

Structure Elucidation of New Monordens Produced by *Humicola* sp. FO-2942

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Structures of three novel compounds designated monordens C to E, isolated from the fermentation broth of amidepsine-producing fungus *Humicola* sp. FO-2942, were elucidated by spectroscopic evidence. Monordens C is 6,7-dihydromonorden A. Monordens D and E lack the epoxide moiety of monordens C and B, respectively.

Humicola sp. FO-2942 was originally discovered as a producing fungus of amidepsines, inhibitors of diacylglycerol acyltransferase (DGAT)¹⁾. Ten compounds including amidepsines A to D were isolated from the culture broth as showing UV spectra similar to amidepsines by LC-UV analyses²⁾. Among them, three were identified as monorden^{3~6)} (radicicol, monorden A in this paper), its tetrahydro-derivative^{4,7)} (monorden B in this paper) and 5-*O*-methylsclerone⁸⁾, but the others are structurally related new compounds designated monordens C, D and E. Tetrahydromonorden (monorden B) and 5-*O*-methylsclerone were originally reported as synthetic compounds, but we showed that they are fungal metabolites²⁾. The structures of monorden A (**1**) to E (**5**) and 5-*O*-methylsclerone (**6**) are shown in Fig. 1. In this paper, we describe the structure elucidation of monordens C to E mainly done by NMR analysis. The detailed spectral data of monorden B and 5-*O*-methylsclerone is also reported here.

Results

Structure Determination

¹H- and ¹³C-NMR spectra of monorden A (**1**) were measured in CDCl₃ (data not shown), which were identical with those of monorden (radicicol) previously reported^{4~6)}. Physico-chemical properties and ¹H- and ¹³C-NMR data in CD₃OD of monordens B (**2**), C (**3**), D (**4**) and E (**5**) are

summarized in Tables 1, 2 and 3 together with those of **1** for comparative purpose. Monorden B (**2**) and 5-*O*-methylsclerone were reported as synthetic compounds.

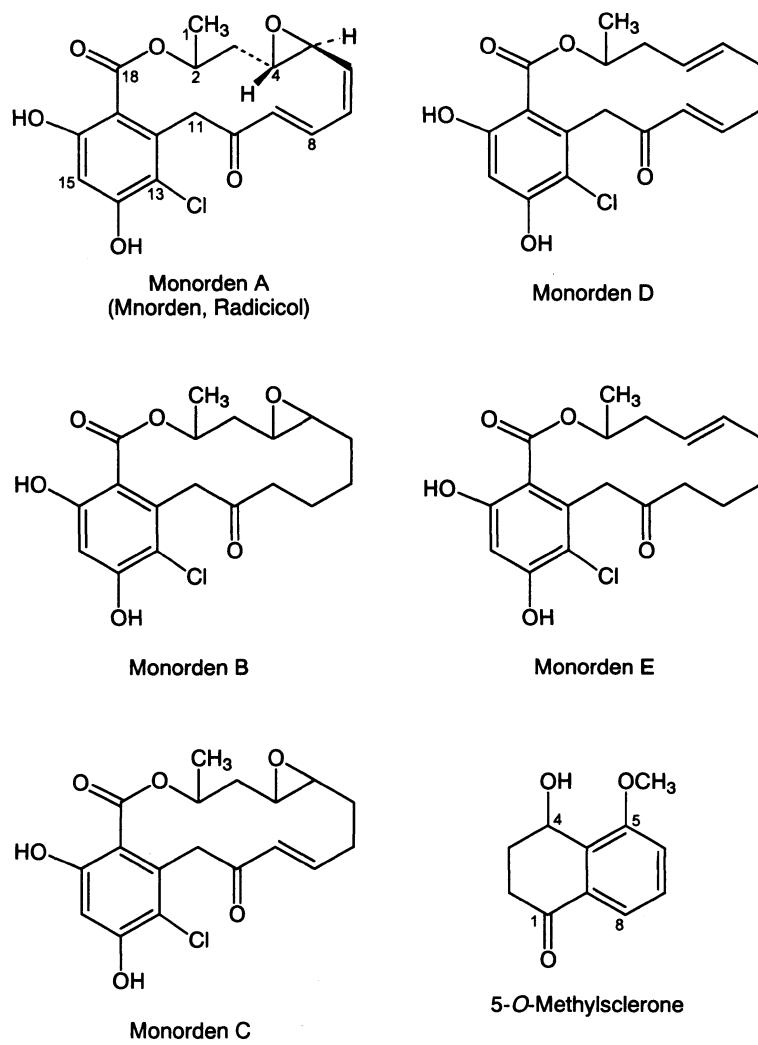
Structure of Monorden C (**3**)

