Menverins A – D, New Highly Oxygenated Guaiane Lactones from Hainan Gorgonian *Menella verrucosa* (BRUNDIN)

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Four new highly oxygenated guaiane lactones, menverins A – D (**1** – **4**), were isolated from the gorgonian *Menella verrucosa* (BRUNDIN) from the South China Sea. Their structures and relative configurations were elucidated on the basis of spectroscopic data. All compounds contain a conjugated α-methyl-substituted α,β-unsaturated γ-lactone moiety, a C(8)=C(9) conjugated with the γ-lactone moiety, and an exocyclic methylene group at C(4) (trivial numbering).

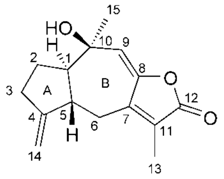
Introduction. – Many guaiane sesquiterpenoids have been isolated from natural sources [1]. However, they are infrequent in marine organisms [2][3]. Gorgonians contain the majority (60%) of marine guaiane analogs [4 – 14], whereas the remaining guaianolides were isolated from soft corals [15 – 19] and sponges [20 – 23]. Many guaianes display an exocyclic C(10)=C(15) bond, whereas the exocyclic C(4)=C(14) bond is quite unusual[1]). Finally, only twice a C(8)=C(9) olefin moiety has been reported [24],[25].

Recently, we have collected the gorgonian *Menella verrucosa* (BRUNDIN) off the coast of Sanya, Hainan Province, China. No chemical study of this gorgonian has been reported until now. This paper describes the isolation and characterization of the four novel guaiane lactones **1** – **4**, all containing both C(4)=C(14) and C(8)=C(9) bonds.

Results and Discussion. – The gorgonian (209 g, dried weight) was collected off the coast of Xiaodong Hai, Hainan Province, China, in December 2001, at a depth of 20 m. The animals were immediately put at $-20°$ and kept frozen until extraction. The Et_2O-soluble portion from the Me_2CO extract was repeatedly subjected to column chromatography (silica gel, *Sephadex LH-20*) and to reversed-phase HPLC to afford four pure compounds, **1** (3.0 mg), **2** (4.6 mg), **3** (2.1 mg), and **4** (1.8 mg), respectively.

Menverin A (**1**) is an opticaly active colorless oil of the molecular formula $C_{15}H_{18}O_3$ as deduced by HR-EI-MS (*m/z* 246.1270 (M^+)). A strong UV absorption at 273 nm (log ε 4.06) revealed the presence of an extensive conjugated system. All further spectral data (^{1}H- and ^{13}C-NMR (*Table 1*), HMQC, ^{1}H,^{1}H-COSY, HMBC, and NOESY (*Table 1*)) strongly suggested a guaiane framework with a conjugated α,β-unsaturated γ-lactone, an exocyclic methylene group at C(4), and an OH group at C(10)[1]) and established the proposed structure. A compound structurally related to **1** is

[1]) Trivial numbering (see **1**); for systematic names, see *Exper. Part*.



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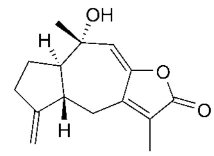

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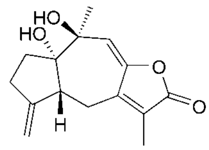

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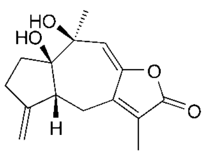

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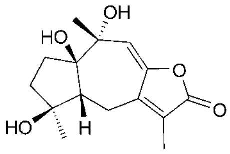

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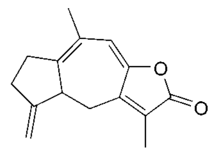

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zedoalactone B (**5**), isolated from the rhizomes of *Curcuma aeruginosa* [24], which was used in Japan as a traditional gastrointestinal medicine.

