Isomeric *ent*-Labdane-Type Diterpenoids from the Stems of *Rhizophora mucronata*

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Two new constitutional isomers of *ent*-labdane-type diterpenoids, **1** and **2**, with an unusual seven-membered lactone moiety (*i.e.*, **1**), together with two known compounds, **3** and **4**, were isolated from the acetone extract of *Rhizophora mucronata*. Their structures were elucidated as rhizomucronol A and B (**1** and **2**, resp.) by spectroscopic analyses and chemical evidence. The absolute configuration of **2** was established by applying the *Mosher* ester procedure.

Introduction. – *Rhizophora mucronata* (Rhizophoraceae) is an evergreen shrub or small tree that occurs in the Indo-Pacific region on the banks of the rivers and on the sea coast [1]. It is used as a folk medicine in Southeast Asia for the treatment of angina, haemorrhage, haematuria, diarrhoea, and diabetes [2]. Previous chemical studies on this plant revealed the presence of a variety of sesquiterpenoids, diterpenoids [3][4], triterpenoids, steroids [5–7], and tannins [8]. Mangroves are widely recognized as an emerging source of novel metabolites with intriguing molecular architectures [9]. In our ongoing program on the bioactive constituents of the Indian mangrove flora [10–12], two new constitutional isomers, named rhizomucronol A and B (**1** and **2**, resp.), together with two known compounds **3** and **4** (*Fig. 1*) were isolated from *R. mucronata*. The structures of the new compounds were elucidated by extensive NMR analysis (HSQC, HMBC, COSY, and NOESY), as well as by chemical transformations. The absolute configuration of compound **2** was established by a convenient modified *Mosher* ester method in NMR tubes. In addition, the two known compounds were characterized as rhizophorin B [13] and manool [14], by comparison of their physical and spectroscopic data with those reported. Epimers of 3-nor-δ-lactones in ring *A* have been already reported [15][16], while constitutional isomers with an ε-lactone in ring *A* are uncommon.

Results and Discussion. – Rhizomucronol A (**1**) was obtained as amorphous, optically active solid ($[\alpha]_D^{27} = -125$ ($c = 0.12$, $CHCl_3$)). The HR-ESI-MS exhibited a sodiated molecular-ion peak at *m/z* 359.2206 ($C_{20}H_{32}NaO_4^+$; calc. 359.2198), in conjunction with the ^{13}C-NMR spectrum, providing the molecular formula $C_{20}H_{32}O_4$. The IR spectrum of **1** displayed absorption bands attributable to OH (3407 cm^{-1}), lactone CO (1712, 1218 cm^{-1}), vinyl (1507, 921 cm^{-1}), and ether (1118 cm^{-1}) groups. The ^{1}H-NMR spectrum of **1** (*Table 1*) displayed diagnostic resonances for a

