# New Casbane Diterpenoids from the Hainan Soft Coral *Sinularia* Species

by **Bin Yang**[a]), **Jingxia Huang**[b]), **Xiuping Lin**[a]), **Shengrong Liao**[a]), **Xuefeng Zhou**[a]), **Juan Liu**[a]), **Junfeng Wang**[a]), **Lishu Wang**[c]), and **Yonghong Liu***[a])

[a]) CAS Key Laboratory of Tropical Marine Bio-resources and Ecology/Guangdong Key Laboratory of Marine Materia Medica/Research Center for Marine Microbes, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, P. R. China (phone/fax: +86-20-89023244; e-mail: yonghongliu@scsio.ac.cn)

[b]) Zhongshan Ophthalmic Center, Sun Yat-Sen University, Guangzhou 510060, P. R. China

[c]) Jilin Provincial Academy of Chinese Medicine Sciences, Changchun 130021, P. R. China

Six new casbane diterpenoids, sinularcasbanes G – L (**1** – **6**, resp.) were isolated from the soft coral *Sinularia* sp. Their structures were established by extensive spectroscopic analyses, especially 2D-NMR and HR-ESI-MS. The configuration was confirmed by CD analyses and by comparison with data reported in the literature. The compounds were evaluated for cytotoxicity against ten human cancer cell lines (H1975, U937, K562, BGC823, MOLT-4, MCF-7, A549, HeLa, HL60, and Huh-7) and showed no activity.

**Introduction.** – *Sinularia* contain a fairly large variety of secondary metabolites, including sesquiterpenoids, diterpenoids, polyhydroxylated steroids, and polyamine compounds, of which diterpenoids that exhibit a range of biological activities are the most commonly encountered ones [1 – 7]. The casbanes are diterpenes derived from the cembranes and differ from the later by the presence of a *gem*-dimethylcyclopropyl moiety instead of an $^{i}$Pr residue fused to the 14-membered ring [8 – 13]. They are considered as the formal parent of several groups of many other diterpenoids, such as jatropholones [14], crotofolanes [15], and tiglianes [16]. In the majority of casbanes described in the literature, the two rings forming the macrocyclic structures are *cis*-fused, whereas very few molecules exhibit a corresponding *trans* junction [11][17 – 19]. During our investigations of biologically active constituents from a *Sinularia* species collected around the Sanya coast, Hainan Province, P. R. China, we have reported 13 cembrane diterpenoids isolated from this coral [2]. Further studies were carried out, which resulted in the isolation of six new casbane diterpenes, named sinularcasbanes G – L (**1** – **6**; *Fig. 1*). All isolated compounds contain a *cis*-fused bicyclic system. In this article, the isolation, the structure elucidation, and cytotoxicity evaluation of these compounds are described.

**Results and Discussion.** – *Isolation and Structure Determination*. The fresh soft corals of *Sinularia* sp. were cut and exhaustively extracted with EtOH. The crude EtOH extracts were partitioned between $CHCl_3$ and $H_2O$. The $CHCl_3$ layer was further partitioned between 85% EtOH and petroleum ether (PE) to yield 85% EtOH and PE fractions. The PE extracts were purified by column chromatography over silica gel,