The molecular formula of the compound **3**, given yellowish amorphous powder, was established as C₁₈H₁₉O₆Cl on the basis of HRFAB-MS [*m/z* 365.0809 (M-H)⁺, 365.0792 for C₁₈H₁₈O₆Cl]. The UV spectrum of **3** showed maxima absorption, λ_{max} nm (ε, CH₃OH): 218 (27,200), 227 (sh, 20,900), 261 (6,900), 313 (4,800). These spectra resemble those of **1**, suggesting that **3** has structure related to **1**.

The ¹³C-NMR spectra of **3** in CD₃OD exhibited 18 carbon signals. Analysis of the ¹H-, ¹³C-NMR, DEPT and HMQC spectral data led to the existence of one doublet methyl, four methylene, three *sp*³ methine, three *sp*² methine, seven quaternary carbons. The ¹H-¹H COSY and HMBC spectra of **3** revealed a partial connection consisting of one methyl, three methylene, three *sp*³ methine and two *sp*² methine, which assigned the sequence from C-1 to C-9. Further structural elucidation was done through interpretation of the HMBC experiment of **3** as shown in Fig. 2. The ¹H-¹³C long-range couplings from 8-H (δ_{H} 7.02) to C-10 (δ_{C} 199.0), and from 9-H (δ_{H} 6.11) to C-10 and C-11 (δ_{C} 45.8), and from 11-H₂ (δ_{H} 4.59 and 4.36) to C-10 and C-9 (δ_{C} 132.0) gave the bond from C-9 to C-11 via C-10. The long-range couplings from 15-H (δ_{H} 6.46) to C-13 (δ_{C} 117.5), C-14 (δ_{C} 164.8), C-16 (δ_{C} 160.8) and C-

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Fig. 1. The structures of monorden A (1), B (2), C (3), D (4), E (5) and 5-*O*-methylsclerone (6).



17 (δ_C 108.2) suggested that **3** contains the pentasubstituted benzene moiety, because 15-H was only observed as a singlet in the low-field signal. The long-range couplings from 11-H to C-12 (δ_C 137.9), C-13 and C-17 indicated that C-12 is linked to C-11. The carbon chemical shifts for benzene moiety showed good agreement with those of **1**, suggesting that the corresponding part is 1,2-disubstituted 3-chloro-4,6-dihydroxybenzene. The long-range coupling through 4 bonds (4J) from 15-H to C-18 (δ_C 171.9) was observed, indicating that they are for 'W' configuration and that C-17 and C-18 are bonded. The geometrical isomerism of C-8 was determined as 'E' by the proton coupling constant of $J_{8,9}$ (16.0 Hz). Thus, the planer structure of **3** was elucidated as 8-chloro-1a,4,5,14,15,15a-hexahydro-9,11-dihydroxy-14-methyl-6*H*-

oxireno[*e*][2]benzoxacyclotetradecin-6,12(7*H*)-dione.

Structure of Monorden D (4)

The molecular formula of the compound **4**, given yellowish oil, was established as $C_{18}H_{19}O_5Cl$ on the basis of HRFAB-MS [m/z 351.0999 ($M+H$) $^+$, 351.1051 for $C_{18}H_{20}O_5Cl$]. The UV and IR of **4** were very similar to those of **1** and **3**.