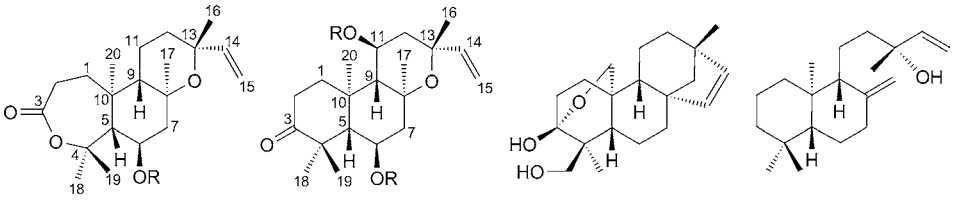

Fig. 1. *Compounds isolated from* Rhizophora mucronata

monosubstituted vinyl moiety (δ(H) 4.99 (*d*, *J* = 18.0, 1 H), 4.96 (*d*, *J* = 10.8, 1 H), and 5.98 (*dd*, *J* = 18.0, 11.4, 1 H)), and five tertiary Me groups (δ(H) 1.41 (*s*, 3 H), 1.29 (*s*, 3 H), 1.71 (*s*, 3 H), 1.59 (*s*, 3 H), and 0.98 (*s*, 3 H)). One O-bearing CH signal at δ(H) 3.92 (*td*, *J* = 10.8, 4.2, 1 H) was shifted downfield to δ(H) 5.00 (*td*, *J* = 11.2, 4.5, 1 H) in the case of its monoacetate **1a**. The ^{13}C-NMR (*Table 1*) spectrum of **1** showed signals corresponding to all 20 C-atoms, including those of five tertiary Me, six CH_2 (one olefinic), and four CH groups (one O-bearing), and five quaternary C-atoms (one lactone CO), as discerned from its DEPT and HSQC spectra. From the ^{13}C-NMR data (*Table 1*), a labdane-type diterpene structure was proposed for **1**. Two O-bearing C-atom signals at δ(C) 74.2 and 73.7 were ascribed to C(8) and C(13) of 13-epimanoyol oxide [17]. The downfield chemical shifts for Me(18) and Me(19) disclosed the position of quaternary OH group at C(4), with the possibility of C(3) carrying a lactone or an acid carboxy group. Also, the location of a OH group at C(4) was further supported by the HMBC from Me(18) and Me(19) to C(4) and C(5). Based on these data, compound **1** possesses a seven-membered lactone in ring *A*. The CH–O signal could be spectroscopically allocated to C(6) or C(11) owing to the multiplicity and *J* values in the tricyclic architecture of the molecule. Accordingly, the oxygenation at C(6) was eventually ascribed by comparing its ^{13}C chemical shift of C(7) (δ(C) 51.6) with the reported values of C(7) (δ(C) 50–53) [18] and C(12) (δ(C) 40–45) [18] in related diterpenoids. This was further supported by HMBCs from H–C(6) to C(4), C(5), and C(7), and from H–C(7) to C(5), C(6), C(8), C(9), and C(17).

The ^{1}H,^{1}H-COSY spectrum (*Table 2* and *Fig. 2*) showed spin systems corresponding to H–C(9)/H–C(11)/H–C(12); H–C(14)/H–C(15); H–C(1)/H–C(2); and H–C(5)/H–C(6)/H–C(7). The relative configuration was assigned on the basis of the NOESY correlations (*Table 2* and *Fig. 3*) H–C(5)/H–C(9); H–C(14)/Me(17); H–C(7)/Me(17); and H–C(6)/Me(17) and Me(20). The absence of correlations between H–C(9) and Me(17), and H–C(5) and Me(20) established the overall configuration of the rings *A*, *B*, and *C* as *trans-trans-trans*, and β-configuration of OH group at C(6). The relative configuration at C(16) was deduced from the ^{13}C chemical-shift value of C(16) (δ(C) 32.6) compared with that of the related epimanoyl oxide series (δ(C) 33.0) [19][20]. It was considered to be an *ent*-derivative in view of its negative specific rotation [21]. This unambiguously established the structure of rhizomucronol A (**1**) as *ent*-8,13-epoxy-6β-hydroxy-13-epilabd-14-en-3,4-olide. 3-Nor δ-lactones in ring *A* are known in the literature belonging to the manoyl oxide series isolated from *Dacrydium colensoi* [15] as well as 13-epimanoyl oxide series from *Excoecaria agallocha* [16], which might be

Table 1. *^{1}H- and ^{13}C-NMR Chemical Shifts* (in $CDCl_3$) *of Compounds* **1**, **1a**, **2**, *and* **2a**. δ in ppm; J in Hz.