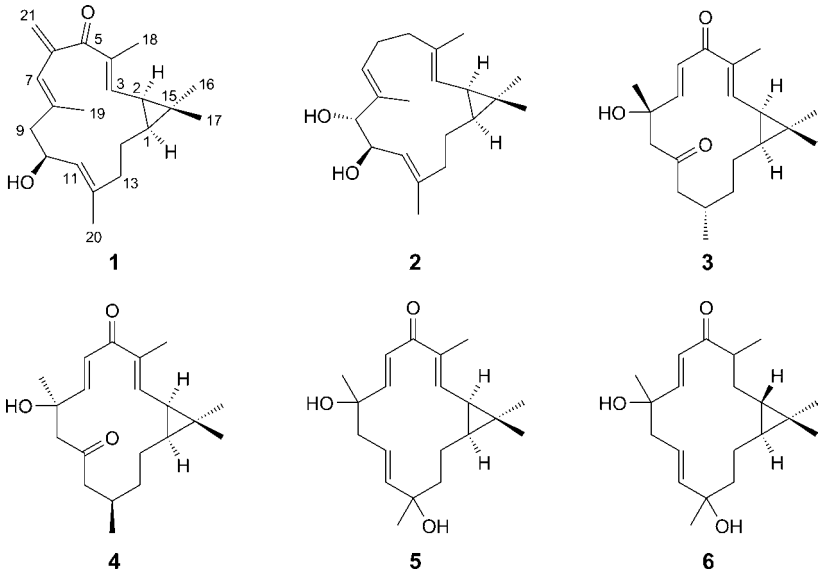


Fig. 1. *Structures of compounds* **1**–**6**

*Sephadex LH-20*, and by RP-HPLC to yield the six new casbane diterpenoids, sinularcasbanes G–L (**1**–**6**).

Compound **1** was isolated as colorless oil. The molecular formula $C_{21}H_{30}O_2$ was deduced by the HR-ESI-MS *pseudo*-molecular-ion peak at *m*/*z* 315.2302 ($[M+H]^+$) and implied seven degrees of unsaturation. The $^1$H-NMR spectrum of **1** contained Me *singlet*s at $\delta$(H) 0.87, 1.17, 1.50, 1.71, and 1.90, which were assigned to two tertiary and three vinyl Me groups (*Table 1*). Three trisubstituted C=C bonds, and one 1,1-disubstituted C=C bond were evident by eight C=C signals in the $^{13}$C-NMR spectrum (*Table 2*) at $\delta$(C) 119.0 (C(21)), 126.8 (C(7)), 128.7 (C(11)), 135.9 (C(4)), 136.2 (C(8)), 140.9 (C(12)), 145.9 (C(3)), and 148.1 (C(6)) and by four olefinic signals in the $^1$H-NMR spectrum at $\delta$(H) 5.07 (*d*, *J* = 9.5, H–C(11)), 5.16 (*s*, $CH_2$(21)), 5.92 (*s*, H–C(7)), and 6.29 (*d*, *J* = 10.5, H–C(3)). The NMR spectra also showed a signal for an C=O group ($\delta$(C) 200.7 (C(5))), and a CH group ($\delta$(H) 4.48–4.53 (*m*, H–C(10), $\delta$(C) 66.4 (C(10))). The signals at $\delta$(C) 28.9 (C(2)), 34.8 (C(1)), 26.2 (C(15)), 15.8 (C(17)), and 29.2 (C(16)) in the $^{13}$C-NMR spectrum (*Table 2*) together with the signals at $\delta$(H) 1.02–1.14 and 0.99–1.02 in the $^1$H-NMR spectrum indicated the presence of a cyclopropyl ring bearing geminal Me groups, which were typical signals for the casbane-type diterpenoid containing a 14-membered macrocyclic ring. Key HMBCs Me(18)/C(3,4,5); $CH_2$(21)/C(5,6,7); Me(19)/C(7,8,9); H–C(9)/C(10); Me(20)/C(11,12,13) permitted the connection of the C-atom skeleton (*Fig. 2*).

The (*E*) geometries of the three C=C bonds C(3)=C(4), C(7)=C(8), and C(11)=C(12) were deduced by the $\delta$(C) values of Me(18), Me(19), and Me(20) (< 20 ppm; *Table 2*) [11]. The junction of the two rings at C(1) and C(2) was suggested to be *cis* on the basis of $^{13}$C-NMR chemical shifts of the geminal Me(16) and Me(17) ($\delta$(C) 29.2 and 15.8, resp.), consistent with the literature concerning *cis*-fused casbane

Table 1. *$^1$H-NMR* (500 MHz; in $CDCl_3$) *Data of Compounds* **1**–**6**. $\delta$ in ppm and $J$ in Hz.