The MS of **1** indicated seven unsaturations assigned by NMR analysis (*Table 1*) to three C=C bonds, a C=O, and three rings. In addition, ^{13}C-NMR and DEPT spectra supported the presence of eight sp^3 C-atoms (2 Me, 3 CH_2, 2 CH, and 1 C). The olefine signals at δ (H) 5.80, 5.05, and 4.91 were assigned to H−C(9) of the trisubstituted C=C bond and to CH_2(14) of the exocyclic C=C bond, respectively. Two Me groups were detected at δ(H) 1.92 (*d*, $J = 1.7$, Me(13)) and 1.46 (*s*, Me(15)). Finally, the *m*s (8 H) between δ 3.08 and 1.84 were assigned to CH_2(2), CH_2(3), CH_2(6), H−C(1), and H−C(5) by HMQC experiments. ^{1}H,^{1}H COSY experiments allowed us to establish the proton sequence. Significant HMBC long-range correlations H−C(9)/C(1), C(8), and C(15), Me(13)/C(7), C(11), and C(12), CH_2(14)/C(3) and C(5), and Me(15)/C(1), C(8), C(9), and C(10) unambiguously confirmed the suggested skeleton. The relative configuration of **1** at the stereogenic centers C(1), C(5), and C(10) was deduced from NOESY experiments (*Table 1*) and analysis of molecular models. The absence of an NOE H−C(5)/H−C(1) suggested a *transoid* fusion of the A and B rings. The suggested configuration was further supported by a series of clear NOE correlations, *i.e.*, H−C(1)/H_α−C(3), H_α−C(6), and Me(15), and H−C(5)/H_β−C(2) and H_β−C(6). In addition, these correlations suggested an α-orientation to the Me group at C(10). Finally, the remarkable pyridine-induced solvent shifts [26] (*Table 2*) for H_β−C(2) ($\Delta\delta = +0.33$) and H−C(5) ($\Delta\delta = +0.43$) supported the β-orientation of the OH group at C(10).

Menverin B (**2**), a colorless optically active oil, showed a UV absorption at 273 nm (log ε 3.69) and had the molecular formula $C_{15}H_{18}O_3$ (HR-EI-MS: *m*/*z* 246.1241 (M^+)), which was identical to that of **1**. HMBC and ^{1}H,^{1}H COSY experiments led to the same framework and proton sequence as those of **1**. The ^{13}C-NMR spectrum of **2** (*Table 1*) was also very similar to that of **1**, with the exception of the resonance of Me(15) (δ 22.9; δ 29.9 in **1**), suggesting a different configuration at C(10), *i.e.*, that **2** is the 10-epimer of **1**.

Clear NOE cross-peaks (*Table 1*) Me(15)/H_β−C(2), H−C(5) and H−C(9) and the absence of an NOE Me(15)/H−C(1) for **2** indicated a *transoid* A/B-ring fusion and a β-orientation of the Me group at C(10). Due to the α-orientation of OH−C(10), the pyridine-induced solvent shifts exhibited deshielding effects for H−C(1) ($\Delta\delta = 0.30$), H_α−C(2) ($\Delta\delta = 0.21$), and H−C(9) ($\Delta\delta = 0.40$) (*Table 2*).

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[2]) Relative configuration.

Table 1. *NMR Data* ($CDCl_3$)[a]) *for Menverin A* (**1**) *and B* (**2**)[b]). Arbitrary numbering[1]).

