorless prisms ($CHCl_3$–MeOH); m.p. 279–281 °C; $[\alpha]_D^{23} = -41.1°$ (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} nm (log ε): 208 (3.87); IR (film) ν_{max} cm^{-1}: 3480, 3148, 2986, 2950, 1736, 1504, 1464, 1429, 1374, 1284, 1228, 1163, 1147, 1119, 1079, 1048, 1025, 976, 925, 893, 876, 804, 753, 666; for ^1H and ^{13}C NMR spectra, see Tables 1 and 2; HRESIMS *m/z* 575.2513 ($[M + H]^+$, calcd for $C_{30}H_{39}O_{11}$, 575.2492).

*3.3.5. 11-Oxocneorin G (**5**)*

Colorless prisms ($CHCl_3$–MeOH); m.p. 274–276 °C; $[\alpha]_D^{23} = 126°$ (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} nm (log ε): 208 (3.85); IR (film) ν_{max} cm^{-1}: 2987, 2947, 1744, 1719, 1504, 1457, 1430, 1394, 1375, 1284, 1227, 1205, 1162, 1123, 1088, 1065, 1025, 918, 898, 876, 806, 753;

Table 1
^1H NMR (500 MHz) spectral data for **1**–**5** in $CDCl_3$ at 300 K

Position	1	2	3	4	5
1	6.72 (*d*, 12.8)	6.60 (*d*, 12.1)	6.59 (*d*, 12.1)	5.22 (*d*, 7.2)	5.60 (*d*, 7.4)
2	5.92 (*d*, 12.8)	5.85 (*d*, 12.1)	5.82 (*d*, 12.1)	3.24 (*d*, 15.6)	3.21 (*d*, 15.8)
				3.20 (*dd*, 15.6, 7.2)	3.09 (*dd*, 15.8, 7.4)
5	2.50 (*dd*, 13.2, 3.2)	2.31 (*dd*, 13.2, 3.3)	2.65 (*dd*, 13.2, 3.2)	2.40 (*m*)	2.36 (*m*)
6	2.10 (*m*)	1.90 (*m*)	1.93 (*m*)	2.07 (*m*)	2.10 (*m*)
	1.92 (*m*)	1.90 (*m*)	1.73 (*m*)	1.88 (*m*)	1.80 (*m*)
7	4.49 (*t*, 3.0)	4.63 (*t*, 2.9)	3.62 (*brs*)	4.45 (*brs*)	4.60 (*brs*)
9	2.29 (*d*, 5.0)	3.40 (*s*)	3.51 (*s*)	2.65 (*d*, 4.7)	3.77 (*s*)
11	4.62 (*m*)			4.20 (*m*)	
12	2.12 (*m*)	2.47 (*d*, 18.9)	2.42 (*d*, 18.8)	2.00 (*m*)	2.37 (*d*, 19.0)
	1.69 (*m*)	2.30 (*d*, 18.9)	2.27 (*d*, 18.8)	1.65 (*m*)	2.13 (*d*, 19.0)
15	3.52 (*s*)	3.64 (*s*)	3.90 (*s*)	3.54 (*s*)	3.59 (*s*)
17	5.63 (*s*)	5.66 (*s*)	5.65 (*s*)	5.63 (*s*)	5.62 (*s*)
18	1.15 (*s*)	1.43 (*s*)	1.42 (*s*)	1.13 (*s*)	1.42 (*s*)
19	1.65 (*s*)	1.58 (*s*)	1.56 (*s*)	1.58 (*s*)	1.50 (*s*)
21	7.41 (*m*)	7.43 (*m*)	7.42 (*m*)	7.40 (*m*)	7.42 (*m*)
22	6.34 (*s*)	6.33 (*s*)	6.34 (*s*)	6.32 (*s*)	6.30 (*s*)
23	7.42 (*m*)	7.44 (*m*)	7.43 (*m*)	7.42 (*m*)	7.43 (*m*)
28	1.31 (*s*)	1.36 (*s*)	1.42 (*s*)	1.36 (*s*)	1.37 (*s*)
29	1.46 (*s*)	1.44 (*s*)	1.46 (*s*)	1.50 (*s*)	1.49 (*s*)
30	1.34 (*s*)	1.15 (*s*)	1.08 (*s*)	1.36 (*s*)	1.11 (*s*)
1-OAc				2.12 (*s*)	2.17 (*s*)
7-OAc	2.11 (*s*)	2.16 (*s*)		2.04 (*s*)	2.01 (*s*)

