Menverins H – L, New Highly Oxygenated Guaiane Lactones from the Gorgonian Coral *Menella kanisa*

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By further chemical investigation of South China Sea gorgonian *Menella kanisa*, five new highly oxygenated guaiane lactones, menverins H – L (**1** – **5**, resp.), were obtained. Their structures were established by employing spectroscopic methods, computer modeling, and comparison of their data with those of related metabolites.

Introduction. – Previous chemical investigations of gorgonian corals of the genus *Menella* (family Plexauridae) have yielded several interesting natural products, including steroids, guainae lactones, and briarane diterpenoids [1 – 10], some of which were shown to possess antitumor and anti-inflammatory activities. To date, there are only a few reports on the bioactive secondary metabolites isolated from *Menella kanisa*. In our study of bioactive compounds from *M. kanisa*, we have reported some diketopiperazines [11]. Further search for bioactive metabolites from this specimen has led to the isolation of five new highly oxygenated guaiane lactones, menverins H – L (**1** – **5**, resp.; *Fig. 1*). Herein, we describe the isolation and structure elucidation of **1** – **5**.

Results and Discussion. – Menverin H (**1**) was isolated as white solid. Its molecular formula was deduced as $C_{23}H_{24}O_7$ on the basis of its HR-ESI-MS (*m/z* 413.1605 ($[M+H]^+$, $C_{23}H_{25}O_7^+$; calc. 413.1600)) and NMR data, implying twelve degrees of unsaturation. Analysis of the ^{1}H-NMR data (*Table 1*) revealed the presence of a 1,4-disubstitued aromatic ring (δ(H) 7.39 (*d*, $J = 7.5$, H–C(2′,6′)), 5.61 (*d*, $J = 7.5$, H–C(3′,5′)), an olefinic H-atom (δ(H) 6.55 (*s*, H–C(6))), a MeO group (δ(H) 3.08 (*s*, MeO–C(8))), three Me groups (δ(H) 1.88 (*s*, Me(13)), 1.51 (*s*, Me(14)), and 1.08 (*d*, $J = 6.8$, Me(15))). The ^{13}C-NMR data of **1** indicated the presence of four Me, two sp^3 CH_2, two sp^3 CH, and five sp^2 CH groups, and three quaternary sp^3 and seven quaternary sp^2 C-atoms (*Table 1*). A COOH group at C(1′) was evidenced by the

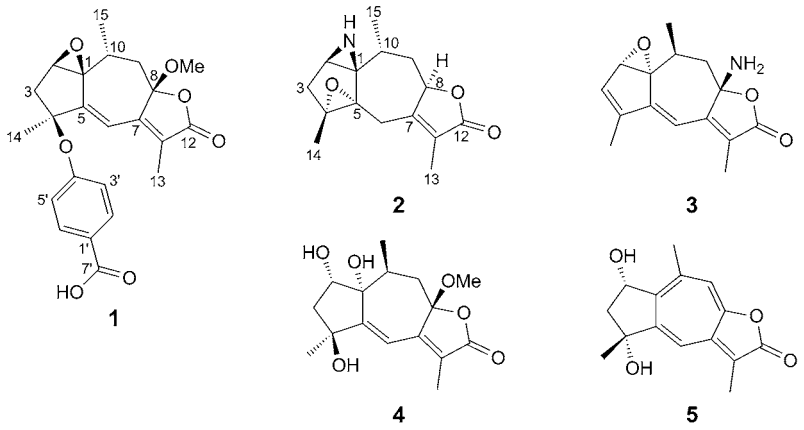

Fig. 1. *Structures of compounds* **1**–**5**

^{13}C-NMR resonance at δ(C) 167.8 (C(7′)). The presence of an α-methyl-α,β-unsaturated γ-lactone moiety was indicated by the C-atom resonances at δ(C) 173.9 (C(12)), 155.1 (C(7)), 126.8 (C(11)), 109.0 (C(8)), and 8.6 (Me(13)) [11]. An additional unsaturated functionality was evidenced by the resonances at δ(C) 165.8 (C(5)) and 115.8 (C(6)), indicating the presence of a trisubstituted olefinic C=C bond. Moreover, an ether bridge between C(1) and C(2) was revealed by the downfield shifted δ values of C(1) and C(2) and the C=C equivalents of this molecule. The above information, in combination with the molecular formula, indicated a pentacyclic molecule.

