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Isolation and Structure of Shimofuridins B ~ G from the Okinawan Marine Tunicate *Aplidium multiplicatum*

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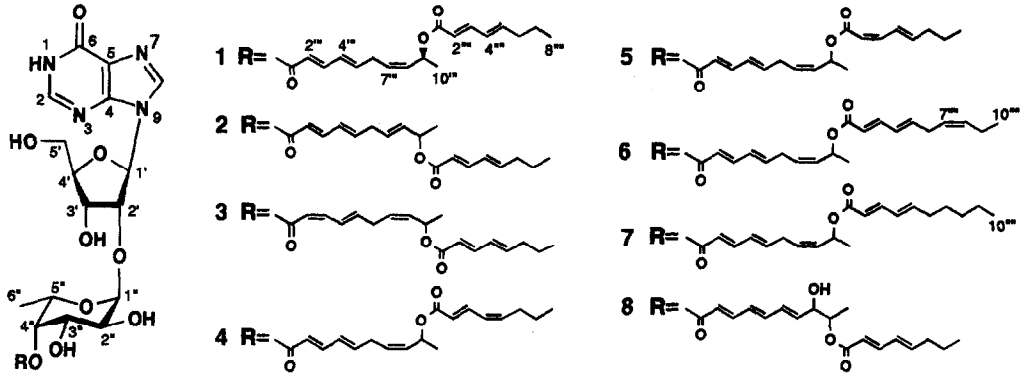
Abstract: Shimofuridins B ~ G (2 ~ 7), six new nucleoside derivatives with acylfucopyranoside moiety, have been isolated from the Okinawan marine tunicate *Aplidium multiplicatum* by careful HPLC separation and their structures elucidated on the basis of spectroscopic data.

During our studies on bioactive substances from Okinawan marine organisms,[1] we recently isolated shimofuridin A (1), a nucleoside derivative containing an acylfucopyranoside moiety, from the Okinawan marine tunicate *Aplidium multiplicatum* Sluiter. This unique nucleoside (1) exhibited cytotoxic and antimicrobial activities and the structure including the absolute stereochemistry of all chiral centers was established by spectral and chemical means.[2] We further continued investigation on extracts of this tunicate and careful studies on the HPLC separation of closely related analogs resulted in the isolation of six new nucleoside derivatives, shimofuridins B ~ G (2 ~ 7). This paper deals with the isolation and structure elucidation of 2 ~ 7. Shimofuridins B ~ E (2 ~ 5) are stereoisomers of shimofuridin A (1) as to the geometry of the double-bonds in the unsaturated acyl chain moieties, while shimofuridins F (6) and G (7) possess homologous acyl chains with two more carbon units.

The tunicate *A. multiplicatum*, collected off Okinawan Island, was extracted with MeOH, and the extract was partitioned between EtOAc and water. The EtOAc-soluble material was subjected to silica gel flash column chromatography ($MeOH/CHCl_3$, 30:70) followed by gel filtration on Sephadex LH-20 ($MeOH/CHCl_3$, 1:1). Further separation using a Sep-Pak® cartridge (C_{18}, 40% ~ 50% CH_3CN) afforded a fraction containing a mixture of shimofuridin analogs, purification of which was subsequently attempted by HPLC using several types of reversed-phase columns (ODS, Ph, TMS, and NH_2) with various solvent systems. Consequently, separation of this fraction was successfully achieved only when a column of Develosil® ODS-HG-5 (Nomura Chemical) was used and eluted with 43% ~ 48% CH_3CN to give shimofuridins B (2, 0.001% wet weight), C (3, 0.003%), D (4, 0.002%), E (5, 0.002%), F (6, 0.0008%), and G (7, 0.0002%), together with the major component, shimofuridin A (1, 0.01%).[2]