Chemical shifts are reported in ppm relative to the residual $CHCl_3$ resonance at 7.26 ppm. Multiplicity and *J* values in Hz are given in parentheses.

Table 2
^{13}C NMR (125 MHz) spectral data for **1–5** in $CDCl_3$ at 300 K

Position	1	2	3	4	5
1	151.4 (*d*)	156.0 (*d*)	157.2 (*d*)	71.8 (*d*)	70.7 (*d*)
2	118.5 (*d*)	120.4 (*d*)	120.3 (*d*)	34.9 (*t*)	35.3 (*t*)
3	167.2 (*s*)	167.0 (*s*)	167.7 (*s*)	169.7 (*s*)	169.8 (*s*)
4	84.3 (*s*)	83.5 (*s*)	84.2 (*s*)	85.1 (*s*)	84.6 (*s*)
5	49.4 (*d*)	48.5 (*d*)	47.5 (*d*)	44.7 (*d*)	42.9 (*d*)
6	26.9 (*t*)	26.7 (*t*)	30.8 (*t*)	26.1 (*t*)	25.8 (*t*)
7	74.3 (*d*)	72.3 (*d*)	69.4 (*d*)	74.3 (*d*)	72.9 (*d*)
8	42.2 (*s*)	42.8 (*s*)	44.2 (*s*)	41.8 (*s*)	43.9 (*s*)
9	46.4 (*d*)	57.2 (*d*)	56.4 (*d*)	40.8 (*d*)	51.7 (*d*)
10	46.3 (*s*)	42.5 (*s*)	42.7 (*s*)	45.7 (*s*)	43.4 (*s*)
11	65.6 (*d*)	205.2 (*s*)	206.8 (*s*)	64.7 (*d*)	205.3 (*s*)
12	39.5 (*t*)	45.6 (*t*)	46.1 (*t*)	39.7 (*t*)	46.2 (*t*)
13	38.0 (*s*)	38.6 (*s*)	38.5 (*s*)	38.0 (*s*)	39.1 (*s*)
14	69.1 (*s*)	68.2 (*s*)	68.8 (*s*)	69.2 (*s*)	68.1 (*s*)
15	55.6 (*d*)	55.5 (*d*)	56.5 (*d*)	55.8 (*d*)	55.0 (*d*)
16	167.1 (*s*)	166.1 (*s*)	167.3 (*s*)	167.2 (*s*)	166.2 (*s*)
17	78.1 (*d*)	76.8 (*d*)	77.4 (*d*)	78.1 (*d*)	77.0 (*d*)
18	16.6 (*q*)	18.3 (*q*)	18.3 (*q*)	16.2 (*q*)	18.5 (*q*)
19	20.2 (*q*)	18.0 (*q*)	18.3 (*q*)	17.9 (*q*)	16.9 (*q*)
20	120.1 (*s*)	119.2 (*s*)	119.6 (*s*)	120.2 (*s*)	119.3 (*s*)
21	141.2 (*d*)	141.1 (*d*)	141.3 (*d*)	141.2 (*d*)	141.1 (*d*)
22	109.9 (*d*)	109.2 (*d*)	109.5 (*d*)	109.9 (*d*)	109.2 (*d*)
23	143.2 (*d*)	143.5 (*d*)	143.6 (*d*)	143.3 (*d*)	143.7 (*d*)
28	31.7 (*q*)	32.1 (*q*)	32.3 (*q*)	34.6 (*q*)	34.3 (*q*)
29	25.2 (*q*)	26.6 (*q*)	27.1 (*q*)	23.6 (*q*)	23.8 (*q*)
30	20.3 (*q*)	19.9 (*q*)	20.1 (*q*)	20.3 (*q*)	19.9 (*q*)
1-OAc (C=O)				170.1 (*s*)	169.3 (*s*)
1-OAc (Me)				21.1 (*q*)	21.0 (*q*)
7-OAc (C=O)	169.9 (*s*)	169.4 (*s*)		170.1 (*s*)	169.1 (*s*)
7-OAc (Me)	21.2 (*q*)	20.9 (*q*)		21.0 (*q*)	21.0 (*q*)