^{1}H,^{1}H-COSY and HMB correlations (*Fig. 2*) were used to establish the molecular skeleton of **1**. Spin systems were revealed by analysis of COSY correlations H–C(2)/CH_2(3) and CH_2(9)/H–C(10)/Me(15). These data, together with the key HMBCs from Me(14) to C(3), C(4), and C(5); from H–C(6) to C(1), C(4), C(5), C(7), C(8), and C(11); from Me(13) to C(7), C(8), and C(12); from CH_2(9) to C(1) and C(8); and from Me(15) to C(1) and C(9), in combination with the δ values of C(8) and C(12), evidenced the presence of a guaiane sesquiterpenoid skeleton with a furan lactone [12] and a C(5)=C(6) bond. Moreover, the MeO group at C(8) was secured by the HMBC MeO–C(8)/C(8). Further, the COSY correlations H–C(2′)/H–C(3′) and H–C(5′)/H–C(6′), together with the HMBCs from H–C(2′) and H–C(6′) to C(7′) and C(4′), and analysis of the molecular formula, indicated the presence of a 4-hydroxybenzoic acid. As there is no further HMBC from outside the benzene with C(4′), it must be attached to a quaternary center, and it must be in a position where sp^2 atoms are close to influence the chemical shifts of H–C(3′) and H–C(5′). C(4) is a suitable candidate which was supported by the downfield shifted δ value of C(4) in accord with those of zedoalactones A and B [12][13]. Therefore, the 4-hydroxybenzoic acid moiety was connected to C(4) *via* an O-bridge.

The relative configuration of **1** was proposed on the basis of key NOESY correlations (*Fig. 3*). The observation of NOESY correlation the Me(15)/H–C(2)

Table 1. *^{1}H- and ^{13}C-NMR Data* (600 and 150 MHz, resp.; in CD_3OD) *of* **1**–**3**. δ in ppm, J in Hz. Arbitrary atom numbering as indicated in *Fig. 1*.

Position	**1**		**2**		**3**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1		85.0		69.1		91.2
2	3.96 (*d*, *J* = 4.5)	76.9	3.59 (*d*, *J* = 3.0)	62.8	4.20 (*s*)	77.1
3	2.29 (*dd*, *J* = 13.8, 4.5), 1.95 (*d*, *J* = 15)	47.0	2.20 (*dd*, *J* = 12, 6.5), 1.27 (*d*, *J* = 12)	33.0	6.09 (*s*)	138.9
4		80.7		68.0		143.4
5		165.8		77.0		156.5
6	6.55 (*s*)	115.8	3.16 (*d*, *J* = 15.5, H_α), 2.67 (*d*, *J* = 15.5, H_β)	27.3	6.49 (*s*)	110.2
7		155.1		153.2		155.6
8		109.0	4.15 (*dd*, *J* = 11.1, 3.5)	61.7		93.5
9	2.13 (*dd*, *J* = 14.3, 2.3, H_α), 1.92 (*d*, *J* = 15, H_β)	40.1	1.96–1.94 (*m*, H_α), 1.67–1.64 (*m*, H_β)	40.5	1.72 (*dd*, *J* = 14.4, 11.4, H_α), 1.60 (*d*, *J* = 14.1, H_β)	39.8
10	2.67–262 (*m*)	33.0	2.64–2.60 (*m*)	29.5	2.49–2.47 (*m*)	41.6
11		126.8		130.7		122.4
12		173.9		175.9		176.8
13	1.88 (*s*)	8.6	1.79 (*s*)	8.9	1.84 (*s*)	7.7
14	1.51 (*s*)	32.6	1.41 (*s*)	17.3	1.95 (*s*)	12.1
15	1.08 (*d*, *J* = 6.8)	17.5	0.88 (*d*, *J* = 7.0)	17.2	0.86 (*d*, *J* = 6.7)	15.7
MeO	3.08 (*s*)	51.0				
1′		135.5				
2′, 6′	7.39 (*d*, *J* = 7.5)	143.7				
4′		153.7				
3′, 5′	5.61 (*d*, *J* = 7.5)	101.8				
7′		167.8				