The molecular weights of shimofuridins B ~ E (2 ~ 5) were all revealed to be equal to that of shimofuridin A (1) from the negative FABMS data [*m/z* 699 $(M-H)^-$ for 2 ~ 5] and the IR and UV absorptions of 2 ~ 5 were also almost identical with those of 1. Shimofuridins B ~ E (2 ~ 5) were therefore inferred as isomers of 1, which was supported by the ^1H and ^{13}C NMR data; their chemical shifts as well as the coupling



constants were parallel to those of **1** respecting the inosine α-fucopyranoside unit, and differences of NMR data were observed only as to the two acyl chain moieties (Tables 1 ~ 3). Assignments of the ^{1}H and ^{13}C NMR data were firmly established on the basis of ^{1}H-^{1}H COSY and HSQC[3] spectra recorded for each compound (**2** ~ **5**) as well as comparison with the data of shimofuridin A (**1**).[2]

Shimofuridin B (**2**) possesses 2'''*E*, 4'''*E*, 7'''*E*- and 2''''*E*, 4''''*E*-configurations for the acyl chain

Table 1. ^{1}H NMR Data of Shimofuridins A ~ G (**1** ~ **7**) in CD_3OD.

position		1	2	3	4	5	6	7
2		8.48 s	8.48 s	8.45 s	8.43 s	8.41 s	8.44 s	8.43 s
8		8.14 s	8.14 s	8.13 s	8.12 s	8.13 s	8.13 s	8.14 s
1'		6.25 d	6.26 d	6.24 d	6.23 d	6.21 d	6.22 d	6.23 d
2'		4.87 dd	4.88 dd	4.85 dd	4.85 dd	4.85 dd	4.88 dd	4.85 dd
3'		4.50 dd	4.49 dd	4.50 dd	4.50 dd	4.50 dd	4.50 dd	4.50 dd
4'		4.23 t	4.23 t	4.23 t	4.23 t	4.23 t	4.23 t	4.23 t
5'	(a)	3.91 dd	3.90 dd	3.91 dd	3.89 dd	3.90 dd	3.91 dd	3.89 dd
	(b)	3.82 dd	3.80 dd	3.80 dd	3.81 dd	3.84 dd	3.80 dd	3.81 dd
1"		5.02 d	5.00 d	5.04 d	5.09 d	5.02 d	5.02 d	4.99 d
2"		3.80 m	3.75 m	3.78 dd	3.80 dd	3.79 dd	3.80 dd	3.80 m
3"		3.98 dd	4.04 dd	3.97 dd	3.97 dd	3.97 dd	3.98 dd	3.98 dd
4"		5.13 t	5.05 t	5.14 t	5.11 t	5.12 t	5.12 brt	5.13 brt
5"		3.70 dq	3.70 dq	3.70 dq	3.68 dq	3.67 dq	3.68 m	3.68 m
6"	(3H)	0.66 d	0.64 d	0.68 d	0.65 d	0.64 d	0.66 d	0.66 d
2"'		5.89 d	5.82 d	5.64 d	5.89 d	5.89 d	5.83 d	5.90 d
3"'		7.30 m	7.28 dd	6.68 t	7.30 dd	7.30 dd	7.28 dd	7.26 dd
4"'		6.31 m	6.28 dd	7.35 dd	6.31 dd	6.31 dd	6.27 dd	6.30 dd
5"'		6.19 m	6.22 m	6.15 dt	6.17 dt	6.22 m	6.23 m	6.22 m
6"'	(2H)	3.10 m	3.10 m	3.10 m	3.11 m	3.12 m	3.10 m	3.10 m
7"'		5.55 m	5.56 m	5.54 m	5.55 m	5.55 m	5.55 m	5.55 m
8"'		5.59 m	5.59 m	5.58 m	5.59 m	5.60 m	5.59 dd	5.58 dd
9"'		5.72 m	5.73 dq	5.71 dq	5.73 dq	5.72 dq	5.72 dq	5.72 dq
10"'	(3H)	1.34 d	1.34 d	1.33 d	1.35 d	1.34 d	1.34 d	1.34 d
2""		5.81 d	5.95 d	5.82 d	5.89 d	5.55 d	5.89 d	5.81 d
3""		7.26 m	7.39 dd	7.27 dd	7.64 dd	6.64 t	7.30 dd	7.29 dd
4""		6.27 m	6.34 m	6.27 dd	6.21 m	7.36 dd	6.31 dd	6.26 dd
5""		6.24 m	6.24 m	6.23 m	5.94 m	6.15 m	6.19 m	6.20 m
6""	(2H)	2.20 m	2.21 m	2.21 m	2.32 m	2.20 m	2.97 t	2.21 dt
7""		1.50 m	1.52 m	1.52 m	1.51 m	1.50 m	5.40 dt	1.51 m
8""		0.97 t	0.96 t	0.98 t	0.98 t	0.98 t	5.54 m	1.46 m
9""	(2H)						2.11 m	1.66 m
10""	(3H)						1.01 t	1.02 t