The ^{13}C -NMR spectra of **4** in CD_3OD exhibited 18 carbon signals as well as those of **1** and **3**. The 1H - and ^{13}C -NMR spectra of **4** showed signals of the 1,2-disubstituted 3-chloro-4,6-dihydroxybenzene moiety (δ_C 162.7, 159.3, 137.1, 116.5, 109.6 and 103.9, δ_H 6.48), two carbonyl (δ_C 198.7 and 170.7) and methylene (δ_C 46.4, δ_H 4.23 and 4.11) between the substituted benzene and

Table 1. Physico-chemical properties of monordens A (1), B (2), C (3), D (4) and E (5).

	1	2	3
Appearance	Yellowish amorphous powder	Yellowish amorphous powder	Yellowish amorphous powder
MP	191°C	187°C	158°C
$[\alpha]_D^{26}$	+160.6° (c 0.1, in CHCl_3)	-9.8° (c 0.1, in CHCl_3)	-10.9° (c 0.4, in CHCl_3)
Molecular formula	$\text{C}_{18}\text{H}_{17}\text{O}_6\text{Cl}$	$\text{C}_{18}\text{H}_{21}\text{O}_6\text{Cl}$	$\text{C}_{18}\text{H}_{19}\text{O}_6\text{Cl}$
HRFAB-MS (m/z)			
Found	363.0636 ($\text{M}-\text{H}^+$)	391.0899 ($\text{M}+\text{Na}^+$)	365.0809 ($\text{M}-\text{H}^+$)
Calcd.	365.0635 (for $\text{C}_{18}\text{H}_{16}\text{O}_6\text{Cl}$)	391.0924 (for $\text{C}_{18}\text{H}_{21}\text{O}_6\text{ClNa}$)	365.0792 (for $\text{C}_{18}\text{H}_{18}\text{O}_6\text{Cl}$)
UV λ_{max} nm (MeOH)	215 (sh, 20,500), 263 (12,700), 315 (sh, 4,200)	217 (16,100), 231 (sh, 9,400), 261 (6,200), 312 (4,500)	218 (27,200), 227 (sh, 20,900), 261 (6,900), 313 (4,800)
IR ν_{max} (KBr) cm^{-1}	3421, 1656, 1604, 1435, 1354, 1305, 1241, 1093	3162, 2364, 1712, 1666, 1608, 1311, 1232, 1114, 837	3000, 2937, 1681, 1646, 1600, 1295, 1249, 1101
	4	5	
Appearance	Yellowish oil	Yellowish oil	
MP	84°C	89°C	
$[\alpha]_D^{26}$	+21.4° (c 0.1, in CHCl_3)	-22.7° (c 0.28, in MeOH)	
Molecular formula	$\text{C}_{18}\text{H}_{19}\text{O}_5\text{Cl}$	$\text{C}_{18}\text{H}_{21}\text{O}_5\text{Cl}$	
HRFAB-MS (m/z)			
Found	351.0999 ($\text{M}+\text{H}^+$)	353.1166 ($\text{M}+\text{H}^+$)	
Calcd.	351.1051 (for $\text{C}_{18}\text{H}_{50}\text{O}_5\text{Cl}$)	353.1156 (for $\text{C}_{18}\text{H}_{22}\text{O}_5\text{Cl}$)	
UV λ_{max} nm (MeOH)	218 (15,900), 232 (sh, 11,000), 256 (sh, 5,100), 311 (3,200)	217 (12,900), 232 (sh, 6,900), 262 (4,300), 311 (2,900)	
IR ν_{max} (KBr) cm^{-1}	3425, 2926, 1651, 1606, 1311, 1246, 1114, 1033	3425, 2925, 1708, 1650, 1608, 1309, 1241, 1116	

Table 2. The ^{13}C -NMR data of monordens A (1), B (2), C (3), D (4) and E (5) in CD_3OD .