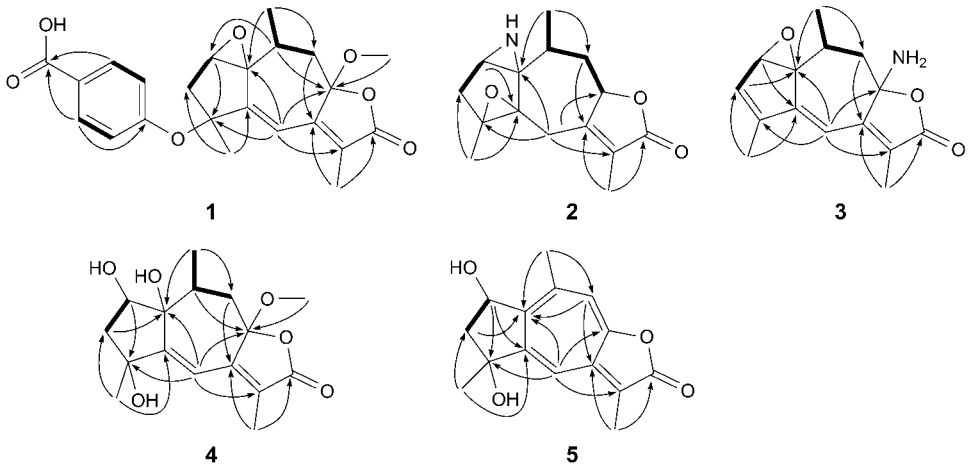

Fig. 2. *Key* $^1H,^1H$*-COSY* (—) *correlations and HMBCs* (H → C) *of* **1**–**5**

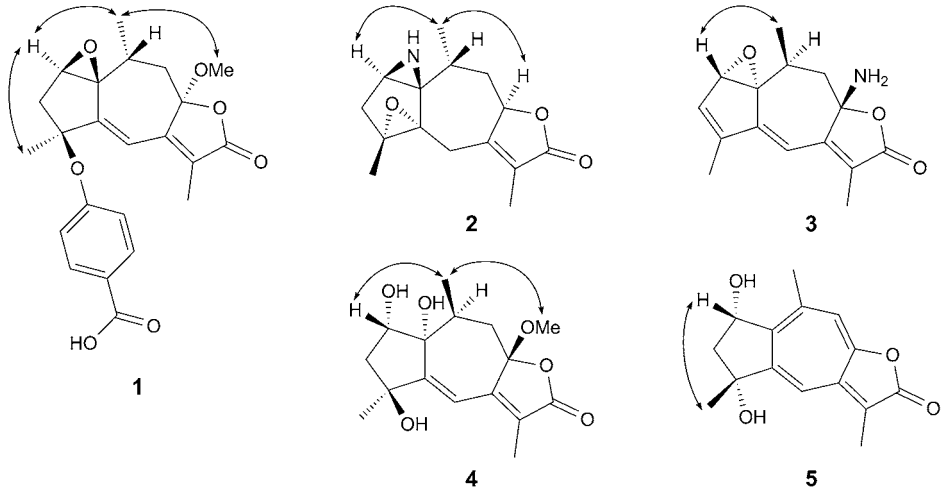

Fig. 3. *The key NOESY* (H ↔ H) *correlations of* **1**–**5**

allowed assignment of the relative configuration at C(2)/C(10) with the Me group at C(10) and H–C(2) in α-orientation, and H–C(10) in β-orientation. A NOESY correlation between H_β–C(9) and Me(15) was also observed. The coupling constants between H–C(9) and H–C(10) ($J(9\alpha,10) = 14.3$, $J(9\beta,10) \leq 1$) required a dihedral angle close to 90° between H–C(10) and H_β–C(9) and of almost 180° between H–C(10) and H_α–C(9). The MeO group at C(8) was predicted to be on the same molecular face as H–C(10), based on the large coupling constant between H–C(10) and H_α–C(9), and combined with the lack of the NOESY correlation between H–C(10) and $H_{\alpha\beta}$–C(9). In addition, NOESY correlation H–C(2)/H_α–C(3), as well as Me(14)/H_α–C(3), were also

observed. All these geometric constraints dictated by the observed NOESY correlations and coupling constants are compatible with a MeO group at C(8) in the β-orientation.