Position	δ(H)				Position	δ(C)	
	1	**1a**	**2**	**2a**		**1**	**2**
1	1.19 (*td*, J = 13.8, 4.2, H_α), 1.70 – 1.72 (*m*, H_β)	2.00 – 2.06 (*m*, H_α), 1.84 (*td*, J = 14.1, 4.4, H_β)	2.42 – 2.50 (*m*, H_α), 1.90 – 2.01 (*m*, H_β)	2.33 – 2.36 (*m*, H_α), 1.91 – 1.97 (*m*, H_β)	1	40.7	40.2
					2	32.4	33.0
2	2.72 (*td*, J = 13.8 ,6.6, H_α), 2.47 (*dt*, J = 7.8, 3.6, H_β)	2.71 (*td*, J = 14.0, 6.2, H_α), 2.50 (*dt*, J = 7.6, 4.2, H_β)	2.70 – 2.80 (*m*, H_α), 2.24 – 2.31 (*m*, H_β)	2.72 – 2.80 (*m*, H_α), 2.24 – 2.30 (*m*, H_β)	3	174.5	206.8
					4	86.1	47.5
5	1.90 (*d*, J = 10.2)	2.24 (*d*, J = 10.9)	1.85 (*d*, J = 10.5)	1.80 (*d*, J = 10.3)	5	57.2	59.3
6	3.92 (*td*, J = 10.8, 4.2)	5.00 (*td*, J = 11.2,4.5)	3.83 (*td*, J = 12.8, 6.0)	4.93 (*td*, J = 11.5, 4.2)	6	68.0	67.8
7	2.05 (*dd*, J = 11.4, 4.2, H_α), 1.51 – 1.55 (*m*, H_β)	2.25 – 2.28 (*m*, H_α), 1.55 – 1.58 (*m*, H_β)	2.05 (*dd*, J = 11.3, 4.5, H_α), 1.55 – 1.62 (*m*, H_β)	2.18 – 2.22 (*m*, H_α), 1.54 – 1.62 (*m*, H_β)	7	51.6	52.3
					8	74.2	75.4
9	1.31 – 1.33 (*m*)	1.36 – 1.38 (*m*)	1.43 (*d*, J = 10.5)	1.46 – 1.51 (*m*)	9	59.5	61.8
11	1.55 – 1.60 (*m*, H_α), 1.55 – 1.60 (*m*, H_β)	1.54 – 1.59 (*m*, H_α), 1.54 – 1.59 (*m*, H_β)	4.13 (*td*, J = 10.5, 4.5, H_α)	5.27 (*td*, J = 8.5, 4.4, H_α)	10	39.2	38.8
					11	17.0	65.6
12	2.26 – 2.28 (*m*, H_α), 1.45 – 1.50 (*m*, H_β)	2.26 – 2.28 (*m*, H_α), 1.46 – 1.59 (*m*, H_β)	2.50 (*dd*, J = 12.8, 3.7, H_α), 1.59 – 1.62 (*m*, H_β)	2.53 (*dd*, J = 13.5, 4.4, H_α), 1.60 – 1.62 (*m*, H_β)	12	34.9	45.5
					13	73.7	74.4
14	5.98 (*dd*, J = 18.0, 11.4)	5.77 (*dd*, J = 18.1, 11.1)	5.94 (*dd*, J = 17.3, 10.5)	5.91 (*dd*, J = 17.7, 10.9)	14	146.7	147.3
15	4.99 (*d*, J = 18.0, H_α), 4.96 (*d*, J = 10.8, H_β)	4.98 (*d*, J = 13.5, H_α), 4.59 (*d*, J = 6.5, H_β)	5.06 (*d*, J = 18.1, H_α), 4.94 (*d*, J = 10.5, H_β)	5.26 (*d*, J = 17.8, 5.04 (*d*, J = 11.1, H_β)	15	110.2	110.1
					16	32.6	32.4
16	1.41 (*s*)	1.12 (*s*)	1.23 (*s*)	1.21 (*s*)	17	23.4	25.1
17	1.29 (*s*)	1.25 (*s*)	1.26 (*s*)	1.25 (*s*)	18	32.5	19.3
18	1.71 (*s*)	1.65 (*s*)	1.28 (*s*)	1.28 (*s*)	19	27.0	31.9
19	1.59 (*s*)	1.34 (*s*)	1.36 (*s*)	1.38 (*s*)	20	19.0	17.1
20	0.98 (*s*)	1.02 (*s*)	0.84 (*s*)	1.05 (*s*)			
Ac		2.04 (*s*)		2.05 (*s*)			