Position	1 δ_{C} (ppm, J in Hz)	2 δ_{C} (ppm, J in Hz)	3 δ_{C} (ppm, J in Hz)	4 δ_{C} (ppm, J in Hz)	5 δ_{C} (ppm, J in Hz)
1	19.2 q	19.5 q	18.5 q	18.5 q	19.4 q
2	72.6 d	72.4 d	74.0 d	73.7 d	74.2 d
3	38.2 t	37.9 t	38.0 t	38.1 t	38.9 t
4	57.0 d	56.4 d	57.2 d	128.1 d	126.5 d
5	57.3 d	58.7 d	58.6 d	133.4 d	135.7 d
6	137.4 d a)	31.5 t	32.4 t	32.1 t	33.2 t
7	132.0 d a)	24.5 t	30.6 t	32.3 t	26.8 t
8	141.1 d a)	23.9 t	150.9 d	149.3 d	23.4 t
9	131.3 d a)	41.4 t	132.0 d	130.8 d	42.1 t
10	200.1 s	209.7 s	199.0 s	198.7 s	209.7 s
11	47.0 t	47.1 t	45.8 t	46.4 t	47.1 t
12	135.6 s	136.1 s	137.9 s	137.1 s	137.1 s
13	115.8 s	116.0 s	117.5 s	116.5 s	116.1 s
14	159.6 s	161.3 s	164.8 s	162.7 s	162.6 s
15	104.3 d	103.9 d	104.5 d	103.9 d	103.9 d
16	158.8 s	159.1 s	160.8 s	159.3 s	159.1 s
17	113.6 s	110.8 s	108.2 s	109.6 s	109.8 s
18	169.6 s	170.6 s	171.9 s	170.7 s	171.1 s

a) Assignments are interchangeable

Table 3. The ^1H -NMR data of monordens A (1), B (2), C (3), D (4) and E (5) in CD_3OD .

Position	1 δ_{H} (ppm, J in Hz)	2 δ_{H} (ppm, J in Hz)	3 δ_{H} (ppm, J in Hz)
1	1.51 d (3H, J = 6.6 Hz)	1.43 d (3H, J = 6.4 Hz)	1.46 d (3H, J = 6.5 Hz)
2	5.37 m (1H)	5.27 m (1H)	5.23 m (1H)
3	2.41 ddd (1H, J = 14.7, 3.4, 3.0 Hz) 1.72 ddd (1H, J = 14.7, 8.6, 3.9 Hz)	2.17 ddd (1H, J = 15.2, 6.9, 4.1 Hz) 1.77 m (1H)	2.04 br. dd (1H, J = 16.1, 3.4 Hz) 1.76 ddd (1H, J = 16.1, 4.8, 4.3 Hz)
4	3.05 ddd (1H, J = 8.6, 3.0, 2.2 Hz)	2.84 ddd (1H, J = 6.4, 4.3, 2.5 Hz)	2.88 m (1H)
5	3.33 m (1H)	2.71 ddd (1H, J = 8.7, 3.0, 2.5 Hz)	2.60 m (1H)
6	5.77 dd (1H, J = 10.7, 3.9 Hz)	2.00 m (1H) 1.20 m (1H)	2.37 m (1H) 1.26 m (1H)
7	2.54 ddd (1H, J = 10.7, 9.8, 1.5 Hz)	1.58 m (1H) 1.47 m (1H)	2.54 m (1H) 2.33 m (1H)
8	7.52 dd (1H, J = 16.9, 9.8 Hz)	1.58 m (1H) 1.77 m (1H)	7.02 ddd (1H, J = 16.0, 10.8, 4.4 Hz)
9	6.11 d (1H, J = 16.9 Hz)	2.56 m (1H) 2.50 m (1H)	6.11 dd (1H, J = 16.0, 1.4 Hz)
11	4.16 d (1H, J = 16.3 Hz) 3.92 d (1H, J = 16.3 Hz)	4.30 d (1H, J = 18.2 Hz) 4.20 d (1H, J = 18.2 Hz)	4.59 d (1H, J = 18.3 Hz) 4.36 d (1H, J = 18.3 Hz)
15	6.46 s (1H)	6.45 s (1H)	6.46 s (1H)