Table 2. ^{1}H-^{1}H Coupling Constants (J in Hz) of Shimofuridins B ~ G (1 ~ 7) in CD_3OD.[a]

H/H	1	2	3	4	5	6	7	H/H	1	2	3	4	5	6	7
1'/2'	6.4	6.4	6.4	6.4	6.4	6.4	6.4	2'''/3'''	15.4	15.4	11.4	15.3	15.4	15.3	15.4
2'/3'	4.5	4.8	4.7	4.6	4.6	4.8	4.5	3'''/4'''		10.1	11.4	10.7	11.9	10.0	10.2
3'/4'	2.9	2.9	2.9	2.8	2.8	2.8	2.7	4'''/5'''		15.3	15.4	15.7	14.9	15.1	15.8
4'/5'a	2.9	2.9	2.9	2.8	2.8	2.8	2.7	7'''/8'''	10.7					11.1	11.4
4'/5'b	2.9	2.9	2.9	2.8	2.8	2.8	2.7	8'''/9'''		7.4	8.1	7.7	8.2	7.7	7.6
5'a/5'b	12.3	12.4	12.4	12.4	12.3	12.1	12.2	9'''/10'''	6.4	6.4	6.4	6.4	6.4	6.4	6.5
1''/2''	3.9	3.9	3.9	3.7	3.7	3.8		2''''/3''''	15.6	15.4	15.4	15.3	11.4	15.3	15.4
2''/3''	10.3	10.6	10.6	10.4	10.3	10.4	10.3	3''''/4''''		10.7	10.0	12.4	11.4	10.7	10.2
3''/4''	3.2	3.0	3.0	2.9	3.1	3.5	3.5	4''''/5''''		14.9	14.9	10.7	15.2	15.4	15.8
4''/5''	3.2	3.0	3.0	2.9	3.1			6''''/7''''						6.5	6.9
5''/6''	6.4	6.3	6.4	6.6	6.6	5.9	5.9	7''''/8''''	7.3	7.4	7.2	7.3	7.4	10.5	
								9''''/10''''						7.5	7.5

[a] J-values for blank positions were not assigned.

moieties, which was revealed by the ^{1}H-^{1}H coupling constants ($J_{2''',3'''}$ = 15.4 Hz and $J_{2'''',3''''}$ = 15.4 Hz) and the ^{13}C chemical shifts for the carbons of allylic positions (C-6''' and C-6''''). The allylic carbon of the second acyl chain (C-6'''') resonated at δ_C 36.0, which agreed well to the ^{13}C chemical shift for C-6 (δ_C 35.0) of 2*E*, 4*E*-octadienoic acid.[4] 4''''*E*-Configuration of **2** was thus deduced since allylic carbons of *cis*-olefins are known to be observed at higher resonances (approximately 27 ppm).[5] The ^{13}C NMR chemical shifts for bis-allylic positions between *cis-cis*, *cis-trans*, and *trans-trans* olefins are described to be approximately 25, 30, and 35 ppm, respectively.[5] The bis-allylic carbon of the first acyl chain of **2** (C-6''') resonated at δ_C 36.0, which implied that C-6''' was located between two *trans* olefins, thus suggesting 4'''*E*, 7'''*E*-configurations.