The $[\alpha]_D^{20}$ value of compound **1** was +14.7 (MeOH), whereas the reported values for americanolides A–C were negative [14][15]. Although we do not have an explanation for the difference in the absolute values of the optical rotations, the configuration at C(8) was assigned to be (*S*) by the aid of NMR assignments and optical rotations compared with the relevant signals of americanolides A–C, whose configurations have been established by a combination of NOE and coupling constant data, supported by distance calculations using the QUANTA/CHARMm molecular-mechanics program as having the same partial substructure as **1** [14][15]. The configuration at C(4) was assigned to be (*S*), because a positive $[\alpha]_D$ was observed, which was in accordance with those observed in zedoalactone A, and analysis of the ^{13}C-NMR chemical shift of C(4) in **1** indicated that it was very similar to that of C(4) in zedoalactone A whose configuration has been established by a synthetic method [16]. From the aforementioned analyses, the configuration of **1** was assumed to be (1*S*,2*R*,4*S*,8*S*,10*R*). On the basis of this cumulative analysis, the structure of **1** was thus established as depicted in *Fig. 1*.

Menverin I (**2**) was obtained as white solid. Its molecular formula of $C_{15}H_{19}NO_3$ was deduced from its HR-ESI-MS (*m*/*z* 262.1432 ($[M+H]^+$, $C_{15}H_{20}NO_3^+$; calc. 262.1443) and NMR data, indicating seven degrees of unsaturation. Analysis of the NMR data (*Table 1*) indicated the presence of three Me, three sp^3 CH_2, and three sp^3 CH groups, and three quaternary sp^3 and three quaternary sp^2 C-atoms. The presence of an α-methyl-α,β-unsaturated γ-lactone moiety in **2** was revealed by the C-atom signals at δ(C) 175.9 (C(12)), 153.2 (C(7)), 130.7 (C(11)), 61.7 (C(8)), and 8.9 (Me(13)) [12]. Analysis of the NMR data indicated that **2** had a guaiane sesquiterpene skeleton with great similarity to that of americanolide A [14]. Careful comparison of the ^{13}C-NMR data of **2** and its molecular formula with those of americanolide A, revealed that an amide bridge was located between C(1) (δ(C) 69.1) and C(2) (δ(C) 62.8). Hence, **2** possessed seven degrees of unsaturation, two of which were due to an ester C=O C-atom and a tetrasubsituted C=C bond, and five due to the rings. The above information, consistent with its molecular formula, displayed the molecule to be pentacyclic.

Spin systems H–C(2)/CH_2(3) and H–C(8)/CH_2(9)/H–C(10)/Me(15) present in **2**, as the analysis of the ^{1}H,^{1}H-COSY correlations revealed, were assembled with the assistance of the HMBC correlations (*Fig. 2*). From the ^{1}H,^{1}H-COSY and HMB correlation spectra, the partial structure of **2** contained a cyclopentane skeleton with an epoxide and an amide bridge (at C(4)/(5) and C(1)/(2), respectively) adjacent to the same CH_2 group. Next to this CH_2 was a deshielded quaternary C-atom on one side, which was shown by HMBC to bear a Me group and a deshielded CH on the opposite side, which was adjacent to N-bearing quaternary C-atom. The Me groups at C(4), C(10), and C(11) were confirmed by the HMBCs from Me(14) to C(3) and C(5); from Me(15) to C(1) and C(9); and from Me(13) to C(7) and C(12). The HMBCs of H–C(2) to C(5); of H–C(6) to C(1), C(4), C(8), and C(11); and of CH_2(9) to C(7) further supported the proposed structure for **2**.