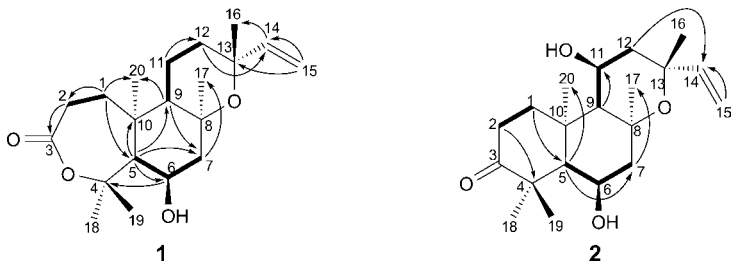

Fig. 2. *$^1H,^1H$-COSY* (—) *and key HMBC* (H → C) *correlations of compounds* **1** *and* **2**

Table 2. *Key HMBCs and $^1H,^1H$-COSY and NOESY Correlations of Compounds* **1** *and* **2**

Position	**1**			**2**		
	HMBC	COSY	NOESY	HMBC	COSY	NOESY
1α	2, 3, 5, 10, 20	2α, 2β		2, 5, 10, 20	1β	20
1β	2, 3, 5, 10, 20	2α		2, 5, 10, 20	1α, 2α	9
2α	1, 3, 10	1α, 2β	18, 5	1, 10	1α, 2β	19
2β	1, 3, 10	2α		1, 10, 4	2α	
5	1, 4, 6, 7, 9, 18, 19, 20	6	2α, 7α, 9	1, 4, 6, 7, 9, 10, 18, 19, 20	6	7β, 9, 19
6	4, 5, 7	5, 7β	17, 19, 20		5, 7β	17, 20
7α	5, 6, 8, 9, 17	7β	5, 17	5, 6, 8, 9, 17	7β	17
7β	5, 6, 8, 9, 17	6, 7α		5, 6, 8, 9, 17	6, 7α	5
9	1, 7, 8, 10, 11, 12, 17, 20	11α, 11β	5	1, 5, 7, 8, 10, 11, 12, 17, 20	11	1β, 5, 16
11α	9, 12, 13	9, 12α, 12β			9, 12β	17, 20
11β	9, 12, 13	9, 12α, 12β				
12α	9, 11, 13, 14	11α, 11β, 12β	16, 15	9, 11, 13, 14	12β	15, 16
12β	9, 11, 13, 14	11α, 11β, 12α		9, 11, 13, 14	11, 12α	
14	12, 16	15α, 15β	17	12	15α, 15β	17
15α	13, 14	14, 15β	12α	13, 14	14, 15β	12α, 17
15β	13, 14	14, 15α		13, 14	14, 15α	
16	12, 13, 14		12α	12, 13, 14		12α, 9
17	7, 8, 9		6, 7α, 14	7, 8, 9		6, 7α, 11, 14, 15, 20
18	4, 5, 19		2α	4, 5, 19		
19	4, 5, 18		6	4, 5, 18		2α, 5
20	1, 5, 9, 10		6, 19	1, 5, 9, 10		1α, 6, 11, 17

derived from a hydroxy acid formed from ring *A* seco derivative after loss of a C-atom as CO_2. Our study revealed that **1** possesses an unusual seven-membered lactone moiety in ring *A*, which might be formed from a seco-hydroxy acid without loosing a C-atom.