In the ^{1}H NMR spectrum of shimofuridin C (**3**), the signals for H-3''' and H-4''' in the first acyl chain were apparently different from those for **1**; H-3''' resonated at higher field by 0.62 ppm while H-4''' was observed at lower field by 1.04 ppm (Table 1). This phenomenon was ascribable to difference in the geometry of the $\Delta^{2''',3'''}$-double bond (2'''*Z* for **3**), which was confirmed by the coupling constant ($J_{2''',3'''}$ = 11.4 Hz). Spectral data for rest of the molecule of **3** were quite parallel to those of **1**. Particularly, the 7'''*Z*-configuration

Table 3. ^{13}C NMR Data of Shimofuridins A ~ E (1 ~ 5) in CD_3OD.[a]

position	1	2	3	4	5	position	1	2	3	4	5
2	148.3		146.5			1'''	164.1		167.3		
4	150.0	149.9	147.1			2'''	120.2	120.2	116.6	120.3	128.9
5	126.1					3'''	147.3	146.7	146.2		144.6
6	158.7					4'''	130.5	130.1	129.6		128.8
8	139.6	140.5	140.8			5'''	141.2	144.0	143.5		142.0
1'	88.0	87.7	87.8	88.5	87.0	6'''	32.1	36.0	32.0	32.2	31.2
2'	82.5	82.0	82.3	82.5	82.5	7'''	132.5	132.4	132.2		131.5
3'	71.5	71.4	71.2	71.5	70.4	8'''	130.0	129.8	128.5	129.7	127.3
4'	88.4	88.4	88.2	88.4	87.0	9'''	67.9	67.9	67.7		
5'	63.0	61.7	62.8	63.0		10'''	21.1	21.0	20.8	21.0	20.1
1''	101.6	109.0	101.3	101.6		1''''	164.5		168.0		
2''	70.0	70.9	69.9	71.3	69.0	2''''	120.4	120.2	120.0	122.5	125.5
3''	69.5	67.7	69.2	71.0	68.4	3''''	146.8	146.7	145.7		
4''	74.9	74.4	74.4	75.8	73.9	4''''	129.9	129.7	129.6		128.8
5''	67.3	66.2	67.1	68.0	66.4	5''''	141.1	139.9	142.8		142.2
6''	16.5	16.1	16.1	17.4	15.2	6''''	36.1	36.0	35.8	32.0	29.7
						7''''	21.1	21.0	22.8	23.6	22.0
						8''''	14.2	14.0	13.8	16.2	13.0

[a] Chemical shifts for blank positions were not assigned.

was ascertained by the NOESY correlations between H_2-6‴ and H-9‴.

The ^{1}H NMR spectrum of shimofuridin D (**4**) was indistinguishable from that of **1** except for the signals due to H-3‴″ and H-5‴″ in the second acyl chain; H-3‴″ was shifted to lower field by 0.38 ppm whereas H-5‴″ to higher field by 0.30 ppm (Table 1), suggesting that differences between **4** and **1** were found only in the geometry of olefins contained in the second acyl chain. The $\Delta^{2'''',3''''}$-double bond was obviously *E* from the coupling constant ($J_{2'''',3''''}$ = 15.3 Hz), while the 4‴″*Z*-configuration was suggested from the NOESY cross-peak observed between H-3‴″ and H_2-6‴″ and the $J_{4'''',5''''}$-value (10.7 Hz) revealed by homo-spin decoupling experiment irradiating at H_2-6‴″.

Shimofuridin E (**5**) showed characteristic ^{1}H NMR signals due to H-3‴″ (δ_H 6.64) and H-4‴″ (δ_H 7.36) in the second acyl chain, which were much different from those for **1** (δ_H 7.26 and 6.27, respectively) but closely corresponded to those for H-3‴ (δ_H 6.68) and H-4‴ (δ_H 7.35) in the first acyl chain of shimofuridin C (**3**). This observation suggested 2‴″*Z*, 4‴″*E*-configurations in the second acyl chain for **5**, which was further verified by the coupling constants ($J_{2'''',3''''}$ = 11.4 Hz and $J_{4'''',5''''}$ = 15.2 Hz). The first acyl chain of **5** possesses the same olefin geometries as that of **1**, deduced from the following observations for **5** ($J_{2'''',3''''}$ = 15.4 Hz, $J_{4'''',5''''}$ = 14.9 Hz; $\delta_{C\text{-}6'''}$ 31.2; NOESY correlation for H_2-6‴/H-9‴).