| Position | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| 1 | 0.99–1.02 (*m*) | 0.64 (*t*, *J* = 9.0) | 0.90–0.97 (*m*) | 0.97–1.02 (*m*) | 1.00–1.03 (*m*) | −0.01 – −0.08 (*m*) |
| 2 | 1.02–1.14 (*m*) | 1.16 (*t*, *J* = 8.0) | 1.30–1.39 (*m*) | 1.20–1.22 (*m*) | 1.43–1.48 (*m*) | −0.01 – −0.08 (*m*) |
| 3 | 6.29 (*d*, *J* = 10.5) | 4.82 (*d*, *J* = 7.5) | 6.04 (*d*, *J* = 10.0) | 5.96 (*d*, *J* = 8.5) | 6.34 (*d*, *J* = 10.0) | 1.99–2.03 (*m*, $H_a$), 1.12–1.13 (*m*, $H_b$) |
| 4 | | | | | | 2.94–2.97 (*m*) |
| 5 | | 2.21–2.23 (*m*, $H_a$), 2.04–2.07 (*m*, $H_b$) | | | | |
| 6 | | 2.17–2.21 (*m*) | 6.20 (*d*, *J* = 16.0) | 6.21 (*d*, *J* = 16.5) | 6.25 (*d*, *J* = 16.5) | 6.28 (*d*, *J* = 16.0) |
| 7 | 5.92 (*s*) | 5.14 (*d*, *J* = 4.5) | 6.57 (*d*, *J* = 16.0) | 6.44 (*d*, *J* = 16.5) | 6.43 (*d*, *J* = 16.5) | 6.82 (*d*, *J* = 16.0) |
| 9 | 2.49–2.52 (*m*, $H_a$), 2.11–2.13 (*m*, $H_b$) | 3.77 (*d*, *J* = 9.5) | 2.82 (*d*, *J* = 17.0, $H_a$), 2.68 (*d*, *J* = 17.0, $H_b$) | 2.98 (*d*, *J* = 18.5, $H_a$), 2.64 (*d*, *J* = 18.5, $H_b$) | 2.40 (*d*, *J* = 6.5) | 2.37–2.48 (*m*) |
| 10 | 4.48–4.53 (*m*) | 4.34 (*t*, *J* = 9.5) | | | 5.50–5.56 (*m*) | 5.55 (*s*) |
| 11 | 5.07 (*d*, *J* = 9.5) | 4.94 (*d*, *J* = 9.5) | 2.32–2.34 (*m*) | 2.10–2.12 (*m*) | 5.66 (*d*, *J* = 16.0) | 5.55 (*s*) |
| 12 | | | 1.93–1.98 (*m*) | 1.78–1.83 (*m*) | | |
| 13 | 2.41–2.45 (*m*, $H_a$), 1.87–1.90 (*m*, $H_b$) | 2.04–2.10 (*m*, $H_a$), 1.74–1.79 (*m*, $H_b$) | 1.20–1.24 (*m*, $H_a$), 0.90–0.97 (*m*, $H_b$) | 1.22–1.25 (*m*) | 1.71–1.76 (*m*, $H_a$), 1.33–1.37 (*m*, $H_b$) | 1.61–1.71 (*m*, $H_a$), 1.36–1.41 (*m*, $H_b$) |
| 14 | 2.00–2.03 (*m*, $H_a$), 1.14–1.18 (*m*, $H_b$) | 1.58–1.60 (*m*, $H_a$), 0.99–1.06 (*m*, $H_b$) | 1.73–1.76 (*m*, $H_a$), 1.30–1.31 (*m*, $H_b$) | 1.69–1.71 (*m*, $H_a$), 1.32–1.34 (*m*, $H_b$) | 1.14–1.19 (*m*) | 1.12–1.14 (*m*) |
| 16 | 1.17 (*s*) | 1.06 (*s*) | 1.16 (*s*) | 1.16 (*s*) | 1.17 (*s*) | 0.99 (*s*) |
| 17 | 0.87 (*s*) | 0.95 (*s*) | 1.00 (*s*) | 0.90 (*s*) | 0.99 (*s*) | 0.97 (*s*) |
| 18 | 1.90 (*s*) | 1.60 (*s*) | 1.87 (*s*) | 1.88 (*s*) | 1.90 (*s*) | 1.10 (*d*, *J* = 7.0) |
| 19 | 1.50 (*s*) | 1.58 (*s*) | 1.28 (*s*) | 1.34 (*s*) | 1.39 (*s*) | 1.45 (*s*) |
| 20 | 1.71 (*s*) | 1.66 (*s*) | 0.99 (*d*, *J* = 7.0) | 1.08 (*d*, *J* = 7.0) | 1.33 (*s*) | 1.18 (*s*) |
| 21 | 5.16 (*s*) | | | | | |