Chemical shifts are reported in ppm relative to the solvent resonance at 77.03 ppm.

for ^1H and ^{13}C NMR spectra see Tables 1 and 2; HRES-IMS *m/z* 573.2363 ($[M + H]^+$, calcd for $C_{30}H_{37}O_{11}$, 573.2336).

3.4. Oxidation of *1* to *2*

Solid TPAP (tetrapropylammonium perruthenate, 0.34 mg, 0.00097 mmol) was added in one portion to a stirred mixture of **1** (5.0 mg, 0.0097 mmol), 4-methylmorpholine *N*-oxide (1.5 mg, 0.013 mmol), and powdered 4 Å molecular sieves (4.4 mg) in CH_2Cl_2 (1 ml), and the whole was stirred at room temperature for 7 h. The mixture was diluted with $CHCl_3$ and washed successively with aqueous Na_2SO_3 and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated to give a residue, which was subjected to ODS-HPLC with MeCN/H_2O (35:65) to afford an oxidation product (4.9 mg), which was identified as **2** by comparison of their NMR and mass spectra.

3.5. Oxidation of *4* to *5*

TPAP oxidation of **4** (5.0 mg) according to the procedure described above gave an oxidation product (4.9 mg), which was shown to be identical to **5** by comparison of their NMR and mass spectra.

3.6. X-ray crystallographic studies of *2*

$C_{28}H_{32}O_9$, $M = 512.555$, $0.58 \times 0.38 \times 0.38$ mm^3, orthorhombic, $P2_12_12_1$, $a = 10.8690(3)$ Å, $b = 13.7380(3)$ Å, $c = 16.3860(3)$ Å, $V = 2446.73(10)$ Å^3, $Z = 4$, $D_x = 1.391$ Mg m^{-3}, μ(Mo Kα) = 0.104 mm^{-1}, 3041 reflection measured, 3031 unique reflections, $R = 0.0482$, $R_w = 0.1193$. The structure was determined by the direct method using the maXus crystallographic software package (Mackay et al., 1999), and the refinement was carried out by the program SHELXL-97 (Sheldrick, 1997).

3.7. X-ray crystallographic studies of *3*

$C_{26}H_{30}O_8$, $M = 470.518$, $0.50 \times 0.30 \times 0.13$ mm^3, orthorhombic, $P2_12_12_1$, $a = 8.0470(2)$ Å, $b = 11.7770(8)$ Å, $c = 24.2800(14)$ Å, $V = 2301.0(2)$ Å^3, $Z = 4$, $D_x = 1.358$ Mg m^{-3}, μ(Mo Kα) = 0.100 mm^{-1}, 2869 reflection measured, 2869 unique reflections, $R = 0.0462$, $R_w = 0.0819$.

3.8. X-ray crystallographic studies of **5**

$C_{30}H_{36}O_{11}$, $M = 572.607$, $0.50 \times 0.50 \times 0.30$ mm^3, orthorhombic, $P2_12_12_1$, $a = 8.7440(3)$ Å, $b = 16.0790(5)$ Å, $c = 19.1330(3)$ Å, $V = 2690.00(13)$ Å^3, $Z = 4$, $D_x = 1.414$ Mg m^{-3}, μ(Mo Kα) = 0.108 mm^{-1}, 3250 reflection measured, 3244 unique reflections, $R = 0.0768$, $R_w = 0.2293$.

CCDC 238269–238271 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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