The molecular formula of shimofuridin F (**6**) was revealed as $C_{36}H_{46}O_{12}N_4$ by HRFABMS [*m/z* 832.3949 (M+diethanolamine+H)$^+$ for $C_{40}H_{58}O_{14}N_5$, Δ -3.2 mmu], which contains two carbons and two hydrogen atoms more than that of shimofuridin A (**1**). The UV, IR, and ^{1}H NMR data of **6** were almost similar to those of **1** and suggested that the inosine α-fucopyranoside unit was also contained in **6**. From the ^{1}H-^{1}H COSY spectrum, structural differences were found only in the second acyl chain moiety, which proved to be a 2*E*, 4*E*, 7*Z*-decatrienoyl group. The configurations of double bonds were revealed by the ^{1}H-^{1}H coupling constants ($J_{2'''',3''''}$ = 15.3 Hz, $J_{4'''',5''''}$ = 15.4 Hz, and $J_{7'''',8''''}$ = 10.5 Hz).

Shimofuridin G (**7**) was shown to have the largest molecular weight (728) with a composition of $C_{36}H_{48}O_{12}N_4$ as established by HRFABMS [*m/z* 727.3216 (M-H)$^-$ for $C_{36}H_{47}O_{12}N_4$, Δ +2.5 mmu], which corresponds to that having two more hydrogen atoms than shimofuridin F (**6**). The ^{1}H NMR data of **7** aided with the ^{1}H-^{1}H COSY spectrum revealed that **7** possesses a 2*E*, 4*E*-decadienoyl group as the second acyl chain, olefin geometries of which were also determined by the ^{1}H-^{1}H coupling constants ($J_{2'''',3''''}$ = 15.4 Hz and $J_{4'''',5''''}$ = 15.8 Hz).[6]

Shimofuridins B ~ G (**2** ~ **7**) are new nucleoside analogs isolated from marine origins, and their structures are related closely to one another and the isolation procedure required careful operations to avoid air-oxidation or photoisomerization.[7] Shimofuridin A (**1**) proved to be stable for several days in MeOH solution under room light. Formation of the isomers **2** ~ **5** was not detected by HPLC examination. We therefore concluded that **2** ~ **5** are not necessarily artificially produced compounds during isolation processes, while shimofuridins F (**6**) and G (**7**) are definitely natural products. Shimofuridin A (**1**), however, suffered from considerable decomposition under irradiation with 400 W high-pressure mercury lamp in MeOH solution. HPLC analysis showed formation of compounds **2** ~ **5**, with the ratio of **1** ~ **5** after 5 min to be 1:0.03:0.16:0.23:0.07. After 20-h irradiation, all of compounds **1** ~ **5** disappeared to yield a complex mixture, from which a peak due to an allyl alcohol (**8**) was detected by HPLC analysis. Compound **8** was isolated previously during HPLC separation of shimofuridins, in spite of taking care of air, and characterized as an air-oxidized product.

Experimental Section[8]

Collection, Extraction, and Isolation. The tunicate *Aplidium multiplicatum* Sluiter was collected off Seragaki Beach, Okinawa Island in May 1992 and kept frozen until used. The tunicate (1.0 kg wet weight) was extracted with MeOH (1.5 L x 2). The MeOH extract (52.8 g) was partitioned between EtOAc (500 mL x 3) and 1M NaCl (500 mL). A portion (1.2 g) of the EtOAc-soluble material (2.4 g) was subjected to silica gel flash column chromatography (45 x 3.0 cm) with stepwise elution of MeOH in $CHCl_3$ (10-100%). The fraction (78.9 mg) eluting with 30% MeOH in $CHCl_3$ was separated by gel filtration on a Sephadex LH-20 column (Pharmacia, 2.0 x 100 cm) with 50% MeOH in $CHCl_3$ to give a fraction (54.6 mg; 125 ~ 160 mL), which was then passed through a Sep-Pak C_{18} cartridge (Waters, 10 x10 mm). The fraction (10.1 mg) eluting with 40% CH_3CN was finally purified by reversed-phase HPLC (Develosil ODS-HG-5, 10 x 250 mm; 43% CH_3CN; flow rate, 2.5 mL/min) to give shimofuridins B (**2**, t_R 74.0 min, 0.6 mg, 0.001% wet weight), C (**3**, t_R 58.4 min, 1.3 mg, 0.003%), D (**4**, t_R 52.8 min, 0.9 mg, 0.002%), E (**5**, t_R 55.6 min, 0.8 mg, 0.002%), and A (**1**, t_R 64.8 min, 6.1 mg, 0.01%) together with the allyl alcohol (**8**, t_R 15.2 min, 0.5 mg, 0.001%). Separation of the fraction (10.7 mg) of the Sep-Pak cartridge eluting with 50% CH_3CN by reversed-phase HPLC (Develosil ODS-HG-5 10 x 250 mm; 48% CH_3CN; flow rate, 2.5 mL/min) to give shimofuridins F (**6**, t_R 40.0 min, 0.4 mg, 0.0008%) and G (**6**, t_R 66.8 min, 0.15 mg, 0.0002%).