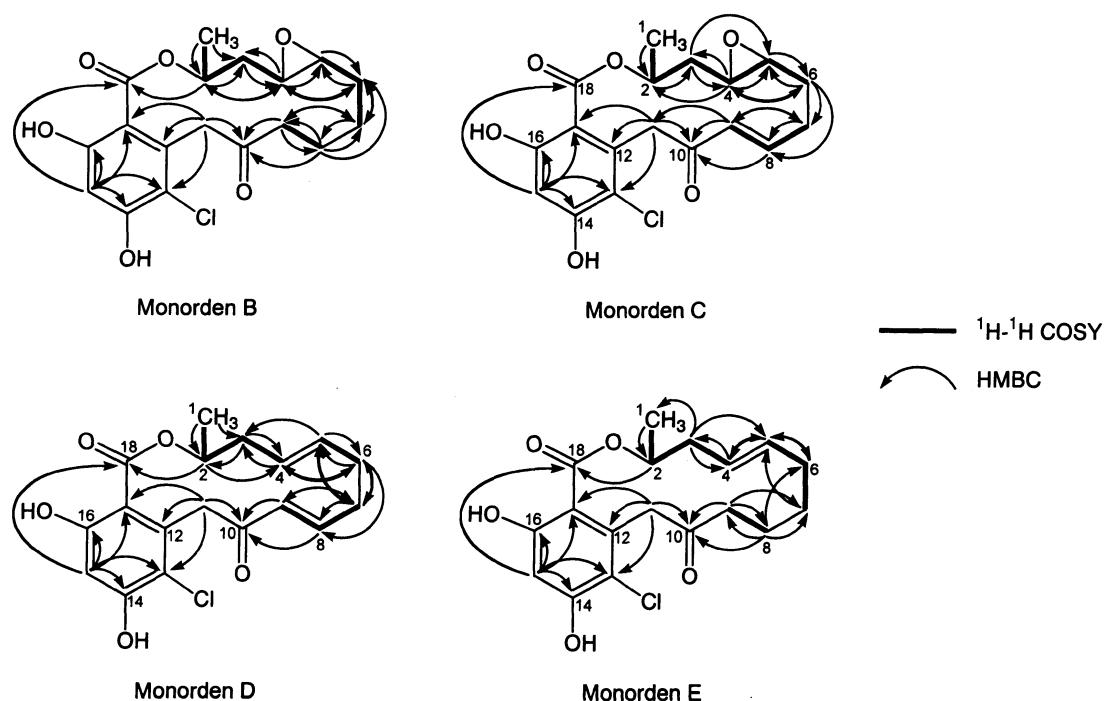
Position	4 δ_{H} (ppm, J in Hz)	5 δ_{H} (ppm, J in Hz)
1	1.29 d (3H, J = 6.4 Hz)	1.37 d (3H, J = 6.0 Hz)
2	5.31 m (1H)	5.31 m (1H)
3	2.54 m (1H) 2.24 m (1H)	2.50 m (1H) 2.31 m (1H)
4	5.28 m (1H)	5.48 m (1H)
5	5.23 m (1H)	5.48 m (1H)
6	2.17 m (2H)	2.08 m (2H)
7	2.28 m (1H) 2.15 m (1H)	1.55 m (1H) 1.47 m (1H)
8	6.72 ddd (1H, J = 15.2, 8.0, 7.0 Hz)	1.65 m (2H)
9	5.81 d (1H, J = 15.2 Hz)	2.52 m (2H)
11	4.23 d (1H, J = 16.0 Hz) 4.11 d (1H, J = 16.0 Hz)	4.37 d (1H, J = 17.0 Hz) 4.09 d (1H, J = 17.0 Hz)
15	6.48 s (1H)	6.46 s (1H)

the ketone, which are common to **1** and **3**. Analysis of the ^1H - ^{13}C -NMR, DEPT, and HMQC spectra revealed the presence of seven quaternary, six methine, four methylene, and one methyl carbons. Four partial structures, $\text{CH}_3\text{--CH}(\text{--O})\text{--}$, $\text{--CH}_2\text{--CH}=\text{}$, $=\text{CH--CH}_2\text{--}$, and $\text{--CH}_2\text{--CH=CH--}$, were shown by ^1H - ^1H -COSY. Their connection was analysed by HMBC (Fig. 2), indicating that **4** contains the olefin bonds between C-8 and C-9 and between C-4 and C-5. Further structural elucidation was also made by interpreting the HMBC experimental data (Fig. 2). Finally, the planar structure of **4** was elucidated as 13-chloro-3,4,7,8-tetrahydro-14,16-dihydroxy-3-methyl-1H-2-benzoxacyclotetradecin-1,11(12H)-dione.