	1			**2**		
	δ(H)	δ(C)[c])	NOESY	δ(H)	δ(C)[c])	NOESY
H−C(1)	2.03 (*ddd*, *J* = 7.0, 9.5, 11.2)	55.4 (*d*)	H_α−C(3), H_α−C(6), Me(15)	2.16 (*ddd*, *J* = 7.3, 8.7, 10.7)	56.5 (*d*)	H_α−C(3), H_α−C(6)
H_α−C(2)	1.91 (*m*)	26.7 (*t*)	Me(15)	2.01 (*m*)	27.1 (*t*)	
H_β−C(2)	1.84 (*m*)		H−C(5), Me(15)	1.72 (*m*)		Me(15)
H_α−C(3)	2.38 (*m*)	32.4 (*t*)	H−C(1), H_a−C(14)	2.39 (*m*)	32.6 (*t*)	H−C(1), H_a−C(14)
H_β−C(3)	2.48 (*m*)		H_a−C(14)	2.44 (*m*)		
C(4)		155.6 (*s*)			155.3 (*s*)	
H−C(5)	2.71 (*ddd*, *J* = 3.2, 9.5, 12.2)	39.9 (*d*)	H_β−C(2), H_β−C(6), H_b−C(14)	2.39 (*m*)	41.5 (*d*)	H_β−C(2), H_b−C(14), Me(15)
H_α−C(6)	2.38 (*ddd*, *J* = 1.7, 12.2, 18.0)	33.9 (*t*)	H−C(1), Me(13), H_b−C(14)	2.39 (*m*)	33.6 (*t*)	H−C(1), Me(13), H_b−C(14)
H_β−C(6)	3.08 (*dd*, *J* = 3.2, 18.0)		H−C(5), Me(13), H_b−C(14)	3.03 (*d*, *J* = 14.3)		Me(13), H_b−C(14)
C(7)		147.9 (*s*)			148.3 (*s*)	
C(8)		148.8 (*s*)			146.4 (*s*)	
H−C(9)	5.80 (*s*)	119.6 (*d*)	Me(15)	5.86 (*s*)	121.9 (*d*)	Me(15)
C(10)		70.9 (*s*)			70.9 (*s*)	
C(11)		127.5 (*s*)			127.4 (*s*)	
C(12)		169.9 (*s*)			169.9 (*s*)	
Me(13)	1.92 (*d*, *J* = 1.7)	8.9 (*q*)	H_α−C(6), H_β−C(6)	1.92 (*s*)	8.9 (*q*)	H_β−C(6)
H_a−C(14)	5.05 (*d*, *J* = 1.3)	106.5 (*t*)	H_α−C(3), H_β−C(3)	5.05 (*d*, *J* = 1.5)	106.4 (*t*)	H_α−C(3)
H_b−C(14)	4.91 (*d*, *J* = 1.3)		H−C(5), H_α−C(6), H_β−C(6)	4.89 (*d*, *J* = 1.5)		H−C(5), H_α−C(6), H_β−C(6)
Me(15)	1.46 (*s*)	29.9 (*q*)	H−C(1), H_α−C(2), H_β−C(2), H−C(9)	1.35 (*s*)	22.9 (*q*)	H_β−C(2), H−C(5), H−C(9)

[a]) *Bruker DRX*-400-MHz spectrometer; chemical shifts in ppm referred to $CHCl_3$ (δ 7.26) and to $CDCl_{13}$ (δ 77.0), *J* in Hz. [b]) Assignments made by ^{1}H,^{1}H COSY, HMQC, and HMBC. [c]) By DEPT sequence.

Menverin C (**3**) was obtained as colorless optically active oil with a UV absorption at 275.5 nm (log ε 4.35) and a molecular formula $C_{15}H_{18}O_4$ (HR-EI-MS *m*/*z* 262.1199 (M^+)), thus containing an additional O-atom in comparison with both **1** and **2**. Comparison of the NMR data (*Table 3*) with those of **1** and **2** and remarkable pyridine-induced solvent shifts (*Table 2*) allowed us to assign a 1-hydroxylated structure to **3**.

The ^{1}H-NMR spectrum of **3** was similar to that of **1**, except for the absence of one proton between δ 3.13 and 1.72, in accordance with the replacement of an sp^3 CH by a tertiary oxygenated C-atom resonating at δ 85.2 (*s*) in the ^{13}C-NMR spectrum. Two separate spin system, CH_2(2)/CH_2(3) and H−C(5)/CH_2(6), revealed by

Table 2. *^{1}H-NMR Data* (C_5D_5N)[a]) *for Menverin A–D* (**1**–**4**). Arbitrary numbering[1]).