Shimofuridin B (2). Colorless amorphous solid; $[\alpha]_D^{20}$ -167° (*c*, 0.1, MeOH); UV (MeOH) λ_{max} 370 (ε 340) and 261 nm (48000); IR (KBr) ν_{max} 3440, 2950, 1700, 1640, 1620, 1390, 1150, 1050, and 1010 cm^{-1}; ^1H and ^{13}C NMR (Tables 1-3); FABMS (negative, diethanolamine matrix) *m/z* 699 $(M-H)^-$, 559 (M - octadienoyloxy group)$^-$, 413 (inosine α-fucopyranoside - H)$^-$, 267 (inosine - H)$^-$, and 135 (hypoxanthine - H)$^-$.

Shimofuridin C (3). Colorless amorphous solid; $[\alpha]_D^{20}$ -110° (*c*, 0.2, MeOH); UV (MeOH) λ_{max} 263 nm (ε 32000); IR (KBr) ν_{max} 3400, 2910, 2840, 1700, 1630, 1260, 1170, 1130, 1080, and 1040 cm^{-1}; ^1H and ^{13}C NMR (Tables 1-3); FABMS (negative, diethanolamine matrix) *m/z* 699 $(M-H)^-$, 559, 413, 267, and 135. HRFABMS *m/z* 699.2858 (M-H; calcd for $C_{34}H_{43}O_{12}N_4$, 699.2877).

Shimofuridin D (4). Colorless amorphous solid; $[\alpha]_D^{20}$ -91° (*c*, 0.1, MeOH); UV (MeOH) λ_{max} 358 (ε 340) and 263 nm (30000); IR (KBr) ν_{max} 3430, 2920, 2830, 1680, 1640, 1260, 1080, and 1040 cm^{-1}; ^1H and ^{13}C NMR (Tables 1-3); FABMS (negative, diethanolamine matrix) *m/z* 699$(M-H)^-$, 559, 413, 267, and 135; HRFABMS *m/z* 699.2905 (M-H; calcd for $C_{34}H_{43}O_{12}N_4$, 699.2877).

Shimofuridin E (5). Colorless amorphous solid; $[\alpha]_D^{20}$ -109° (*c*, 0.1, MeOH); UV (MeOH) λ_{max} 338 (ε 630) and 262 nm (42000); IR (KBr) ν_{max} 3420, 2930, 1690, 1640, 1180, 1080, and 1040 cm^{-1}; ^1H and ^{13}C NMR (Tables 1-3); FABMS (negative, diethanolamine matrix) *m/z* 699 $(M-H)^-$, 559, 413, 267, and 135; HRFABMS *m/z* 699.2853 (M-H, calcd for $C_{34}H_{43}O_{12}N_4$, 699.2877).

Shimofuridin F (6). Colorless amorphous solid; $[\alpha]_D^{20}$ -59° (*c*, 0.07, MeOH); UV (MeOH) λ_{max} 353 (ε 330) and 263 nm (18000); IR (KBr) ν_{max} 3410, 2920, 1680, 1630, and 1040 cm^{-1}; ^1H NMR (Tables 1 and 2); FABMS (positive, diethanolamine matrix) *m/z* 832 $(M+DEA+H)^+$, 665, 269; HRFABMS *m/z* 832.3949 (M+DEA+H; calcd for $C_{40}H_{58}O_{14}N_5$, 832.3981).

