Juncins I−M, Five New Briarane Diterpenoids from the Indian Ocean Gorgonian *Junceella juncea* Pallas

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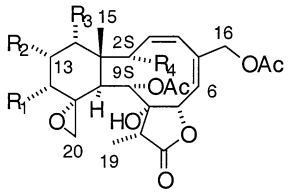
Five new diterpenoids, juncins I−M (**1**−**5**), of the briarane skeleton have been isolated from the Indian Ocean gorgonian *Junceella juncea* in addition to four known derivatives, gemmacolides A−C (**6**−**8**) and juncin H (**9**). The structures of **1**−**5** were established by the interpretation of spectroscopic data.

The gorgonian species of the genus *Junceella*[1−9] (Gorgonaceae) are a rich source of several closely related briarane diterpenoids having a 10-membered carbocyclic system. Six new briarane diterpenoids, juncins A−F, were reported from *Junceella juncea* collected from the Gulf of Eilat and Gulf of Suez in the Red Sea.[2] Working with samples of this species collected from the Gulf of Mannar in the Indian Ocean (Mandapam coast), we have recently reported the isolation of two new briarane diterpenoids, juncins G and H, in addition to the known gemmacolides A and B and three polyhydroxy sterols.[7] We now report five new briarane diterpenoids [juncins I−M (**1**−**5**)] in addition to four known derivatives [gemmacolides A−C (**6**−**8**)[3] and juncin H] from the ethyl acetate solubles of the initial methanolic extract of the same species collected from the Tuticorin coast of the Indian Ocean.

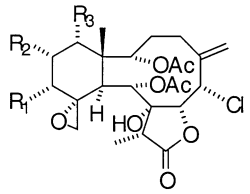
Results and Discussion

Juncin I (**1**), $C_{35}H_{46}O_{16}$ (HRESIMS, 745.2675 $[M + Na]^+$), juncin J (**2**), $C_{38}H_{52}O_{16}$ (HRESIMS, 787.3172 $[M + Na]^+$), and juncin K (**3**), $C_{36}H_{50}O_{14}$ (HRESIMS, 729.3105 $[M + Na]^+$) were recognized as closely related new briarane diterpenoids by a study of their physical and spectral characteristics. All three were found to be nonhalogenated but with common functionalities in the 10-membered carbocyclic ring and the attached γ-lactone. Two secondary acetates located at C-2 and C-9, a tertiary hydroxyl at C-8, an acetoxymethyl at C-5, and a conjugated 3,5-diene system were present in all three compounds. They also each possessed an exocyclic C-11/C-20 epoxy system in the cyclohexyl part of the ring system, and they only differed in the number and location of isovalerate and acetate groups at the remaining carbons: C-12, C-13, or C-14.

The structure of juncin I (**1**) differed from that of gemmacolide F (**10**)[3] only by the presence of an isovalerate rather than an acetate ester at C-13 and acetylation of the 2-hydroxyl group. The assignment of the isovalerate ester at C-13 was based on HMBC correlations to the isovalerate carbonyl carbon [δ 171.6 (s)] from H-13 (δ 5.07), H_2-2′ (δ 2.02), and H-3′ (δ 1.92), and $^1H-^1H$ COSY correlations between H-12, H-13, and H-14. In the presence of consecutive esters at C-12, C-13, and C-14, the signal for the middle carbon (C-13) resonates around δ 66.0, while signals for



1 $R_1 = R_3 = R_4 = OAc$, $R_2 = OCOCH_2CH(CH_3)_2$
2 $R_1 = R_2 = OCOCH_2CH(CH_3)_2$, $R_3 = R_4 = OAc$
3 $R_1 = R_3 = OCOCH_2CH(CH_3)_2$, $R_2 = H$, $R_4 = OAc$
10 $R_1 = R_2 = R_3 = OAc$, $R_4 = OH$



4 $R_1 = R_2 = OCOCH_2CH(CH_3)_2$, $R_3 = OAc$
5 $R_1 = R_3 = OCOCH_2CH(CH_3)_2$, $R_2 = H$
6 $R_1 = R_2 = R_3 = OAc$
7 $R_1 = R_3 = OAc$, $R_2 = OCOCH_2CH(CH_3)_2$
8 $R_1 = R_3 = OAc$, $R_2 = H$
9 $R_1 = OAc$, $R_2 = H$, $R_3 = OCOCH_2CH(CH_3)_2$