In the NOESY spectrum (*Fig. 3*), the correlations H–C(2)/Me(15) and Me(15)/H–C(8) revealed their α-orientations. The configuration at C(8) was assigned to be

(*R*), because a negative *Cotton* effect at 220 nm ($\Delta\varepsilon$ −12.28), in accordance with those of menverin F, 1-deoxymenverin F, and menverin G [3], and also by aid of NMR assignments compared with the corresponding signals assigned for americanolides A–D [14]. These findings suggested that **2** had the absolute configuration (1*R*,2*R*,4*R*,5*S*,8*R*,10*R*). Thus, the structure of **2** was elucidated as shown in *Fig. 1*.

Menverin J (**3**) was isolated as white solid. Its molecular formula of $C_{15}H_{17}NO_3$ was assigned through its HR-ESI-MS (*m*/*z* 260.1278 ($[M+H]^+$, $C_{15}H_{18}NO_3^+$; calc. 260.1287)) and NMR data, requiring eight degrees of unsaturation. The NMR data for **3** confirmed the presence of three Me groups, one sp^3 CH_2 group, two sp^3 CH and two sp^2 CH groups, and two quaternary sp^3 and five quaternary sp^2 C-atoms (*Table 1*). An α-methyl-α,β-unsaturated γ-lactone moiety in **3** was supported by the resonances at δ(C) 176.8 (C(12)), 155.6 (C(7)), 122.4 (C(11)), 93.5 (C(8)), and 7.7 (Me(13)) [12]. Apart from four degrees of unsaturation due to a lactone C=O C-atom and three C=C bonds, a tetracyclic structure was required for **3** to fulfill the unsaturation requirement.

The molecular framework was established by ^{1}H,^{1}H-COSY and HMB correlations (*Fig. 2*). Comprehensive analysis of ^{1}H,^{1}H-COSY correlations of **3** established spin systems of H–C(2)/H–C(3) and CH_2(9)/H–C(10)/Me(15). The Me groups at C(4), C(10), and C(11) were confirmed by the HMBCs from Me(14) to C(3) and C(5); from Me(15) to C(1) and C(9); and from Me(13) to C(7) and C(12). The planar structure of **3** was further confirmed by HMBCs from H–C(2) to C(5); from H–C(3) to C(1); from H–C(6) to C(1), C(4), C(8), and C(11); and from CH_2(9) to C(7). Analysis of its molecular formula and ^{13}C-NMR data, an ether bridge between C(1) and C(4) was supported by the downfield shifted δ values of C(1) and C(2), and the NH_2 group at C(8) was indicated by the downfield shifted δ value of C(8).

The relative configuration of **3** was deduced from the NOESY spectrum as shown in *Fig. 3*. The NOESY correlation H–C(2)/Me(15) indicated β-orientation of H–C(2) and Me(15). The configuration at C(8) was assigned as (*S*), based on a positive *Cotton* effect at 218 nm ($\Delta\varepsilon$ +6.22), in line with those of menverin F, 1-deoxymenverin F, and menverin G [3]. On the basis of these analyses, the configuration of **3** was assigned as (1*R*,2*S*,8*S*,10*S*). Therefore, the structure of compound **3** was established as shown in *Fig. 1*.

Menverin K (**4**) was isolated as colorless oil. Its molecular formula of $C_{16}H_{22}O_6$ was provided by its HR-ESI-MS (*m*/*z* 333.1315 ($[M+Na]^+$, $C_{16}H_{22}NaO_6^+$; calc. 333.1314)) and NMR data, revealing six degrees of unsaturation. The NMR data of **4** and its molecular formula revealed the presence of four Me, two sp^3 CH_2, and two sp^3 CH, a sp^2 CH group, and three quaternary sp^3 and four quaternary sp^2 C-atoms, and finally three OH groups (*Table 2*). The characteristic signals of an α-methyl-α,β-unsaturated γ-lactone moiety (δ(C) 171.5 (C(12)), 153.4 (C(7)), 128.3 (C(11)), 108.0 (C(8)), and 9.0 (Me(13))) were detected in the ^{13}C-NMR specimen of **4** [12]. An additional unsaturated functionality was indicated by resonances at δ(C) 160.4 (C(5)) and 115.8 (C(6)), revealing the presence of a trisubstituted olefinic C=C bond. Given that the molecular formula implied six degrees of unsaturation and the molecule contained a lactone C=O C-atom and two C=C bonds, the remaining unsaturations were due to a tricyclic skeleton.

