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Capillosananes S–Z, new sesquiterpenoids from the soft coral *Sinularia capillosa*

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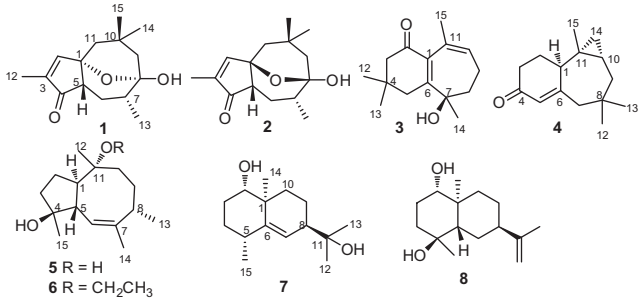
ABSTRACT

Chemical examination of the soft coral *Sinularia capillosa* resulted in the isolation of eight new sesquiterpenoids named capillosananes S–Z (**1**–**8**) and six known sesquiterpenes. The structures of the new compounds were determined on the basis of extensive spectroscopic analysis, including CD effects and Mosher method for the assignment of their absolute configurations. Capillosananes S–U (**1**–**3**) presented as the novel carbon skeletons with bicyclo[3,6,0] and bicyclo[4,5,0] systems, while capillosananane V (**4**) was characteristic of an unprecedented tricyclic skeleton. Capillosananes W–X (**5**–**6**) were assigned to the unusual dumortane-type sesquiterpenes. In addition, the absolute configurations of the stereoisomers of isodaucene-9,14-diol were assigned for the first time.

The soft coral *Sinularia capillosa* has been recognized as a rich source of secondary metabolites with structural novelty and a wide range of structural diversities. For instance, the soft coral *S. capillosa* inhabiting at Dongsha Atoll was reported to contain furanosesquiterpenoids, tetraprenylbenzoquinone,[1] furanobenzosesquiterpenoids,[2] unprecedented bicycle[7.2.0] undecane sesquiterpene,[3] and unprecedented farnesyl quinoid. Furanosesquiterpene derivatives were also isolated from the Australian soft coral *S. capillosa*.[4,5] Cembranoids, the typical metabolites of the genus *Sinularia*, are also found from *S. capillosa*.[6] In our previous work, the chemical examination of *S. capillosa* from the Sanya Bay of South China Sea resulted in the isolation of asteriscane-type sesquiterpenoids.[7] These findings suggested that *S. capillosa* possesses more biogenetic pathways to derive various metabolites for the chemical defense, while geographic environments also induce the structural variation. As part of a continuing search for chemical diversity from soft corals located in South China Sea, the soft coral *S. capillosa* from the Sanya Bay was re-collected. Analysis of the ^{1}H NMR and HPLC/UV spectra of the ethyl estate (EtOAc) extract revealed that the NMR signals and the retention times of HPLC peaks differed from those published previously.[7] Chromatographic separation of the EtOAc extract resulted in the isolation of 14 sesquiterpenoids, of which **1**–**8** were determined as new compounds.



Capillosanane S (**1**)[8] was obtained as a colorless oil. Its HRESIMS data with a pseudomolecular ion peak at *m/z* 273.1462 $[M+Na]^+$ were in accordance with a molecular formula of $C_{15}H_{22}O_3$, requiring five degrees of unsaturation. The IR absorptions at 1655 and 1710 cm^{-1} suggested the presence of olefinic and carbonyl functionalities. The spectrum of the Attached Proton Test (APT) displayed a total of 15 resonances, including four methyl, three methylene, three methine, and five quaternary carbons, while the HSQC spectrum assigned the resonances of all protons and their associated carbons. The NMR data (Tables 1 and 2) of **1** were characteristic of a sesquiterpene, but were incomparable to those reported from the same organism.[7] A methylcyclopentenone ring was established from the resonances for a α,β-unsaturated ketone

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Table 1
^{1}H NMR data for compounds **1**–**8**

No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
1				2.19, dt (3.3,10.7)	1.52, m	1.79, ddd (6.3, 10.8,11.3)		
2	7.13, s	7.11, s		1.91, m	1.62, m	1.59, m	3.10, ddd (3.8,4.9,11.5)	2.99, ddd (4.6,4.8,9.4)
				1.85, m	1.43, m	1.39, m		
3			2.28, d (15.0)	2.36, m	1.51, m	1.52, m	1.72, m	1.46, m
			2.10, d (15.0)	2.34, m	1.45, m	1.46, m	1.49, m	1.42, m
4							1.48, m	1.55, m
							1.40, m	1.40, m
5	2.36, dd (6.6, 12.6)	2.05, d (8.0)	2.63, d (19.3)	5.74, s	2.34, dd (8.9, 10.8)	2.42, dd (8.7, 11.3)	2.38, m	
			2.48, d (19.3)					
6	1.84, ddd (5.6,6.6,12.6)	2.09, dd (5.8,14.8)			5.37, d (8.9)	5.38, d (8.7)		1.19, dd (2.1,13.1)
	1.07, q (12.6)	1.52, m						
7	1.99, m	1.28, m		2.62, d (13.0)			5.52, d (2.5)	2.02, br d (13.4)
				1.93, d (13.0)				1.42, dd(13.1,13.4)
8			2.13, m		2.66, m	2.65, m	1.91, m	2.30, m
			1.75, m					
9	1.59, d (13.6)	1.55, d (13.7)	1.88, m	1.77, dd (4.9,14.5)	1.57, m	1.59, m	1.50, m	1.76, br d (13.9)
	1.40, d (13.6)	1.20, d (13.7)	1.77, m	1.00, dd (7.0,14.5)	1.14, m	1.21, m	1.45, m	1.60, ddd (4.3,5.2,13.9)
10			5.75, t (7.0)	0.77, m	1.56, m	1.53, m	1.57, m	1.53, m
					1.46, m	1.50, m	1.35, m	1.10, dt (3.1, 13.6)
11	1.60, d (13.6)	1.84, d (13.9)						
	1.34, d (13.6)	1.49, d (13.9)						
12	1.70, s	1.71, s	1.02, s	1.03, s	1.07, s	1.09, s	1.02, s	4.88, s; 4.85, s
13	0.83, d (6.9)	0.78, d (6.9)	0.98, s	0.83, s	0.93, d (6.8)	0.95, d (6.8)	1.03, s	1.70, s
14	1.02, s	0.97, s	1.27, s	0.51, dd (4.6,8.0)	1.55, s	1.55, s	0.97, s	0.81, s
				0.25, t (4.6)				
15	1.12, s	1.18 s	1.79, s	0.91, s	1.09, s	1.12, s	1.10, d (6.9)	0.95, s
OH-2							4.47, d (4.9)	4.28, d (4.8)
OH-4					4.26, s	4.29, s		
OH-5								4.00, s
OH-7			4.78, s					
OH-8	5.67, s	5.69, s						
OH-11					3.97, s		4.15, s	
EtO						3.24, q (6.9)		
						0.97, t (6.9)		