C-12 and C-14 come around δ 73.0 and 74.0 as in juncin E.[2] The presence of acetate esters at C-2 and C-9 was supported by comparison of chemical shifts for the methine protons (δ 5.56 and 4.72) with those of related compounds.[3]

While the proton assignments for gemmacolide F (**10**)[3] and juncin I (**1**) agreed, discrepancies were noticed in the ^{13}C NMR assignments. On the basis of HMQC and HMBC data the carbons C-2, C-7, C-8, C-9, C-10, and C-17 in juncin I (**1**) were assigned the values δ 74.0 (d), 78.6 (d), 80.9 (s), 63.6 (d), 32.5 (d), and 43.9 (d), respectively, while the same carbons in gemmacolide F (**6**) were assigned the values δ 64.1 (d), 73.5 (d), 81.5 (s), 78.8 (d), 44.4 (d), and 32.8 (d), respectively. While the ^{13}C values for both compounds remain the same, their assignments differ, in particular, the values of carbons C-7 and C-17, which appeared interchanged, and so also the values of C-2, C-7, and C-9. [Our assignment is based on HMQC and HMBC data, in particular, the following HMBC correlations: δ 32.5 (C-10) with H-9,-12,-14,-15; δ 43.9 (C-17) with H-9,-18; δ 63.6 (d) (C-9) with H-10.] The assigned chemical shift

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values in juncin I (**1**), in fact, agree closely with those of briaranes C−L.[10] The other HMBC correlations observed were in full agreement with the structure and the location of the functional groups.

The NOESY correlations observed between H-10 and both H-9 and H-2 suggested a *cis* relationship between these three protons. The *cis* orientation of H_3-15 and the epoxide carbon as well as the *cis* relationship of H-12, H-13, and H-14 was established by observation of the following NOESY correlations: H-15 with H-14, H-13, and H-20; H-20 with H-12, H-13, and H-15. A 1.5 Hz *W*-coupling between H-12 and H-14 also indicated a 1,3-*cis* diequatorial arrangement of these protons. The NOESY correlation observed between H-7 and H-17 revealed the stereochemistry between the 10-membered and γ-lactone rings. The structure and stereochemistry of juncin I (**1**) were thus established as shown in **1**.

The ^{1}H and ^{13}C NMR spectral data of juncin J (**2**) suggested that it has a structure identical with respect to the 10-membered carbocylic and fused γ-lactone ring systems as found in juncin I (**1**). For example, **2** has secondary acetates at C-2 and C-9, a primary acetate at C-5, and a conjugated 3,5-diene, but it differs from **1** in the cyclohexane part in having two isovalerate groups and one acetate instead of one isovalerate and two acetate groups as found in juncin I (**1**). Of the five signals attributable to protons geminal to secondary ester groups (δ 5.54, 4.72, 4.90, 5.09, 5.20), the first two were assigned to H-2 and H-9 as in juncin I (**1**). The proton signals at δ 4.90 and 5.09 showed HMBC correlations with overlapped isovalerate carbonyl carbon resonances at δ 171.7 (s), while the proton resonance at δ 5.20 showed HMBC correlation with the ester carbonyl at δ 170.3 (s). The two isovalerate and one acetate groups have to be located at C-12, C-13, and C-14. In the spectrum of juncin I (**1**) the carbon signals at δ 73.6 and 73.1 were assigned to C-14 and C-12, both of which bear acetates, and the signal at δ 66.3 was assigned to C-13, which bears an isovalerate. In comparison, the oxygenated carbon signals at δ 73.6 and 66.2 in juncin J (**2**) could be assigned, respectively, to C-14 bearing an acetate and C-13 carrying an isovalerate group, leaving the second isovalerate group located at C-12. Replacement of the C-12 acetate group of juncin I (**1**) by an isovalerate resulted in an upfield shift of 0.4 ppm for the C-12 signal in the ^{13}CNMR spectrum of juncin J (**2**). The following important NOESY correlations were observed in the spectrum of juncin J (**2**): H-10/H-2, H-9; H-9/H_3-19; H_3-15/H-14, H-13; H-12/H-20. These data confirmed that the corresponding chiral centers in **2** have the same stereochemistry as in juncin I (**1**).