Table 2. *$^{13}$C-NMR* (125 MHz; in $CDCl_3$) *Data of Compounds* **1**–**6**

| Position | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| 1 | 34.8 | 30.2 | 33.1 | 31.4 | 32.6 | 31.3 |
| 2 | 28.9 | 25.6 | 27.8 | 27.0 | 27.0 | 28.5 |
| 3 | 145.9 | 121.1 | 144.5 | 142.6 | 144.1 | 33.0 |
| 4 | 135.9 | 136.5 | 137.7 | 139.1 | 137.8 | 43.2 |
| 5 | 200.7 | 25.0 | 197.5 | 197.5 | 195.9 | 204.4 |
| 6 | 148.1 | 39.0 | 128.8 | 127.2 | 127.3 | 126.9 |
| 7 | 126.8 | 130.5 | 148.4 | 147.2 | 148.1 | 150.6 |
| 8 | 136.2 | 133.5 | 72.0 | 71.3 | 73.5 | 73.3 |
| 9 | 50.1 | 82.2 | 53.3 | 50.8 | 46.5 | 46.3 |
| 10 | 66.4 | 69.9 | 213.2 | 213.0 | 122.5 | 122.6 |
| 11 | 128.7 | 122.3 | 52.4 | 50.8 | 141.2 | 140.3 |
| 12 | 140.9 | 142.0 | 30.1 | 32.5 | 72.7 | 73.6 |
| 13 | 40.4 | 39.1 | 37.3 | 34.2 | 42.0 | 43.4 |
| 14 | 26.5 | 23.1 | 25.0 | 24.0 | 18.8 | 25.5 |
| 15 | 26.2 | 19.7 | 26.2 | 25.2 | 25.7 | 21.8 |
| 16 | 29.2 | 28.8 | 29.3 | 29.1 | 29.1 | 21.6 |
| 17 | 15.8 | 15.7 | 16.3 | 16.3 | 16.0 | 20.2 |
| 18 | 11.0 | 16.2 | 12.0 | 12.5 | 12.0 | 17.0 |
| 19 | 18.3 | 11.8 | 28.5 | 26.1 | 28.9 | 27.2 |
| 20 | 18.6 | 19.0 | 22.0 | 20.9 | 30.5 | 27.1 |
| 21 | 119.0 | | | | | |

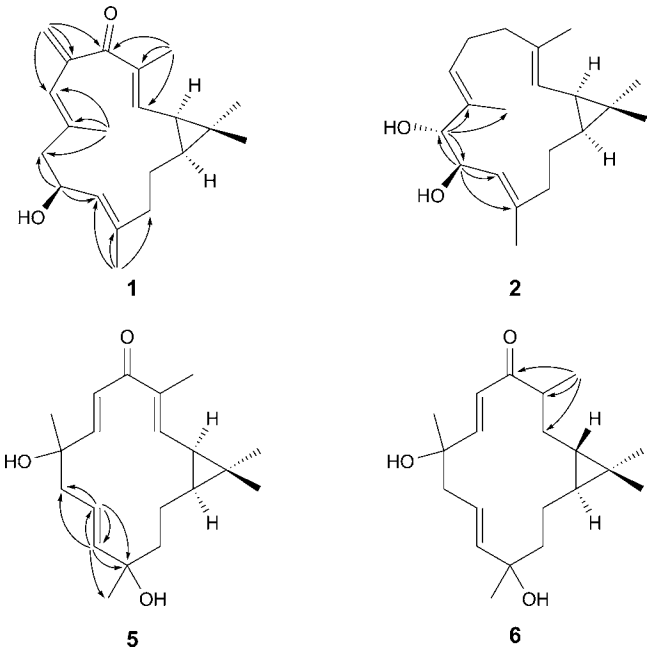


Fig. 2. *Key HMBCs* (H → C) *of compounds* **1**, **2**, **5**, *and* **6**

diterpenes [11]. On biogenetic considerations, the relative configuration of C(10) in **1** was assumed as in [12].