	1	**2**	**3**	**4**
H–C(1) or C(1)	2.00 (*ddd*, *J* = 6.9, 9.2, 11.1)	2.46 (*m*)		
H_α–C(2)	1.89 (*m*)	2.22 (*m*)	2.11 (*ddd*, *J* = 1.6, 8.0, 13.6)	2.14 (*dd*, *J* = 7.2, 12.5)
H_β–C(2)	2.17 (*m*)	1.84 (*m*)	2.83 (*m*)	2.58 (*ddd*, *J* = 7.7, 7.9, 12.5)
H_α–C(3)	2.40 (*m*)	2.38 (*m*)	2.89 (*m*)	2.50 (*dd*, *J* = 7.9, 14.4)
H_β–C(3)	2.47 (*m*)	2.38 (*m*)	2.57 (*m*)	2.96 (*m*)
H–C(5)	3.14 (*m*)	2.44 (*m*)	3.69 (br. *d*, *J* = 12.2)	3.09 (br. *d*, *J* = 9.9)
H_α–C(6)	2.30 (*ddd*, *J* = 2.0, 12.5, 18.0)	2.30 (*ddd*, *J* = 1.8, 7.7, 17.4)	3.13 (*ddd*, *J* = 1.9, 12.2, 18.2)	3.04 (*dd*, *J* = 3.5, 15.0)
H_β–C(6)	3.04 (*dd*, *J* = 3.0, 18.0)	2.94 (*dd*, *J* = 2.7, 17.4)	3.01 (*dd*, *J* = 4.0, 18.2)	3.60 (*dd*, *J* = 9.9, 15.0)
H–C(9)	6.12 (*s*)	6.26 (*s*)	6.10 (*s*)	6.31 (*s*)
Me(13)	1.80 (*d*, *J* = 2.0)	1.80 (*d*, *J* = 1.8)	1.79 (*d*, *J* = 1.9)	1.86 (*s*)
H_a–C(14)	5.09 (*s*)	5.09 (*s*)	5.19 (*d*, *J* = 1.6)	5.13 (*s*)
H_b–C(14)	4.99 (*s*)	4.98 (*s*)	5.12 (*d*, *J* = 1.6)	5.08 (*s*)
Me(15)	1.55 (*s*)	1.48 (*s*)	1.88 (*s*)	1.90 (*s*)

[a]) *Bruker DRX*-400-MHz spectrometer; chemical shifts in ppm referred to C_5H_5N (δ 7.20, 7.57, 8.73), *J* in Hz.

^{1}H,^{1}H COSY experiments, allowed us to assign the O bearing tertiary C-atom to C(1). HMBC Correlations C(1)/H_α–C(2) (δ 1.72), H_β–C(3) (δ 2.48), H–C(9) (δ 5.65) and Me(15) (δ 1.55) supported the suggested structure. The relative configuration of **3** was suggested by both NOESY (*Table 3*) and pyridine-induced solvent shifts (*Table 2*), supported by analysis of molecular models. The *s* at δ 1.55 (Me(15)) exhibited NOE correlations with H_α–C(2), H_β–C(2), and H–C(9), whereas no NOEs Me(15)/H–C(5) and H–C(6) were observed. In addition, the multiplicity of H–C(5) (br. *dd*, *J* = 12.2, 3.9 Hz) revealed coupling with the two protons at C(6), which was almost identical to that observed for H–C(5) of **1** (see *Table 1*). This comparison strongly supported, in analogy with **1**, a *transoid* A/B-ring junction. The α-orientation of Me(15) suggested by the absence of an NOE Me(15)/H–C(5), was further supported by the pyridine-induced solvent shifts. In fact, in accordance with a β-orientation of OH–C(10), relevant pyridine-induced shifts were observed for H_β–C(2) ($\Delta\delta = +0.45$) and H–C(5) ($\Delta\delta = +0.56$). Finally, the remarkable deshielding effect for H_α–C(2) ($\Delta\delta = +0.39$), H_α–C(3) ($\Delta\delta = +0.31$), and H_α–C(6) ($\Delta\delta = +0.42$), attributed to their interactions with the axial OH–C(1), was consistent with the assigned relative structure of **3**.

Menverin D (**4**) was a colorless oil with a UV absorption at 277.5 nm (log ε 4.43) and a molecular formula $C_{15}H_{18}O_4$ (HR-EI-MS: *m*/*z* 262.1214 (M^+)), identical to that of **3**. Also, the same framework and proton sequence as those of **3** were revealed by HMBC and ^{1}H,^{1}H COSY experiments of **4**. Further comparison of the NMR data (*Table 3*) and analysis of the pyridine-induced solvent shifts (*Table 2*) suggested that **4** had to be the 1-epimer of **3**. The absolute configuration of **4** remains to be established.