The ^{1}H and ^{13}C NMR spectral data of juncin K (**3**) indicated the presence of a structure identical with respect to the 10-membered carbocyclic and fused γ-lactone systems as found in juncin I (**1**) and juncin J (**2**), but differing with respect to the functional groups attached to the cyclohexane ring. Two isovalerate groups were found to be present along with an unsubstituted methylene group at C-12, C-13, or C-14, unlike in juncins I (**1**) and J (**2**), where all these three carbons were substituted with the ester groups. Since the carbon-13 signals for all the ring carbons in **1**−**3** are nearly identical except for that of C-13 (δ 28.9 vs ~66.2), the unsubstituted methylene unit in **3** was assigned to C-13, and this was consistent with the H−H COSY correlations observed [H-12 and H-14 are each coupled with H-13,-13′ but not with each other]. In view of the minute quantity of juncin K (**3**) available, all the HMBC correlations could not be observed in the spectrum, but the correlations that were observed were in full support of the structure. In view of the similarity between **3** and **1** in terms of NMR chemical shifts and coupling constants, **3** was assigned the same stereochemistry as **1** at all common chiral centers.

Juncin L (**4**), $C_{36}H_{51}O_{14}Cl$ (HRESIMS, 765.2859 [M + Na]$^+$), and juncin M (**5**), $C_{34}H_{49}O_{12}Cl$ (HRESIMS, 707.3004 [M + Na]$^+$), were recognized as new 6-chlorobriarane diterpenoids closely related to the 6-chlorobriaranoids gemmacolides A−C (**6**−**8**) and juncin H (**9**) from their ^{1}H and ^{13}C NMR spectral data. Both **4** and **5** have identical substituents: a halogen at C-6, exococyclic methylene at C-5, a tertiary hydroxyl at C-8, and two secondary acetates at C-2 and C-9 as found in the chlorobriaranoids mentioned above. They also have the C-11−C-20 exocyclic epoxy group in common. While juncin L (**4**) showed the presence of two isovalerate groups and one secondary acetate in the cyclohexane ring, juncin M (**5**) showed only two isovalerate groups, but no acetate functionality. The ^{1}H and ^{13}C assignments of juncins L (**4**) and M (**5**) were made in comparison with the values of gemmacolides A−C and juncin H.

Two isovalerate groups and one acetate group have to be located in juncin L (**4**) at the available positions C-12, C-13, and C-14. Although the location of an isovalerate or an acetate group at one of these carbons is difficult to determine in view of the close carbon chemical shifts of the respective oxygenated carbons, the ^{1}H chemical shifts of the respective methine protons H-12, H-13, and H-14 can be distinguished by their coupling constants and assigned to the specific carbons. For example, in these compounds, H-13 appears as a triplet, while H-12 and H-14 appear as dd's with vicinal and small *W*-coupling. Besides, the chemical shift of H-12 appears at higher field when compared to the values of H-13 and H-14. Considering the coupling constants of the methine protons deshielded by the ester groups, the values at 4.88 dd (J = 3.0, 1.0 Hz), 5.25 t (J = 3.0 Hz), and 5.22 dd (J = 3.0, 1.0 Hz) could be assigned respectively to H-12, H-13, and H-14. From the HMBC correlations noticed between the isovalerate carbonyl carbon at δ 171.4 (s) and the proton at δ 4.88, one isovalerate group could be located at C-12. It has been noticed that the carbon substituted with an isovalerate group appears at slightly higher field ($\cong\delta$ 0.3−0.5) when compared to the same carbon bearing an acetate group as noticed in gemmacolide B (C-13, δ 66.5) with an isovalerate group and gemmacolide A (C-13, δ 66.8) with an acetate group.[3] The value at δ 66.3 in juncin L (**4**) suggested the presence of a second isovalerate group at C-13 and consequently the acetate at C-14. This is also consistent with the chemical shift C-14, δ 72.9 vs 73.0 for C-14 in gemmacolide B. The various HMBC correlations observed fully supported the location of the functional groups, and hence juncin L was assigned the structure **4** with relative stereochemistry the same as in briaranes **1**−**3** because for the centers that **4** has in common with gemmacolide B, the proton and carbon chemical shifts and proton coupling constants match well. In view of the small quantity of the compound available, NOESY information could not be obtained.