The basic skeleton of **4** was confirmed by analysis of the COSY and HMB correlations. The ^{1}H,^{1}H-COSY correlations H–C(2)/CH_2(3), and CH_2(9)/H–C(10)/

Table 2. *^{1}H- and ^{13}C-NMR Data* (600 and 150 MHz, resp.; in CD_3OD) *of* **4** *and* **5**. δ in ppm, J in Hz. Arbitrary atom numbering as indicated in *Fig. 1*.

Position	**4**		**5**	
	δ(H)	δ(C)	δ(H)	δ(C)
1		82.1		141.4
2	4.07 (*t*, *J* = 6.8)	72.6	5.15 (*d*, *J* = 6.0)	72.4
3	2.19 (*dd*, *J* = 15.9, 3.0, H_α), 2.11 (*d*, *J* = 15.9, H_β)	45.7	2.22 (*dd*, *J* = 16.2, 3.0, H_α), 2.20 (*d*, *J* = 16.2, H_β)	49.2
4		77.0		81.7
5		160.4		156.5
6	6.53 (*s*)	115.8	7.16 (*s*)	118.7
7		153.4		146.1
8		108.0		156.4
9	2.29 (*dd*, *J* = 14.3, 3.8, H_α), 2.02 (*dd*, *J* = 12.9, 7.5, H_β)	38.2	6.73 (*s*)	116.5
10	2.64 (*dd*, *J* = 14.3, 4.1)	37.1		141.0
11		128.3		106.7
12		171.5		170.3
13	1.90 (*s*)	9.0	2.00 (*s*)	8.0
14	1.39 (*s*)	27.7	1.69 (*s*)	32.1
15	1.09 (*d*, *J* = 7.4)	16.1	2.44 (*s*)	23.5
MeO–C(8)	3.05 (*s*)	50.2		

Me(15), coupled with the HMBCs H–C(2)/C(4); CH_2(3)/C(1); Me(14)/C(3) and C(5); H–C(6)/C(1), C(4), C(8), and C(11); Me(13)/C(7) and C(12); CH_2(9)/C(7); H–C(10)/C(8); and Me(15)/C(1) and C(9) of **4** indicated a guaiane sesquiterpene skeleton [12]. Moreover, the MeO group at C(8) was secured by the HMBC of MeO–C(8) to C(8). Comparison of **4** with **1** revealed that **4** differed from **1** by the presence of three OH groups attached at C(1), C(2), and C(4).

The relative configuration of **4** was mainly established by a NOESY spectrum (*Fig. 3*). Two cross-peaks H–C(2)/Me(15) and Me(15)/MeO–C(8) revealed that they were β-oriented. The Me(14) group at C(4) was α-oriented based on the missing NOESY correlation between Me(14) and H–C(2). The configuration at C(8) was assigned as (*S*), on the basis of a positive *Cotton* effect at 220 nm ($\Delta\varepsilon$ +6.42) in accordance with those observed in menverin F, 1-deoxymenverin F, menverin G [3], and **1**. These findings allowed the assignment of the (1*R*,2*S*,4*S*,8*S*,10*S*)-configuration. The structure of compound **4** was thus determined as shown in *Fig. 1*.

Menverin L (**5**) was obtained as yellow solid, and its molecular formula, $C_{15}H_{16}O_4$, was deduced from its HR-ESI-MS (*m*/*z* 261.1122 ($[M+H]^+$, $C_{15}H_{17}O_4^+$; calc. 261.1127)) and NMR data, implying eight degrees of unsaturation. The NMR data of **5** and its molecular formula indicated the presence of three Me groups, one sp^3 CH_2, and one sp^3 CH group, two sp^2 CH_2 groups, one quaternary sp^3 and seven quaternary sp^2 C-atoms, and two OH groups (*Table 2*). The characteristic chemical shifts of an α-methyl-α,β-unsaturated γ-lactone (δ(C) 170.3 (C(12)), 156.4 (C(8)), 146.1 (C(7)), 106.7 (C(11)), and 8.0 (Me(13))) were observed in the ^{13}C-NMR spectrum. In addition, the ^{13}C-NMR data indicated the presence of three trisubstituted olefinic C=C bonds

(δ(C) 156.5 (C(5)), 156.4 (C(8)), 141.4 (C(1)), 141.0 (C(10)), 118.7 (C(6)), and 116.5 C(9)), accounting for three degrees of unsaturation. From these findings, compound **5** was proposed to be tricyclic.

