Nagelamide J, Novel Dimeric Bromopyrrole Alkaloid from Sponge *Agelas* Species

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Supporting Information

Experimental Section

Figure S1. ^1H NMR spectrum of nagelamide J (**1**) in $\text{DMSO-}d_6$.

Figure S2. ^{13}C NMR spectrum of nagelamide J (**1**) in $\text{DMSO-}d_6$.

Figure S3. $^1\text{H-}^1\text{H}$ COSY spectrum of nagelamide J (**1**) in $\text{DMSO-}d_6$.

Figure S4. TOCSY spectrum of nagelamide J (**1**) in $\text{DMSO-}d_6$.

Figure S7. NOESY spectrum of nagelamide J (**1**) in $\text{DMSO-}d_6$.

Figure S6. HMQC spectrum of nagelamide J (**1**) in $\text{DMSO-}d_6$.

Figure S7. HMBC spectrum of nagelamide J (**1**) in $\text{DMSO-}d_6$.

Experimental Section

General Experimental Procedures. Optical rotation was recorded on a JASCO P-1030 polarimeter. IR and UV spectra were recorded on a Shimadzu UV-1600PC and a JASCO FT/IR-5300 spectrophotometers, respectively. ^1H , ^{13}C and 2D NMR spectra were measured on a JEOL ramuda-400 spectrometer and a Bruker AMX-600 spectrometer using 5 and 2.5 mm micro cells (Shigemi Co., Ltd.) for $\text{DMSO-}d_6$, respectively. Positive mode ESIMS spectra were obtained on a JEOL JMS 700-TZ spectrometer at -80 V as a focus voltage using a sample dissolved in MeOH with flow rate of 200 mL/min.

Sponge Description. The sponge (SS-1077) *Agelas* sp. (order, Agelasida, family Agelasiidae) was collected off Gesashi, Okinawa, and kept frozen until used. SS-1077 was open textured sponge with convoluted surface with numerous superficial depressions and occasional oscules. The sponge was very firm, slightly compressible and springy. Its surface was faintly hispid and the skeleton was a dense reticulation of sparsely cored fibres. Spicules were verticillate spined acanthostyles which sparsely core and echinate the fibres. Verticillate spined acanthostyles were short, thick, squat, and 140 x 18 μm . The voucher specimen was deposited at Graduate School of Pharmaceutical Sciences, Hokkaido University.

Extraction and Isolation. The sponge (0.70 kg, wet weight) was extracted with MeOH (2L x 2), and the extract was partitioned between EtOAc (500 mL x 3) and H_2O (500 mL). Parts (3 g) of the EtOAc soluble materials (6.35 g) were subjected to a Silicagel column ($\text{CHCl}_3/n\text{-BuOH/AcOH/H}_2\text{O}$, 1.5:6:1:1) and then a C_{18} column (Cosmosil 140 C_{18} PREP, Nakarai Tesque Inc.; eluent, $\text{MeOH/H}_2\text{O/CF}_3\text{CO}_2\text{H}$, 80:20:0.1) to give a crude fraction of alkaloids. Part of the crude fraction was purified by C_{18} HPLC [YMC Pack ODS-AM, YMC Co., Inc., 10 x 250 mm; eluent, $\text{CH}_3\text{CN/H}_2\text{O/CF}_3\text{CO}_2\text{H}$, 25:75:0.1 to 33:67:0.1; flow rate, 2.5 mL/min; UV detection at 255 nm] to afford nagelamide J (**1**, 1.9 mg, 0.0011 %, wet weight).

Nagelamide J (1): colorless amorphous solid; $[\alpha]_D^{20}$ -19 (c 0.2, MeOH); UV (MeOH) λ_{max} 216 nm (ϵ 32000) and 279 nm (18000); IR (KBr) ν_{max} 3420, 1680, and 1640 cm^{-1} ; ESIMS (pos.) m/z 805, 807, 809, 811, and 813 [1:4:6:4:1, $(\text{M}+\text{H})^+$]; HRESIMS (pos.) m/z 808.8799 [$(\text{M}+\text{H})^+$, calcd for $\text{C}_{23}\text{H}_{25}\text{N}_{10}\text{O}_3^{79}\text{Br}_2^{81}\text{Br}_2$, 808.8803]

Figure S1. ^1H NMR spectrum of nagelamide J (**1**) in $\text{DMSO}-d_6$.

Figure S2. ^{13}C NMR spectrum of nagelamide J (1) in $\text{DMSO}-d_6$.

Figure S3. ^1H - ^1H COSY NMR spectrum of nagelamide J (**1**) in $\text{DMSO}-d_6$.

Figure S4. TOCSY spectrum of nagelamide J (1) in DMSO- d_6 .

Figure S5. NOESY spectrum of nagelamide J (1) in DMSO- d_6 .

Figure S6. HMQC spectrum of nagelamide J (**1**) in DMSO- d_6 .

Figure S7. HMBC spectrum of nagelamide J (1) in DMSO- d_6 .