In contrast to juncin L (**4**), juncin M (**5**) possessed only two isovalerate groups and two acetate groups. The acetate residues were assigned to C-2 and C-9 by analogy and because there were proton and carbon NMR chemical shifts in the spectra of **5** that were nearly identical to those observed for H/C-2,-9 in **4**. The two isovalerate groups could be located at vicinal positions C-12, C-13 or C-13, C-14 or

Table 1. ^{1}H NMR (500 MHz) Spectral Data of Juncins I−M (**1**−**5**) in $CDCl_3$

position	1	2	3	4	5
H-2	5.56 (t, 9.5)	5.54 (t, 10.0)	5.65 (t, 10.0)	5.87 (d, 7.5)	5.89 (d, 8.0)
H-3	5.61 (dd, 10.0, 9.5)	5.58 (dd, 10.0, 10.0)	5.60 (t, 9.5)	2.68 (m)	2.76 (m)
				1.60 (m)	1.62 (m)
H-4	6.27 (d, 10.0)	6.28 (d, 9.5)	6.27 (d, 10.5)	2.42 (m)	2.42 (m)
H-6	5.69 (dd, 9.0, 2.0)	5.70 (dd, 9.0, 2.0)	5.73 (dd, 9.0, 2.0)	4.60 (br s)	4.60 (br s)
H-7	4.96 (d, 9.0)	4.96 (d, 9.0)	4.97 (d, 10.5)	4.44 (br s)	4.43 (br s)
OH-8				3.42 (br s)	3.40 (br s)
H-9	4.72 (d, 5.0)	4.72 (d, 5.0)	4.79 (d, 5.0)	5.67 (br s)	5.71 (br s)
H-10	3.60 (br s)	3.58 (br s)	3.66 (d, 5.0)	3.64 (br s)	3.62 (br s)
H-12	4.86 (dd, 3.5, 1.5)	4.90 (d, 3.0)	4.52 (br s)	4.88 (dd, 3.0, 1.0)	4.60 (br s)
H-13	5.07 (t, 3.5)	5.09 (dd, 7.0, 3.0)	2.20 (m)	5.25 (t, 3.0)	2.16 (m)
			1.90 (m)		2.10 (m)
H-14	5.19 (dd, 3.5, 1.5)	5.20 (d, 3.0)	4.95 (d, 2.0)	5.22 (dd, 3.0, 1.0)	4.93 (br s)
H_3-15	1.07 (s)	1.11 (s)	1.04 (s)	1.23 (s)	1.14 (s)
H-16	5.37 (d, 15.5)	5.40 (d, 16.0)	5.36 (d, 15.0)	5.78 (br s)	5.79 (br s)
H-16	4.63 (d, 15.5)	4.64 (d, 16.0)	4.66 (d, 15.0)	5.49 (br s)	5.51 (br s)
H-17	2.30 (m)	2.30 (m)	2.30 (m)	2.92 (m)	2.82 (m)
H_3-19	1.08 (d, 6.5)	1.12 (d, 6.5)	1.15 (d, 7.0)	1.24 (d, 6.5)	1.24 (d, 6.5)
H-20	3.60 (s)	3.59 (d, 3.0)	3.52 (d, 3.0)	2.96 (d, 6.0)	2.96 (d, 6.0)
H-20	2.90 (s)	2.94 (d, 2.5)	2.78 (s)	2.36 (d, 4.0)	2.34 (d, 4.0)
H_2-2′	2.02 (m)	2.20 (m)	2.22 (m)	2.05 (m)	2.02 (m)
H-3′	1.92 (m)	1.94 (m)	1.98 (m)	1.95 (m)	1.96 (m)
H_3-4′	0.86 (d, 6.5)	0.98 (d, 6.5)	0.95 (br s)	0.88 (d, 6.0)	0.94 (d, 6.0)
H_3-5′	0.88 (d, 6.5)	0.99 (d, 6.5)	0.97 (br s)	0.90 (d, 6.0)	0.96 (d, 6.0)
H_2-2″		2.04 (m)	2.10 (m)	2.15 (m)	2.15 (m)
H-3″		1.92 (m)	1.96 (m)	2.05 (m)	2.02 (m)
H_3-4″		0.89 (d, 6.5)	0.93 (d, 6.5)	0.92 (d, 6.0)	0.90 (d, 6.0)
H_3-5″		0.91 (d, 6.5)	0.95 (d, 6.5)	0.94 (d, 6.0)	0.92 (d, 6.0)
OAC	2.18 (s)	2.18 (s)	2.18 (s)	2.18 (s)	2.18 (s)
	2.14 (s)	2.14 (s)	2.14 (s)	2.14 (s)	2.14 (s)
	2.12 (s)	2.12 (s)	2.12 (s)	2.12 (s)	2.12 (s)
	2.07 (s)	2.07 (s)	2.07 (s)	2.07 (s)	2.07 (s)
	1.93 (s)	1.93 (s)	1.93 (s)	1.93 (s)	1.93 (s)