Structure of Monorden E (5)

The molecular formula of the compound **5** was established as $\text{C}_{18}\text{H}_{21}\text{O}_5\text{Cl}$ on the basis of HRFAB-MS [m/z 353.1166 ($\text{M}+\text{H}$) $^+$, 353.1156 for $\text{C}_{18}\text{H}_{22}\text{O}_5\text{Cl}$], which is additional in two hydrogens compared with **4**. The UV and IR of **5** were very similar to those of **1**, **3** and **4**.

The NMR spectra of **5** were almost the same as those of **4** except C-7 (δ_{C} 26.8, δ_{H} 1.47 and 1.55), C-8 (δ_{C} 23.4, δ_{H} 1.65), and C-9 (δ_{C} 42.1, δ_{H} 2.52). Their alignment was elucidated by ^1H - ^1H -COSY, and ^1H - ^{13}C long-range couplings between $\text{H}_2\text{-6}$ (δ_{H} 2.08) and C-8, between $\text{H}_2\text{-7}$ and C-5 (δ_{C} 135.7), between H-8 and C-10 (δ_{C} 209.7), and between H-9 and C-10, suggesting that **5** is 8,9-dihydromorden D. Further structural elucidation was

Fig. 2. ^1H - ^1H COSY and HMBC correlations of monorden B (2), C (3), D (4) and E (5).

made by interpreting the HMBC experimental data as shown in Fig. 2. Finally, the planar structure of **5** was elucidated as 13-chloro-3,4,7,8,9,10-hexahydro-14,16-dihydroxy-3-methyl-1*H*-2-benzoxacyclotetradecin-1,11(12*H*)-dione.

Structure of Monorden B (2)

The molecular formula of the compound **2** was established as $\text{C}_{18}\text{H}_{21}\text{O}_6\text{Cl}$ on the basis of HRFAB-MS [m/z 391.0899 ($\text{M}+\text{Na}$) $^+$, 391.0924 for $\text{C}_{18}\text{H}_{21}\text{O}_6\text{ClNa}$], which is 2*H* larger than **3**. The UV and IR of **2** were very similar to those of **3**.

The ^{13}C -NMR spectra of **2** in CD_3OD exhibited 18 carbon signals as well as those of **3**. The ^1H - and ^{13}C -NMR spectra of **2** were almost the same as those of **3** except C7 (δ_{C} 24.5, δ_{H} 1.58 and 1.47), C8 (δ_{C} 23.9, δ_{H} 1.77 and 1.58), and C9 (δ_{C} 41.4, δ_{H} 2.56 and 2.50). The ^1H -, ^{13}C -NMR, DEPT and HMQC spectral data of **2** indicated the existence of one doublet methyl, six methylene, three sp^3 methine, one sp^2 methine and seven quaternary carbons, which were two more methylene and two less sp^2 methine than those of **3**. The connection from C-1 to C-10 via C-2, 9 was proved by ^1H - ^1H COSY and ^1H - ^{13}C long-range couplings, suggesting that **2** has additional two hydrogens at C-8 and

C-9 of **3**. Further structural elucidation was made by interpreting the HMBC experimental data as shown in Fig. 2. Finally, the structure of **2** was elucidated as 8-chloro-1*a*,2,3,4,5,14,15,15*a*-octahydro-9,11-dihydroxy-14-methyl-6*H*-oxireno[*e*][2]benzoxacyclotetradecin-6,12(7*H*)-dione.