The ^{1}H,^{1}H-COSY correlation H–C(2)/CH_2(3), combined with HMBCs from H–C(2) to C(4) and C(5); from CH_2(3) to C(1); from H–C(6) to C(1), C(4), C(8), and C(11); and from H–C(9) to C(1) and C(7) (*Fig. 2*) permitted elucidation of the C-skeleton of **5**. The Me groups at C(4), C(10), and C(11) were confirmed by the HMBCs from Me(14) to C(3) and C(5); from Me(15) to C(1) and C(9); and from Me(13) to C(7) and C(12). The NMR data of **5** displayed similarities with those of zedoalactone F [17], and **5** differed from zedoalactone F by the presence of two additional olefinic C-atoms (δ(C) 156.5 (C(5)) and 118.7 (C(6))) and one OH group at C(2).

The relative configuration of **5** was ascertained mainly on the basis of a NOESY spectrum (*Fig. 3*). The NOESY correlation H–C(2)/Me(14) indicated that they were β-oriented. The relative configuration at C(4) was confirmed to be (*R**) by comparison of the chemical shifts at δ(C) 81.7 (C(4)) in **5** with those at δ(C) 77.0 (C(4)) in **4**, and at δ(C) 80.9 (C(4)) in zedoalactone E [17]. On the basis of these evidences, the configuration of **5** was elucidated as (2*S**,4*R**).

Conclusions. – In conclusion, our investigation on the chemical constituents of gorgonian *M. kanisa* led to the identification of new highly oxygenated guaiane lactones, menverins H – L (**1** – **5**, resp.).

This study was supported by grants from the *National Natural Science Foundation of Chin*a (No. 31100260, 81260480), the *Natural Science Foundation of Guangxi* (2012GXNSFAA053160, 2012GXNSFEA053001), the *Knowledge Innovation Program of Chinese Academy of Sciences* (KSCX2-EW-J-28), the *Program of Guangzhou City* (No. 12C14061559), the *Key Project of Science and Technology Department of Guangxi* (143001 – 7), and the *Cooperation Projects of SIDSSE and Sanya* (2013YD73). *R. H.* acknowledges a *CAS Academic Visitor Fellowship*, working with Dr. *Ian S. Blagbrough*, University of Bath.

Experimental Part

General. TLC: Silica gel GF_{254} (*Qingdao Marine Chemical Factory*, Qingdao, China); visualization under UV light or by heating after spraying with 5% H_2SO_4 in EtOH. HPLC: *Waters-2695* system, using a *Sunfire*™ C_{18} column (250 × 10 mm i.d., 10 μm) coupled to a *Waters 2998* photodiode-array detector. Optical rotations: *Perkin–Elmer Model 341* polarimeter. NMR Spectra: *Bruker AC 500* spectrometer; δ in ppm rel. to Me_4Si as internal standard; *J* in Hz. HR-ESI-MS: *Bruker Maxis* mass spectrometer;
in *m*/*z*.

Extraction and Isolation. The *M. kanisa* (3 kg, wet weight) was extracted with EtOH (95%). EtOH was evaporated *in vacuo* to afford a syrupy residue, which was suspended in dist. H_2O and fractionated successively with petroleum ether (PE), AcOEt, and BuOH. The AcOEt-soluble portion (7.21 g) was subjected to column chromatography (CC; SiO_2; $CHCl_3$/Me_2CO 10 : 0, 9 : 1, 8 : 2, 7 : 3, and $CHCl_3$/MeOH 10 : 1, 10 : 2, 10 : 3, 0 : 10), to give eleven fractions, *Frs. A – K*. *Fr. E* was subjected to CC to afford two subfractions, *Fr. E1* and *Fr. E2*. *Fr. E1* was separated by HPLC (MeOH/H_2O 15 : 85) to yield **5** (2.8 mg). *Fr. E2* was separated by HPLC (MeOH/H_2O 5 : 95) to furnish **2** (4.8 mg) and **3** (4.2 mg). *Fr. G* was subjected to CC to yield two subfractions, *Fr. G1* and *Fr. G4*. *Fr. G4* was separated by HPLC (MeOH/H_2O 35 : 65) to give **4** (3.1 mg). The BuOH-soluble portion (5.01 g) was subjected to CC (SiO_2; $CHCl_3$/