Compound **2** was isolated as colorless oil. The molecular formula $C_{20}H_{32}O_2$ was deduced by the HR-ESI-MS *pseudo*-molecular-ion peak at *m*/*z* 327.2262 ($[M+Na]^+$) and implied five degrees of unsaturation. The $^1$H- and $^{13}$C-NMR spectra of **2** were similar to those of casbene [8], expect for the presence of two additional HO–CH groups at $\delta$(H) 3.77 (*d*, *J* = 9.5, H–C(9)) and 4.34 (*t*, *J* = 9.5, H–C(10)) (*Table 1*). This assumption was confirmed by both the $^1$H,$^1$H-COSY correlation of H–C(9)/H–C(10)/H–C(11) and the HMBCs of H–C(9)/C(8,19,10) and H–C(10)/C(9,11,12) (*Fig. 2*). The (*E*) geometries of the three C=C bonds C(3)=C(4), C(7)=C(8), and C(11)=C(12) were deduced by NMR data. The junction of the two rings at C(1) and C(2) was suggested to be *cis* on the basis of $^{13}$C-NMR chemical shifts of the geminal Me(16) and Me(17) (*Table 2*). According to the coupling constant, H–C(9) and H–C(10) were then deduced to have a *trans* relative configuration [20].

Compound **3** was isolated as colorless oil. The molecular formula $C_{20}H_{30}O_3$ was deduced by the HR-ESI-MS *pseudo*-molecular-ion peak at *m*/*z* 341.2086 ($[M+Na]^+$) and implied six degrees of unsaturation. The $^1$H- and $^{13}$C-NMR spectral data of **3** showed close similarity to those of microclavatin [21], except for the disappearance of the 8,9-epoxy ring of the known analog. The geometries of the C(3)=C(4) and C(6)=C(7) bonds were suggested to be (*E*) by the coupling constant values. The configuration of the *cis* ring junction was assumed to be (1*S*,2*S*), in analogy to that of **1**. By biogenetic considerations, the same relative configuration at C(12) in **3** was assumed as described in [11].

Compound **4** was isolated as colorless oil. The molecular formula $C_{20}H_{30}O_3$ was deduced by the HR-ESI-MS *pseudo*-molecular-ion peak at *m*/*z* 341.2078 ($[M+Na]^+$) and implied six degrees of unsaturation. Comparison of **4** with **3** revealed that they had not only the same molecular formula but also very similar spectral data. The $^1$H- and $^{13}$C-NMR spectroscopic data of **4** were very similar to those of **3** except for the up-field shifts of C(8), C(9), C(11), C(13), C(19), and C(20) (*Table 2*). Due to the similarity of the CD curves of **4** with **3**, the absolute configuration of **4** was defined as (1*S*,2*S*). Based on the observed up-field shifts the relative configurations of C(8) and C(12) in **4** were determined to be inversed compared to **3**.

Compound **5** was isolated as colorless oil. The molecular formula $C_{20}H_{30}O_3$ was deduced by the HR-ESI-MS *pseudo*-molecular-ion peak at *m*/*z* 341.2109 ($[M+Na]^+$) and implied six degrees of unsaturation. The spectroscopic data of **5** revealed structural similarity to **3**. The presence of an additional C=C bond suggested by both the $^1$H-NMR signals at $\delta$(H) 5.50–5.56 (*m*, H–C(10)) and 5.66 (*d*, *J* = 16.0, H–C(11)) and the corresponding $^{13}$C-NMR signals at $\delta$(C) 122.5 and 141.2. The assignments were supported by the HMBCs H–C(10)/C(9,11,12) and H–C(12)/C(9,10,12,20) (*Fig. 2*). The $^{13}$C-NMR spectrum of **5** also contained a signal at $\delta$(C) 72.7 (C(12)) attributable to an O-bearing C-atom, thus indicating the presence of a second OH group located at C(12). The geometries of C(3)=C(4), C(6)=C(7), and C(10)=C(11) were suggested to be (*E*) based on the NMR data, whereas the configurations at C(8) and C(12) were not determined.

Compound **6** was isolated as colorless oil. The molecular formula $C_{20}H_{32}O_3$ was deduced by the HR-ESI-MS *pseudo*-molecular-ion peak at *m*/*z* 343.2241 ($[M+Na]^+$)

and implied five degrees of unsaturation. The $^1$H- and $^{13}$C-NMR data of **6**, fully assigned through 2D-NMR experiments, closely resembled those of **5**. One difference was the absence of signals for a trisubstituted C=C bond. This conclusion was confirmed by the HMBCs Me(18)/C(3,4,5) (*Fig. 2*). Another difference was found in the $^{13}$C-NMR values of C(16) ($\delta$(C) 21.6) and C(17) ($\delta$(C) 20.2) that were significantly shifted in comparison with those of **5** (C(16) ($\delta$(C) 29.1) and C(17) ($\delta$(C) 16.0)), suggesting that **6** had a different ring junction at C(1) and C(2) (*Table 2*). The CD curve of **6** was identical with that of 2-*epi*-10-oxo-11,12-dihydrodepressin [11], suggesting the same (1*S*,2*R*) absolute configuration at the junction asymmetric centers.

