Calyciphylline D, a Novel Alkaloid with an Unprecedented Fused-Pentacyclic Skeleton from *Daphniphyllum calycinum*

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Supporting Information

Experimental Section

Figure S1. ¹H NMR spectrum of calyciphylline D (**1**) in CD₃OD.

Figure S2. ¹³C NMR spectrum of calyciphylline D (**1**) in CD₃OD.

Figure S3. ¹H-¹H COSY spectrum of calyciphylline D (**1**) in CD₃OD.

Figure S4. TOCSY spectrum of calyciphylline D (**1**) in CD₃OD.

Figure S5. HMQC spectrum of calyciphylline D (**1**) in CD₃OD.

Figure S6. HMBC spectrum of calyciphylline D (**1**) in CD₃OD.

Figure S7. NOESY spectrum of calyciphylline D (**1**) in CDCl₃.

Experimental Section

General Experimental Procedures. 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 Bruker AMX-600 spectrometer using 2.5 mm micro cells for CD_3OD (Shigemi Co., Ltd.). Positive-mode ESIMS were obtained on a JEOL JMS 700-TZ spectrometer using a sample dissolved in MeOH.

Extraction and Separation. The leaves of *Daphniphyllum calycinum* (1.8 kg) were crushed and extracted with MeOH. The MeOH extract was treated with 3% tartaric acid (pH 2) and then partitioned with EtOAc. The aqueous layer was treated with saturated Na_2CO_3 (aq) to pH 10 and extracted with CHCl_3 to give a crude alkaloidal fraction. The alkaloidal fraction was purified by an amino silica gel column (hexane/AcOEt, 1:0 $\rightarrow$ 4:6, and then CHCl_3 /MeOH, 1:0 $\rightarrow$ 0:1). The fractions eluted with hexane/EtOAc (3:2) was purified repeatedly by silica gel columns (CHCl_3 /MeOH, 1:0 $\rightarrow$ 0:1) to afford calyciphylline D (**1**, 2.5 mg, 0.00013% yield).

Calyciphylline D (1): colorless amorphous solid; $[\alpha]_{\text{D}}^{24} -25.6^\circ$ (c 0.5, MeOH); IR (neat) ν_{max} 1680 cm^{-1} ; ^1H and ^{13}C NMR, see Table 1; ESIMS m/z 456 ($\text{M}+\text{H}$) $^+$; HRESIMS (m/z 456.3452 [$\text{M}+\text{H}$] $^+$; calcd for $\text{C}_{29}\text{H}_{46}\text{NO}_3$, 456.3478).

Figure S1. ^1H NMR spectrum of calyciphylline D (**1**) in CD_3OD .

Figure S2. ^{13}C NMR spectrum of calyciphylline D (**1**) in CD_3OD .

Figure S3. ^1H - ^1H COSY spectrum of calyciphylline D (**1**) in CD_3OD .

Figure S4. TOCSY spectrum of calyciphylline D (**1**) in CD₃OD.

Figure S5. HSQC spectrum of calyciphylline D (**1**) in CD₃OD.

Figure S6. HMBc spectrum of calyciphylline D (**1**) in CD₃OD.

Figure S7. NOESY spectrum of calyciphylline D (**1**) in CDCl_3 .