in 1,3 positions at C-12 and C-14. In the presence of vicinal ester functionalities as found in nui-inoalide A with acetate groups at C-13 and C-14, the C-14 signal appeared at δ 72.75 and that of C-13 at δ 67.49.[11] In juncin M (**5**) the oxygenated carbon signals in question appeared at δ 72.8 and 73.0, supporting the location of the two isovalerate groups at C-12 and C-14, and in the HMBC spectrum a correlation was observed between the nearly overlapping carbon signals at 72.8−73.0 and the H-15 signal, confirming that one of the isovalerate groups is at C-14. Hence structure **5** is proposed for juncin M. Due to the small quantity of the compound available, the HMBC spectrum did not reveal all the correlations, but those observed all supported this structure. The stereochemistry of **5** was assigned as shown because of the similarity of proton NMR chemical shifts and coupling constants with those of **4** and juncin H.

Compounds **6**−**8** were characterized as (+)-gemmacolide A, (+)-gemmacolide B, and (+)-gemmacolide C, respectively, and compound **9** was identified as juncin H by comparing their spectral data with those recorded in the literature.[3,7]

Experimental Section

General Experimental Procedures. Optical rotations were measured with a Rudolph Autopol III automatic polarimeter. FABMS and ESIMS data were obtained on VG ZAB-E and Micromass Q-TOF mass spectrometers, respectively. NMR experiments were performed on a Varian VXR-500 spectrometer equipped with a 3 mm ^{1}H/^{13}C switchable gradient microprobe (MDG-500-3) and a pulsed field gradient driver, using standard Varian software. NMR signals are reported in parts per million (δ), referenced to $CDCl_3$ (δ 7.24; δ_C 77). Vacuum flash column chromatography was carried out on Si gel 60H (Merck) and LRP-2 (Whatman), and preparative HPLC was performed using an RI detector and Phenomenex ODS Prep (250 × 10 mm) column. Si gel 60 (Merck, 230−400 mesh) was used for open column chromatography.

Animal Material. The gorgonians (4.5 kg) were collected from Tuticorin Coast of the Indian Ocean in March 2000. These were cut into small species and stored in methanol at room temperature until extraction. The gorgonian was identified as *Junceella juncea* by P. A. Thomas, Scientist, Vizinjam Research Centre, CMFRI, Trivendrum. Voucher specimens (Code: AU1/198) are deposited at the Marine Museums of the School of Chemistry, Andhra University, and the National Institute of Oceanography, Goa.

Extraction and Isolation. Methanol (10 L) used for storing the specimens was decanted. The material was extracted seven times with cold methanol over a 3-day period. The combined methanolic extract (80 L) was concentrated under reduced pressure, and the residue (45 g) was extracted into ethyl acetate (4 × 1 L). The combined ethyl acetate extract (4 L) was concentrated under reduced pressure to leave a gummy residue (35 g). A part of the above residue (25 g) was chromatographed on a Si gel column (100−200 mesh, Acme) using gradient elution, starting from hexane and progressing through EtOAc to MeOH.

The residue from the column fractions 102−110 (*n*-hexane/EtOAc, 8.5:1.5) when subjected to HPLC furnished juncin L (6 mg, **4**) and juncin M (<1 mg, **5**), the residue from the column fractions 122−134 (*n*-hexane/EtOAc, 8.0:2.0) furnished gemmacolide A (40 mg, **6**) and gemmacolide B (35 mg, **7**), the residue from the column fractions 140−144 (*n*-hexane/EtOAc, 7.5:2.5) furnished juncin H (100 mg, **9**), and the residue from the column fractions 152−166 (*n*-hexane/EtOAc, 6.5:3.5) when subjected to HPLC furnished juncin I (9.5 mg, **1**), juncin J (4.6 mg, **2**), juncin K (0.7 mg, **3**), and gemmacolide C (2.6 mg, **8**).

Juncin I (1): white, amorphous powder; $[\alpha]_D^{25}$ −40.6° (*c* 0.48, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz), see Table 1; ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 2; HRESIMS *m*/*z* 745.2675 $[M + Na]^+$ (calcd for $C_{35}H_{46}O_{16}Na$, 745.2684).