Rhizomucronol B (**2**) was obtained as an amorphous optically active solid ($[\alpha]_D^{27} = -105$ ($c = 0.13$, $CHCl_3$)). The HR-ESI-MS of **2** exhibited a *pseudo*-molecular ion ($[M+Na]^+$) peak at *m/z* 359.2199 ($C_{20}H_{32}NaO_4^+$; calc. 359.2198), providing the same molecular formula $C_{20}H_{32}O_4$ as for compound **1**. However, **2** showed different spectral

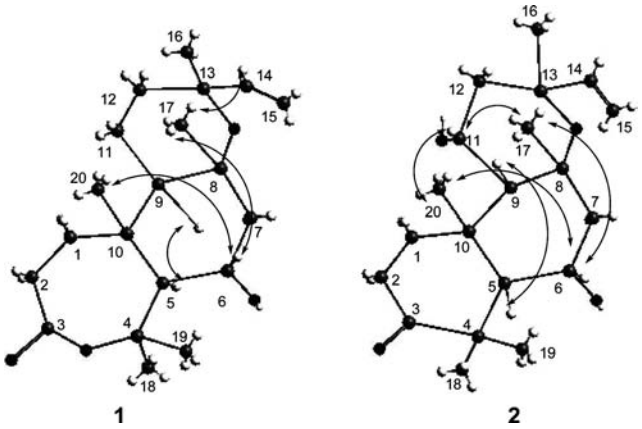

Fig. 3. *Key NOESY* (H ↔ H) *correlations of compounds* **1** *and* **2**

features (IR, ^{1}H-, ^{13}C-NMR, DEPT, HSQC, HMBC, COSY, and NOESY) compared with those of **1**, and was designated as a constitutional isomer of **1**. The IR spectrum of **2** displayed absorptions for OH (3413 cm^{-1}), CO (1716 cm^{-1}), vinyl (1605, 920 cm^{-1}), and ether (1115 cm^{-1}) groups. Acetylation of **2** gave a diacetate **2a**, which showed signals of two *O*-Ac acetyl groups at δ(H) 2.05 (*s*, 6 H), indicating the presence of two OH groups in the molecule. Further, the ^{1}H-NMR spectrum of **2** exhibited signals of five tertiary Me groups, a vinyl group, and two carbinol H-atoms, which were shifted to downfield in the case of its diacetate from δ(H) 3.83 (*td*, J = 12.8, 6.0, 1 H), 4.13 (*td*, J = 10.5, 4.5, 1 H) to δ(H) 4.93 (*td*, J = 11.5, 4.2, 1 H), 5.27 (*td*, J = 8.5, 4.4, 1 H), respectively. The ^{13}C-NMR spectrum with DEPT and HSQC experiments exhibited 20 C-atom resonances, including those of five tertiary Me, five CH_2, and five CH groups, and five quaternary C-atoms. The two O-bearing C-atom signals at δ(C) 67.8 and 65.6 might be attributed to C(6), analogous to compound **1**, and to C(11) on the basis of multiplicity, J values, and chemical shifts. This is in accordance with the observed chemical shift of C(12) (δ(C) 45.5), comparable with that of the related 11-hydroxyepimanoyl oxides [18] (δ(C) 40–45). Further, the HMBCs from H–C(7) to C(5), C(6), C(8), C(9), and C(17), and from H–C(12) to C(9), C(11), C(13), and C(14) supported oxygenations at C(6) and C(11). The partial connectivities H–C(9)/H–C(11)/H–C(12); and H–C(15)/H–C(16), deduced from the COSY spectrum, indicated that the vinyl group was located at C(13), suggesting that **2** contains an epimanoyl oxide C-atom framework, which was further confirmed by the HMBC spectrum (*Table 2* and *Fig. 2*). The relative configurations at C(6) and C(11) were established as β-OH due to significant correlations between H_α–C(6), and Me(17) and Me(20); and H_α–C(11), and Me(17) and Me(20) in the NOESY spectrum. The absolute configuration at the OH bearing centres were determined by application of the *Mosher* ester method, which can be carried out in NMR tubes [22]. Treatment of compound **2** with (*R*)- and (*S*)-MTPA ((*R*)- and (*S*)-methoxy(trifluoromethyl)phenylacetic acid, resp.) chloride in the presence of (D_5)pyridine in NMR tubes at room temperature afforded the (*R*)- and (*S*)-MTPA ester derivatives **2b** and **2c**, respectively. The signals due to H-atoms at C(2), C(14), C(16), C(18), and C(19), C(20) in **2b**