Shimofuridin G (7). Colorless amorphous solid; $[\alpha]_D^{20}$ -74° (*c*, 0.05, MeOH); UV (MeOH) λ_{max} 327 (ε 780) and 262 nm (16000); IR (KBr) ν_{max} 3410, 2920, 1730, and 1630 cm^{-1}; ^1H NMR (Tables 1 and

2); FABMS (negative, diethanolamine matrix) *m/z* 727 $(M-H)^-$; HRFABMS *m/z* 727.3216 (M-H; calcd for $C_{36}H_{47}O_{12}N_4$, 727.3191).

Compound 8. Colorless amorphous solid; UV (MeOH) λ_{max} 386 (ε 320), 296 (10000), and 267 nm (12000); ^1H NMR (CD_3OD) δ_H 8.45 (1H, s, H-8), 8.14 (1H, s, H-2), 7.36 (1H, m, H-3'"), 7.31 (1H, m, H-3""), 6.71 (1H, dd, *J* = 1.09, 15.2 Hz, H-5'"), 6.50 (1H, m, H-4'"), 6.47 (1H, m, H-5""), 6.28 (1H, dd, *J* = 10.0, 15.3 Hz, H-4""), 6.24 (1H, d, *J* = 6.4 Hz, H-1'), 6.22 (1H, m, H-5""), 6.02 (1H, dd, J = 6.3, 14.8 Hz, H-7'"), 6.01 (1H, d, *J* = 6.4 Hz, H-2'"), 5.87 (1H, d, *J* = 15.3 Hz, H-2""), 5.15 (1H, t, *J* = 3.4 Hz, H-4"), 5.04 (1H, d, *J* = 3.9 Hz, H-1"), 5.00 (1H, m, H-9'"), 4.65 (1H, dd, *J* = 4.5, 6.4 Hz, H-2'), 4.45 (1H, dd, *J* = 2.7, 4.5 Hz, H-3'), 4.27 (1H, dd, *J* = 5.2, 6.3 Hz, H-8'"), 4.23 (1H, br t, H-4'), 3.88 (1H, dd, *J* = 3.4, 10.4 Hz, H-3"), 3.92 (1H, dd, *J* = 2.7, 12.3 Hz, H-5'), 3.82 (1H, dd, *J* = 2.7, 12.3 Hz, H-5'), 3.80 (1H, dd, *J* = 3.9, 10.4 Hz, H-2"), 3.68 (1H, m, H-5"), 2.20 (2H, m, H-6""), 1.52 (2H, dq, *J* = 7.2, 14.8 Hz, H-7""), 1.26 (3H, d, *J* = 6.5 Hz, H-10'"), 0.98 (3H, t, *J* = 7.5 Hz, H-8""), and 0.65 (3H, d, *J* = 6.4 Hz, H-6"); FABMS (positive, diethanolamine matrix) *m/z* 699 $(M-H_2O+H)^+$ and 680.

Photoisomerization of Shimofuridin A (1). Shimofuridin A (1, 0.1 mg) was dissolved in MeOH (1 mL) and placed under the 400 W high pressure Hg lamp in a quartz cell at ambient temperature. HPLC analysis was carried out using Develosil ODS-HG-5 (10 x 250 mm; eluent, 43% CH_3CN; flow rate, 2.5 mL/min; detection at UV 254 nm).

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References and Notes

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6. Although we were unable to obtain satisfactory ^{13}C NMR data for compounds **6** and **7** because of the small quantity of the available samples, the structures of these compounds were securely assigned on the basis of other spectral data and comparison with the data of **1** ~ **5**. Degradation experiments of **2** ~ **7** to elucidate the absolute stereochemistries were not carried out due to the paucity of the samples. We, however, assume that the absolute stereochemistries of **2** ~ **7** were parallel to that of **1** because of the similarity of the spectral and optical data as well as formation of **2** ~ **5** from **1** via photoreaction.
7. All HPLC operations were carried out using well-degassed solvents under light-blocked conditions.
8. General methods are the same as those described in the previous reports.[1,2]

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