*Cytotoxic Activity.* Compounds **1**–**6** were tested for their cytotoxicity against ten human tumor cell lines (H1975, U937, K562, BGC823, MOLT-4, MCF-7, A549, HeLa, HL60, and Huh-7) by the MTT (= 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2*H*-tetrazolium bromide) method [22]. However, they showed no cytotoxic activity against all cell lines at 50 μM.

## Experimental Part

*General.* TLC: Silica gel $GF_{254}$ (0.4–0.5 mm; *Qingdao Marine Chemical Factory*, Qingdao, P. R. China). Column chromatography (CC): silica gel ($SiO_2$, 100–200, 200–300 mesh; *Qingdao Marine Chemical Factory*, Qingdao, P. R. China), *Sephadex LH-20* (40–70 μm, *Amersham Pharmacia Biotech AB*, Uppsala, Sweden), and *YMC Gel ODS-A* (12 nm, S-50 μm; *YMC*, MA, USA). HPLC: *Shimadzu LC-10ATvp* with *YMC* ODS series (*YMC-Pack ODS-A*, 250 × 10 mm i.d., S-5 μm, 12 nm). CD Spectra: *Chirascan* circular dichroism spectrometer (*Applied Photophysics*). NMR Spectra: *Bruker AC 500 NMR* spectrometer; $\delta$ in ppm rel. to $Me_4Si$ as internal standard, *J* in Hz. HR-ESI-MS: *AQUITY UPLC/Q-TOF* mass spectrometer; in *m*/*z*.

*Animal Material.* The soft coral *Sinularia* sp. was collected from Dongluo Island, Hainan Province of China in March 2010 (7–10 m depth) and identified by Prof. *Hui Huang*, South China Sea Institute of Oceanology, Chinese Academy of Sciences. A voucher specimen (No. M100301) was deposited with the CAS Key Laboratory of Tropical Marine Bio-resources and Ecology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou, P. R. China.

*Extraction and Isolation.* The soft coral *Sinularia* sp. (7 kg) was extracted three times with 95% EtOH. The extract was concentrated under reduced pressure, and partitioned between $H_2O$ (4 l) and $CHCl_3$ (4 l); the $CHCl_3$ layer (101 g) was further partitioned between 85% EtOH (4 l) and petroleum ether (PE; 4 l) to yield 85% EtOH (30 g) and PE (55.3 g) fractions. The PE extract was subjected to $SiO_2$ CC, using a gradient of AcOEt in PE, to give 13 fractions (*Frs.* $X_1$ – $X_{13}$). *Fr.* $X_8$ (2.7 g) was subjected to $SiO_2$ CC, using a gradient of AcOEt in PE, to give seven fractions (*Frs.* $X_{8\text{-}1}$–$X_{8\text{-}7}$). *Fr.* $X_{8\text{-}4}$ (430 mg) was further purified on a *Sephadex LH-20* column to give three subfractions (*Frs.* $X_{8\text{-}4\text{-}1}$–$X_{8\text{-}4\text{-}6}$). *Fr.* $X_{8\text{-}4\text{-}2}$ was purified by RP HPLC (66.5% MeOH in $H_2O$) to afford **1** (7.5 mg). *Fr.* $X_{8\text{-}4\text{-}3}$ was purified by RP HPLC (67% MeOH in $H_2O$) to afford **3** (7.5 mg) and **4** (6.6 mg). *Fr.* $X_{8\text{–}7}$ was purified by RP-HPLC (73% MeOH in $H_2O$) to afford **2** (2.5 mg). *Fr.* $X_{11}$ (1.5 g) was subjected to $SiO_2$ CC, using a gradient of AcOEt in PE, to give six fractions (*Frs.* $X_{11\text{-}1}$–$X_{11\text{-}6}$). *Fr.* $X_{11\text{-}4}$ (532 mg) was further purified on a *Sephadex LH-20* column to give four subfractions (*Frs.* $X_{11\text{-}4\text{-}1}$–$X_{11\text{-}4\text{-}4}$). *Fr.* $X_{11\text{-}4\text{-}2}$ was purified by RP-HPLC (65% MeOH in $H_2O$) to afford **5** (3.5 mg) and **6** (3.1 mg).