appeared at higher fields than those of **2c** ($\Delta\delta$: negative), while the signals due to H-atoms at C(1), C(5), C(6), C(7), C(9), and C(11), C(12), C(17) in **2b** appeared at lower fields than those of **2c** ($\Delta\delta$(H): positive). Consequently, the configurations at C(6) and C(11) were deduced as (*R*) and (*S*) respectively. Thus the structure of rhizomucronol B (**2**) was deduced as *ent*-8,13-epoxy-6,11-dihydroxy-13-epilabd-14-en-3-one (*Fig. 4*).

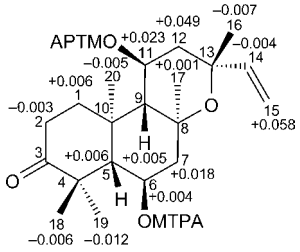

Fig. 4. *$\Delta\delta$(H) Values* ($\Delta\delta(H)\,[ppm] = \delta(H)_S - \delta(H)_R$) *obtained for the (*2S*)- and (*2R*)-MTPA esters of rhizomucronol B* (**2**)

In conclusion, we identified two new isomers of *ent*-labdane-type diterpenoids in the stems of *Rhizophora mucronata*.

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Experimental Part

General. IR Spectra: *Nicolet-740* FT-IR spectrophotometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker Avance* (300 MHz), *Varian Inova* (400 MHz), and *Bruker Avance II* (600 MHz) for ^{1}H-NMR, and 75, 100, and 150 MHz for ^{13}C-NMR spectra; in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. ESI-MS *Agilent 1100 MSD* with *ESI SL Trap*; in *m*/*z*. HR-ESI-MS *Agilent 6510 Q-TOF* and ESI probe; in *m*/*z*.

Plant Material. The stems of *Rhizophora mucronata* were collected from the Ernakulam mangrove forest (latitude, 10° 00′ N; and longitude, 76° 25′ E; India, March 2009), and were authenticated by Prof. *M. Venkaiah*, Department of Botany, Andhra University, Visakhapatnam. A voucher specimen (#IIC-MG-110) has been deposited with the Herbarium of Natural Product Chemistry, I.I.C.T.

Extraction and Isolation. The air-dried and powdered stems (1.0 kg) of *R. mucronata* were extracted with acetone (10 l) in a *Soxhlet* apparatus for 18 h to give a crude extract (25.0 g). A part of the acetone extract (20.0 g) was subjected to vacuum liquid chromatography (VLC) on silica gel (SiO_2; 230–400 mesh) and eluted with binary mixtures of hexane and acetone of increasing polarity to give ten fractions of 800 ml each. The identical fractions were pooled, based on the TLC profile. A total of four main fractions with prominent spots on TLC were obtained. These fractions were further subjected to CC (SiO_2) to afford compounds **1**–**4**. Compound **4** (1.5 mg) was obtained from *Fr. 1*; and compound **1** (2.0 mg) was obtained from *Fr. 3*, while compounds **2** (5.0 mg) and **4** (2.0 mg) were isolated from *Fr. 4*.

Acetylation of Compounds **1** *and* **2**. Compound **1** or **2** (each 1 mg) was dissolved in a mixture of pyridine (0.1 ml) and Ac_2O (0.1 ml), and the soln. was left overnight at r.t. After usual workup, the product was purified by recrystallization from hexane to afford **1a** (1 mg), and **2a** (1 mg), resp.

*Preparation of the (*R*)- and (*S*)-MTPA (=(*R*)- and (*S*)-Methoxy(trifluoromethyl)phenylacetic Acid) Ester Derivatives of* **2** *by* Mosher *Ester Procedure* [22]. Two equal portions of compound **2** were treated with (*R*)- and (*S*)-MTPA chloride (6 µl), resp., in the presence of (D_5)pyridine (0.75 ml) in separate NMR tubes at r.t. for 6 h to afford the (*R*)- and (*S*)-MTPA esters, **2b** and **2c**, resp.