Juncin J (2): white, amorphous powder; $[\alpha]_D^{25}$ −22.4° (*c* 0.38, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz), see Table 1; ^{13}C

Table 2. ^{13}C NMR (125 MHz) Spectral Data of Juncins I−M (**1**−**5**) in $CDCl_3$

carbon no.	**1**[a]	**2**[a]	**3**[a]	**4**[b]	**5**[b]
1	46.3	46.3	47.1	47.2	47.8
2	74.0	74.1	74.4	72.6	72.7
3	131.9	132.0	132.4	28.2	28.2
4	127.6	127.6	127.4	33.0	33.5
5	139.6	139.6	139.8	146.8	146.8
6	122.4	122.4	122.3	51.5	51.6
7	78.6	78.6	78.8	81.1	81.2
8	80.9	80.9	81.1	81.3	81.3
9	63.6	63.7	64.0	72.0	72.1
10	32.5	32.7	32.7	35.3	35.6
11	58.2	58.4	59.2	56.8	57.5
12	73.1	72.7	72.9	73.0	73.0
13	66.3	66.2	28.9	66.3	29.6
14	73.6	73.6	73.0	72.9	72.8
15	14.3	14.4	14.1	14.2	14.1
16	63.0	63.0	62.8	121.0	121.3
17	43.9	44.0	44.1	50.5	50.7
18	175.2	175.2	175.3	174.5	174.4
19	6.2	6.2	6.3	6.2	6.1
20	48.7	48.9	49.0	50.5	50.7
OAc	170.2	170.3	170.2	171.3	170.7
	170.1	170.1	170.0	170.1	169.3
	169.9	169.9	169.0	169.3	
	169.6	169.5			
	169.5				
	21.4	21.5	21.5	21.6	21.3
	21.2	21.3	21.2	21.2	21.2
	21.2	20.8	21.1	20.9	
	20.7	20.8			
	20.7				
1′	171.6	171.7	172.2	171.4	172.4
2′	42.5	43.4	43.2	42.6	42.4
3′	24.8	25.6	25.6	25.6	25.5
4′	22.3	22.4	22.6	22.3	22.4
5′	22.2	22.3	22.4	22.3	22.4
1″		171.7	171.9	171.6	171.7
2″		42.5	42.8	43.4	43.5
3″		24.9	24.7	24.9	24.6
4″		22.4	22.4	22.3	22.7
5″		22.3	22.4	22.3	22.5

[a] Assignments aided by HMQC and HMBC. [b] Many but not all signals assigned by HMQC and HMBC.

NMR ($CDCl_3$, 125 MHz), see Table 2; HRESIMS *m*/*z* 787.3172 $[M + Na]^+$ (calcd for $C_{38}H_{52}O_{16}Na$, 787.3153).

Juncin K (3): white, amorphous powder; $[\alpha]_D^{25}$ −61.7° (*c* 0.06, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz), see Table 1; ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 2; HRESIMS *m*/*z* 729.3105 $[M + Na]^+$ (calcd for $C_{36}H_{50}O_{14}Na$, 729.3098).

Juncin L (4): colorless needles; mp 234−237 °C; $[\alpha]_D^{25}$ −7.4° (*c* 0.50, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz), see Table 1; ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 2; HRESIMS *m*/*z* 765.2859 $[M + Na]^+$ (calcd for $C_{36}H_{51}O_{14}ClNa$, 765.2865).

Juncin M (5): white, amorphous powder; $[\alpha]_D^{25}$ +47.6° (*c* 0.042, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz), see Table 1; ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 2; HRESIMS *m*/*z* 707.2901 $[M + Na]^+$ (calcd for $C_{34}H_{49}O_{12}ClNa$, 707.2810).

Gemmacolide A (6): colorless needles (*n*-hexane/acetone); mp 270−272 °C; $[\alpha]_D^{25}$+ 2.6° (*c* 0.4, $CHCl_3$); spectral data (IR, ^1H NMR, ^{13}C NMR) were identical with literature values.[7]

Gemmacolide B (7): colorless needles (*n*-hexane/chloroform); mp 296−298 °C; $[\alpha]_D^{25}$+ 5.8° (*c* 0.3, $CHCl_3$); spectral data (IR, ^1H NMR, ^{13}C NMR) were identical with literature values.[7]

Gemmacolide C (8): colorless oil; $[\alpha]_D^{25}$ +12.8° (*c* 0.1, $CHCl_3$); spectral data (IR, ^1H NMR, ^{13}C NMR) were identical with literature values.[3]

Juncin H (9): colorless needles (*n*-hexane/chloroform); mp 248−250 °C; $[\alpha]_D^{25}$ +9.4° (*c* 0.2, $CHCl_3$); spectral data (IR, ^1H NMR, ^{13}C NMR) were identical with literature values.[7]

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