MeOH 10:0, 10:1, 10:2, 10:3.5, 0:10) to provide four fractions, *Frs. L1–L4*. *Fr. L3* was separated by HPLC (MeOH/H_2O 5:95) to yield **1** (4.1 mg).

Menverin H (=*4-[[(1a*R,*3*S,*7a*S,*9*R,*9a*S*)-2,3,6,7a,8,9-Hexahydro-7a-methoxy-3,5,9-trimethyl-6-oxo-1a*H*-oxireno[1,8a]azuleno[6,5-*b*]furan-3-yl]oxy]benzoic Acid*; **1**). White solid. M.p. 284–286°. $[\alpha]_D^{20} = +14.7$ ($c = 0.21$, MeOH). CD (MeOH): $\Delta\varepsilon_{220} = -2.28$. ^{1}H- and ^{13}C-NMR: see *Table 1*. HR-ESI-MS: 413.1605 ($[M+H]^+$, $C_{23}H_{25}O_7^+$; calc. 413.1600).

Menverin I (=*(2a*R,*3a*R,*4*R,*5a*R,*9a*S*)-1a,2,2a,3,5,5a-Hexahydro-1a,4,8-trimethyl-4*H*-furo[3′,2′:5,6]-oxireno[3,3a]azuleno[1,8a-*b*]azirin-7(9*H*)-one*; **2**). White solid. M.p. 291–295°. $[\alpha]_D^{20} = -28.1$ ($c = 0.24$, MeOH). CD (MeOH): $\Delta\varepsilon_{220} = -12.28$. ^{1}H- and ^{13}C-NMR: see *Table 1*. HR-ESI-MS: 262.1432 ($[M+H]^+$, $C_{15}H_{20}NO_3^+$; calc. 262.1443).

Menverin J (=*(1a*S,*7a*S,*9*S,*9a*R*)-7a-Amino-7a,8-dihydro-3,5,9-trimethyl-9*H*-oxireno[1,8a]azuleno[6,5-*b*]furan-6(1a*H*)-one*; **3**). White solid. M.p. 305–307°. $[\alpha]_D^{20} = -12.1$ ($c = 0.15$, MeOH). CD (MeOH): $\Delta\varepsilon_{220} = +6.22$. ^{1}H- and ^{13}C-NMR: see *Table 1*. HR-ESI-MS: 260.1278 ($[M+H]^+$, $C_{15}H_{18}NO_3^+$; calc. 260.1287).

Menverin K (=*(5*S,*7*S,*7a*R,*8*S,*9a*S*)-6,7,7a,8,9,9a-hexahydro-5,7,7a-trihydroxy-9a-methoxy-3,5,8-trimethylazuleno[6,5-*b*]furan-2(5*H*)-one*; **4**). Colorless oil. $[\alpha]_D^{20} = -14.5$ ($c = 0.16$, MeOH). CD (MeOH): $\Delta\varepsilon_{220} = +6.42$. ^{1}H- and ^{13}C-NMR: see *Table 2*. HR-ESI-MS: 333.1315 ($[M+Na]^+$, $C_{16}H_{22}NaO_6^+$; calc. 333.1314).

Menverin L (=*(5*R**,7*S**)-6,7-Dihydro-5,7-dihydroxy-3,5,8-trimethylazuleno[6,5-*b*]furan-2(5*H*)-one*; **5**). Yellow solid. M.p. 285–287°. $[\alpha]_D^{20} = +13.3$ ($c = 0.14$, MeOH). CD (MeOH): $\Delta\varepsilon_{218} = -2.15$. ^{1}H- and ^{13}C-NMR: see *Table 2*. HR-ESI-MS: 261.1122 ($[M+H]^+$, $C_{15}H_{17}O_4^+$; calc. 261.1127).

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Received June 27, 2014