The main difference in the ^{1}H-NMR spectra of **3** and **4** was the pattern of the H–C(5) signal (**4**: br. *dd*, *J* = 7.1, 4.5 Hz; **3**: br. *dd*, *J* = 12.2, 3.9 Hz) and CH_2(6) (**4**: *dd*, *J* = 4.5, 16.0 Hz for H_α–C(6) and *dd*, *J* = 7.1, 16.0 Hz for H_β–C(6); **3**: *ddd*, *J* = 1.9, 12.2, 18.5 Hz for H_α–C(6) and *dd*, *J* = 3.9, 18.5 Hz for H_β–C(6). This observation suggested a different A/B-ring junction. This was supported by the ^{13}C-NMR data, which were similar to those of **3**, except for the downfield-shifted signals assigned to C(1) and C(5) at δ 89.2 (*s*) and 51.6 (*d*) (**3**: δ 85.2, 42.1), respectively. The *cisoid* A/B-ring junction was clearly confirmed by the NOE Me(15) (δ 1.62)/H_α–C(6) (δ 2.86), whereas no NOE Me(15)/H–C(5) was observed. The α-orientation of Me(15) was also determined in turn. The pyridine-induced deshielding effects on H_β–C(3) ($\Delta\delta = +0.36$) and H_α–C(3) ($\Delta\delta = +0.15$) could be explained by the β-orientation of OH–C(1).

Table 3. *NMR Data* ($CDCl_3$)[a]) *for Menverin C* (**3**) *and D* (**4**)[b]). Arbitrary numbering[1]).

	3			**4**		
	δ(H)	δ(C)[c])	NOESY	δ(H)	δ(C)[c])	NOESY
C(1)		85.2 (*s*)			89.2 (*s*)	
H_α–C(2)	1.72 (*ddd*, *J* = 1.6, 8.3, 13.2)	34.2 (*t*)	Me(15)	1.76 (*dd*, *J* = 7.7, 13.3)	35.0 (*t*)	H_α–C(3), H_β–C(3)
H_β–C(2)	2.38 (*ddd*, *J* = 3.0, 9.1, 13.2)		H–C(5), Me(15)	2.01 (*ddd*, *J* = 7.7, 7.9, 13.3)		H_α–C(3), H_β–C(3)
H_α–C(3)	2.58 (*m*)	29.8 (*t*)		2.35 (*dd*, *J* = 7.9, 15.2)	31.3 (*t*)	H_α–C(2, H_β–C(2), H_a–C(14)
H_β–C(3)	2.48 (*m*)		H–C(5), H_a–C(14)	2.60 (*m*)		H_α–C(2), H_β–C(2)
C(4)		154.2 (*s*)			153.9 (*s*)	
H–C(5)	3.13 (br. *dd*, *J* = 3.9, 12.2)	42.8 (*d*)	H_β–C(2), H_β–C(3)	2.72 (br. *dd*, *J* = 4.5, 7.1)	51.6 (*d*)	H_α–C(6), H_β–C(6)
H_α–C(6)	2.71 (*ddd*, *J* = 1.9, 12.2, 18.5)	26.4 (*t*)	Me(13)	2.86 (*dd*, *J* = 4.5, 16.0)	27.6 (*t*)	H–C(5), Me(13), Me(15)
H_β–C(6)	2.91 (*dd*, *J* = 3.9, 18.5)		Me(13), H_b–C(14)	3.11 (*dd*, *J* = 7.1, 16.0)		H–C(5), Me(13)
C(7)		148.3 (*s*)			148.0 (*s*)	
C(8)		149.2 (*s*)			150.7 (*s*)	
H–C(9)	5.65 (*s*)	116.3 (*d*)	Me(5)	5.85 (*s*)	117.6 (*d*)	Me(15)
C(10)		73.5 (*s*)			75.3 (*s*)	
C(11)		127.6 (*s*)			126.4 (*s*)	
C(12)		169.9 (*s*)			170.3 (*s*)	
Me(13)	1.93 (*d*, *J* = 1.9)	8.9 (*q*)	H_α–C(6), H_β–C(6)	1.92 (*s*)	8.6 (*q*)	H_α–C(6), H_β–C(6)
H_a–C(14)	5.05 (*d*, *J* = 1.6)	107.1 (*t*)	H_β–C(3)	5.02 (*s*)	105.9 (*t*)	H_α–C(3)
H_b–C(14)	4.89 (*d*, *J* = 1.6)		H–C(5), H_β–C(6)	4.86 (*s*)		H_α–C(6), H_β–C(6)
Me(15)	1.55 (*s*)	26.1 (*q*),	H_α–C(2), H_β–C(2), H–C(9)	1.62 (*s*)	26.5 (*q*),	H_α–C(6), H–C(9)

[a]) *Bruker DRX*-400-MHz spectrometer; chemical shifts in ppm referred to $CHCl_3$ (δ 7.26) and to $CDCl_3$ (δ 77.0), *J* in Hz. [b]) Assignments made by ^{1}H,^{1}H COSY, HMQC and HMBC. [c]) By DEPT sequence.