*Sinularcasbane G* (= *(1*R*,2*E*,6*E*,9*S*,10*E*,14*S*)-9-Hydroxy-3,7,11,15,15-pentamethyl-5-methylidene-bicyclo[12.1.0]pentadeca-2,6,10-trien-4-one*; **1**). Colorless oil. CD ($c$ = 0.2, EtOH): $\Delta\varepsilon_{203}$ +8.7, $\Delta\varepsilon_{231}$ −2.0. $^1$H- and $^{13}$C-NMR: *Tables 1* and *2*, resp. HR-ESI-MS: 315.2302 ($[M+H]^+$, $C_{21}H_{31}O_2^+$; calc 315.2319).

*Sinularcasbane H* (= *(1*S*,4*E*,6*R*,7*R*,8*E*,12*E*,14*R*)-4,8,12,15,15-Pentamethylbicyclo[12.1.0]pentadeca-4,8,12-triene-6,7-diol*; **2**). Colorless oil. CD ($c$ = 0.2, EtOH): $\Delta\varepsilon_{212}$ −48. $^1$H- and $^{13}$C-NMR: *Tables 1* and *2*, resp. HR-ESI-MS: 327.2262 ($[M+Na]^+$, $C_{20}H_{32}NaO_2^+$; calc. 327.2300).

*Sinularcasbane I* (=*(1*R,*2*E,*5*E,*7*S,*11*S,*14*S*)-7-Hydroxy-3,7,11,15,15-pentamethylbicyclo[12.1.0]pentadeca-2,5-diene-4,9-dione*; **3**). Colorless oil. CD ($c = 0.2$, EtOH): $\Delta\varepsilon_{210}$ +8, $\Delta\varepsilon_{229}$ −6.9, $\Delta\varepsilon_{276}$ +10.5. $^1$H- and $^{13}$C-NMR: *Tables 1* and *2*, resp. HR-ESI-MS: 341.2086 ($[M+Na]^+$, $C_{20}H_{30}NaO_3^+$; calc. 341.2093).

*Sinularcasbane J* (=*(1*R,*2*E,*5*E,*7*R,*11*R,*14*S*)-7-Hydroxy-3,7,11,15,15-pentamethylbicyclo[12.1.0]pentadeca-2,5-diene-4,9-dione*; **4**). Colorless oil. CD ($c = 0.2$, EtOH): $\Delta\varepsilon_{210}$ +6, $\Delta\varepsilon_{230}$ −1.6, $\Delta\varepsilon_{279}$ +5. $^1$H- and $^{13}$C-NMR: *Tables 1* and *2*, resp. HR-ESI-MS: 341.2078 ($[M+Na]^+$, $C_{20}H_{30}NaO_3^+$; calc. 341.2093).

*Sinularcasbane K* (=*(1*R,*2*E,*5*E,*9*E,*14*S*)-7,11-Dihydroxy-3,7,11,15,15-pentamethylbicyclo[12.1.0]pentadeca-2,5,9-trien-4-one*; **5**). Colorless oil. CD ($c = 0.2$, EtOH): $\Delta\varepsilon_{274}$ −10, $\Delta\varepsilon_{228}$ −12, $\Delta\varepsilon_{210}$ +10. $^1$H- and $^{13}$C-NMR: *Tables 1* and *2*, resp. HR-ESI-MS: 341.2109 ($[M+Na]^+$, $C_{20}H_{30}NaO_3^+$; calc. 341.2093).

*Sinularcasbane L* (=*(1*S,*5*E,*9*E,*14*S*)-7,11-Dihydroxy-3,7,11,15,15-pentamethylbicyclo[12.1.0]pentadeca-5,9-dien-4-one*; **6**). Colorless oil. CD ($c = 0.2$, EtOH): $\Delta\varepsilon_{203}$ +10.5, $\Delta\varepsilon_{236}$ +8.5. $^1$H- and $^{13}$C-NMR: *Tables 1* and *2*, resp. HR-ESI-MS: 343.2241 ($[M+Na]^+$, $C_{20}H_{32}NaO_3^+$; calc. 343.2249).

*Cytotoxicity.* Determination of cytotoxicity was done according to the procedure described in the literature [22].

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