Structure of 5-*O*-Methylsclerone (6)

The molecular formula of the compounds **6**, $[\alpha]_{D}^{26} -14.0^\circ$ (*c* 0.05, in CHCl_3); given yellowish oil, were established as $\text{C}_{11}\text{H}_{12}\text{O}_3$ on the basis of HREI-MS [m/z 192.0709 (M^+), 192.0786 for $\text{C}_{11}\text{H}_{12}\text{O}_3$]. The UV spectrum of **6** showed maxima absorption, λ_{max} nm (ϵ , CH_3OH): 226 (10,800), 258 (3,300), 318 (1,200). The IR spectrum of **6** showed absorption band, ν_{max} (KBr) cm^{-1} : 3382, 1681, 1384, 1211 and 1136.

The ^{13}C -NMR spectra of **6** in CDCl_3 exhibited 11 carbon signals. Analysis of the ^1H -, ^{13}C -NMR, DEPT and HMQC spectral data led to the existence of one singlet methyl (δ_{C} 55.8, δ_{H} 3.94), two methylene (δ_{C} 33.7, δ_{H} 2.99, 2.55; δ_{C} 29.4, δ_{H} 2.34, 2.31), one sp^3 methine (δ_{C} 62.2, δ_{H} 5.29), three sp^2 methine (δ_{C} 129.1, δ_{H} 7.39; δ_{C} 119.0, δ_{H} 7.65; δ_{C} 115.3, δ_{H} 7.12), one carbonyl (δ_{C} 198.0) and three aromatic quaternary (δ_{C} 157.0, 132.5, 132.3) carbons. The chemical shift of methyl, sp^3 methine and one aromatic quaternary

carbons suggested that **6** had three oxygenated carbons at δ_C 55.7, δ_C 62.2 and δ_C 157.0. The 1H -NMR data gave spin network system among C-6 (δ_H 7.12, $J=8.24, 1.10$ Hz), C-7 (δ_H 7.39, $J=8.24, 7.87$ Hz) and C-8 (δ_H 7.65, $J=7.87, 1.10$ Hz) as *ortho*- and/or *meta*-coupling on the benzene ring. Further structural elucidation was made by interpreting the HMBC experimental data for **6** (data not shown). Finally, the structure of **6** was determined as 2,3-dihydro-4-hydroxy-5-methoxy-1-naphthalenone.

Discussion

Analogs of monorden A (radicicol)³⁾ such as monocillins I to V⁹⁾, nordinone and nordinonediol¹⁰⁾ have been reported as fungal metabolites. Although most of them lack the residue, only monorden A and 13-chloro-6,7,8-dehydro-4-hydroxymonocillin IV¹¹⁾ possess the chlorine residue at C-13. As described in this paper, all the monordens isolated from the amidepsine producer were found to have the 13-chlorine residue in common. Monordens B, C, D and E correspond to 13-chlorinated monocillins III, V, II and IV, respectively. Monorden B^{4,7)} and 5-*O*-methylsclerone⁸⁾ were reported as synthetic compounds, but they were isolated as metabolites of this fungus.

Experimental

Spectral and physico-chemical data for monorden A to E and 5-*O*-methylsclerone were obtained by the following instruments: mp, Yanagimoto Micro Melting Point Apparatus MP-S3; IR, HORIBA FT-210; UV, HITACHI 340 Recording Spectrophotometer; Optical rotations, JASCO DIP-1000 Digital Polarimeter with a 5 cm cell; and NMR, Varian UNITY 400. FAB-MS data for monordens A to E were obtained by JOEL JSM-700 MS station, and EI-MS data for 5-*O*-methylsclerone was obtained by JOEL JSM-AX 505 HA. All NMR spectra for monorden A to E were measured in methanol-*d*₄, and peak positions are expressed in parts per million (ppm) based on the reference of methanol peak at δ 3.30 ppm for 1H -NMR and δ 49.0 ppm for ^{13}C -NMR. Monorden A were also measured in chloroform-*d*. All NMR spectra for 5-*O*-methylsclerone were also measured in chloroform-*d*, and peak positions are expressed in parts per million (ppm) based on the reference of chloroform peak at δ 7.24 ppm for 1H -NMR and δ 77.0 ppm for ^{13}C -NMR. All FAB-MS spectra were measured using 3-nitrobenzylalcohol and

thioglycerol for matrix.

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