The instability of all the compounds prevented further spectral experiments. In particular, the color of **2** changed to yellow in the NMR tube. After a mini column chromatography (silica gel), a light yellow oil was obtained (menverin E (**6**; 0.6 mg), with a molecular formula $C_{15}H_{16}O_2$ (HR-EI-MS: *m*/*z* 228.1149 (M^+)), in accordance with the loss H_2O from **2**). The structure of **6** was readily deduced from its spectral data and confirmed by comparison of the ^{13}C-NMR data of **2** and **6**.

The ^{1}H-NMR spectrum of **6** was similar to that of **2** with three olefinic protons (δ 5.97, 5.08, 4.96) and three proton *s* at δ 1.93. However, one proton was absent in the high-field region between δ 3.21 and 2.32, whereas Me(15) was remarkably downfield-shifted to δ 1.87 (δ 1.35 in **2**), a typical shift value of a Me group attached to a conjugated system.

The study of the gorgonian *M. verrucosa* revealed a series of guaiane sesquiterpenoids exhibiting new structural features. The high instability of the sesquiterpenoids

prevented both full characterization of their configurations and screening of their bioactivities.

After this preliminary study, further studies are necessary to complete the chemical and biological investigation of this interesting class of compounds.

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Experimental Part

General. Column chromatography (CC): silica gel (*Qing Dao Hai Yang Chemical Group Co.*; 200–300 and 400–600 mesh). Anal. TLC: precoated silica-gel plates (*Yan Tai Zi Fu Chemical Group Co.*; *G60 F-254*). Optical rotations: *Perkin-Elmer 341* polarimeter. UV Spectra: *Varian Cary-300* spectrophotometer; λ_{max} (log ε) in nm. NMR Spectra: *Bruker DRX-400* spectrometer; at 400 MHz for ^{1}H and 100 MHz for ^{13}C; chemical shifts δ in ppm, with residual $CHCl_3$ (δ(H) 7.26, δ(C) 77.0) or C_5H_5N (δ(H) 7.20, 7.57, 8.73) as internal standard, coupling constants J in Hz; assignments supported by ^{1}H,^{1}H-COSY, HMQC, HMBC, and NOESY experiments. EI-MS and HR-EI-MS: *Finnigan MAT-95* mass spectrometer; in m/z.

Animal Material. The specimen of the gorgonian *Menella verrucosa* (BRUNDIN) was collected along the cost of Xiaodong hai, Hainan Province, China, in December 2001, at a depth of 20 m, and was frozen immediately after collection. The species of gorgonian was identified by Prof. *Ren-lin Zhou*. A voucher specimen is available for inspection at the Institute of Materia Medica, SIBS-CAS.

Extraction and Purification. The frozen animals (209 g, dried weight) were cut into pieces and extracted exhaustively with acetone at r.t. (3×1.5 l). The org. extract was evaporated to give a residue, which was partitioned between Et_2O and H_2O. The Et_2O soln. was evaporated to give a dark green residue (3.3 g), which was fractionated by CC (silica gel, $0 \rightarrow 100\%$ acetone/petroleum ether) yielding some fractions showing interesting yellow TLC spots on TLC ($CHCl_3$/Et_2O 9:1) after spraying with H_2SO_4: R_f 0.5, 0.45, and 0.15. The three fractions were purified by CC (*Sephadex LH-20* petroleum ether/$CHCl_3$/MeOH 2:1:1) followed by normal-phase CC (silica gel): **1** (3.0 mg) and **2** (4.6 mg) and a more-polar mixture. The latter was subjected to reversed-phase HPLC (semi-prep. *ODS-HG-5* (5μ, 250×10 mm), MeCN/H_2O 3:1, 2.5 ml/min): **3** (2.1 mg; t_R 24.7 min) and **4** (1.8 mg; t_R 29.4 min).

Menverin A (= rel-*(4a*R,*7a*S,*8*S*)-4a,5,6,7,7a,8-Hexahydro-8-hydroxy-3,8-dimethyl-5-methyleneazuleno[6,5-*b*]furan-2(4*H*)-one*; **1**): Colorless oil. $[\alpha]_D^{20} = -160$ ($CHCl_3$, $c = 0.09$). UV (MeOH): 273 (4.06). ^{1}H-NMR ($CDCl_3$, 400 MHz) and ^{13}C-NMR ($CDCl_3$, 100 MHz): *Table 1*. ^{1}H-NMR (C_5D_5N, 400 MHz): *Table 2*. EI-MS: 246 (M^+), 231, 228, 217, 203, 185, 167, 149, 97, 57 (100). HR-EI-MS: 246.1270 ($C_{15}H_{18}O_3^+$; calc. 246.1256).

Menverin B (= rel-*(4a*R,*7a*S,*8*R*)-4a,5,6,7,7a,8-Hexahydro-8-hydroxy-3,8-dimethyl-5-methyleneazuleno[6,5-*b*]furan-2(4*H*)-one*; **2**): Colorless oil. $[\alpha]_D^{20} = -53$ ($CHCl_3$, $c = 0.08$). UV (MeOH): 273 (3.69). ^{1}H-NMR ($CDCl_3$, 400 MHz) and ^{13}C-NMR ($CDCl_3$, 100 MHz): *Table 1*. ^{1}H-NMR (C_5D_5N, 400 MHz): *Table 2*. EI-MS: 246 (M^+), 231 (100), 228, 217, 203, 185, 167, 149, 97, 57. HR-EI-MS: 246.1241 ($C_{15}H_{18}O_3^+$; calc. 246.1256).

Menverin C (= rel-*(4a*R,*7a*S,*8*S*)-4a,5,6,7,7a,8-Hexahydro-7a,8-dihydroxy-3,8-dimethyl-5-methyleneazuleno[6,5-*b*]furan-2(4*H*)-one*; **3**): Colorless oil. $[\alpha]_D^{20} = -152$ ($CHCl_3$, $c = 0.375$). UV (MeOH): 275.5 (4.35). ^{1}H-NMR ($CDCl_3$, 400 MHz) and ^{13}C-NMR ($CDCl_3$, 100 MHz): *Table 3*. ^{1}H-NMR (C_5D_5N, 400 MHz): *Table 2:* EI-MS: 262 (M^+), 244, 229, 201, 187, 167, 124 (100), 96. HR-EI-MS: 262.1199 ($C_{15}H_{18}O_4^+$; calc. 262.1205).

Menverin D (= rel-*(4a*R,*7a*R,*8*S*)-4a,5,6,7,7a,8-Hexahydro-7a,8-dihydroxy-3,8-dimethyl-5-methyleneazuleno[6,5-*b*]furan-2(4*H*)-one*; **4**): Colorless oil. UV (MeOH): 273 (4.06). ^{1}H-NMR ($CDCl_3$, 400 MHz) and ^{13}C-NMR ($CDCl_3$, 100 MHz): *Table 3*. ^{1}H-NMR (C_5D_5N, 400 MHz): *Table 2*. EI-MS: 262 (M^+), 244, 229, 201, 167, 124 (100), 96. HR-EI-MS: 262.1220 ($C_{15}H_{18}O_4^+$; calc. 262.1205).

Menverin E (=*4a,5,6,7-Tetrahydro-3,8-dimethyl-5-methyleneazuleno[6,5-b]furan-2(4*H*)-one*; **6**): Light yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.97 (*s*, H–C(9)); 5.08, 4.96 (2*s*, CH_2(14)); 3.21 (br. *d*, $J = 14.7$, H–C(5)); 2.96 (*d*, $J = 15.0$, 1 H–C(6)); 2.30–1.58 (complex, CH_2(2), CH_2(3), 1 H–C(6)); 1.93 (*s*, Me(13)); 1.87 (*s*, Me(15)). ^{13}C-NMR (100 MHz, $CDCl_3$): 170.0 (*s*), 154.1 (*s*); 150.8 (*s*); 147.5 (*s*); 147.0 (*s*); 123.2 (*s*); 122.3 (*s*); 115.0 (*d*); 106.1 (*t*); 44.5 (*d*); 32.6 (*t*); 31.5 (*t*); 29.8 (*t*); 21.0 (*q*); 8.6 (*q*). EI-MS: 228 (M^+), 213, 199, 185, 167, 149, 111, 97, 57 (100). HR-EI-MS: ($C_{15}H_{16}O_2^+$; calc. 228.1150).

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