*(*R*)-MTPA Ester of Rhizomucronol B*, **2b**. ^{1}H-NMR ($CDCl_3$, 300 MHz): 6.13 (*dd*, *J* = 17.8, 10.9, H–C(14)); 5.17 (*d*, *J* = 17.7, H_α–C(15)); 4.94 (*d*, *J* = 11.5, H_β–C(15)); 4.43 (*td*, *J* = 9.9, 4.1, H–C(11)); 4.15 (*td*, *J* = 11.1, 4.1, H–C(6)); 3.03–3.04 (*m*, H_α–C(2)); 2.93–2.94 (*m*, H_α–C(1)); 2.79 (*dd*, *J* = 13.1, 4.1, H_α–C(12)); 2.50 (*dd*, *J* = 11.7, 4.1, H_α–C(7)); 2.34–2.40 (*m*, H_β–C(2)); 2.30 (*td*, *J* = 14.3, 3.2, H_β–C(1)); 2.22 (*d*, *J* = 10.8, H–C(5)); 2.11 (*t*, *J* = 11.5, H_β–C(7)); 1.98 (*dd*, *J* = 12.9, 9.9, H_β–C(12)); 1.79 (*d*, *J* = 10.3, H–C(9)); 1.72 (*s*, Me(19)); 1.67 (*s*, Me(18)); 1.42 (*s*, Me(17)); 1.35 (*s*, Me(16)); 1.01 (*s*, Me(20)).

*(*S*)-MTPA Ester of Rhizomucronol B*, **2c**. ^{1}H-NMR ($CDCl_3$, 300 MHz): 6.13 (*dd*, *J* = 17.7, 10.9, H–C(14)); 5.22 (*d*, *J* = 17.8, H_α–C(15)); 4.95 (*d*, *J* = 10.9, H_β–C(15)); 4.45 (*td*, *J* = 9.9, 3.9, H–C(11)); 4.15 (*td*, *J* = 11.1, 4.1, H–C(6)); 3.03–3.04 (*m*, H_α–C(2)); 2.93–2.94 (*m*, H_α–C(1)); 2.84 (*dd*, *J* = 13.1, 3.9, H_α–C(12)); 2.52 (*dd*, *J* = 11.7, 4.1, H_α–C(7)); 2.38–2.39 (*m*, H_β–C(2)), 2.30 (*td*, *J* = 14.9, 4.1, H_β–C(1)); 2.22 (*d*, *J* = 10.8, H–C(5)); 2.12 (*t*, *J* = 11.5, H_β–C(7)); 1.99 (*dd*, *J* = 12.9,10.0, H_β–C(12)); 1.79 (*d*, *J* = 10.3, H–C(9)); 1.72 (*s*, Me(19)); 1.68 (*s*, Me(18)); 1.42 (*s*, Me(17)); 1.34 (*s*, Me(16)); 1.09 (*s*, Me(20)).

Rhizomucronol A (= *(3*R*,4a*S*,6*R*,6a*R*,11a*S*,11b*S*)-3-Ethenyldecahydro-6-hydroxy-3,4a,7,7,11a-pentamethyl-1*H*-oxepino[4,3-f]chromen-9(4a*H*)-one*; **1**). Amorphous solid. R_f (hexane/acetone 7:3) 0.5. $[\alpha]_D^{27} = -125$ (*c* = 0.12, $CHCl_3$). IR (KBr): 3407, 2942, 1712, 1507, 1451, 1383, 1218, 1118, 1143, 1038, 921, 764, 666. ^{1}H-, ^{13}C-, and 2D-NMR: see *Tables 1* and *2*, and *Figs. 2 and 3*. HR-ESI-MS: 359.2206 ($[M+Na]^+$, $C_{20}H_{32}NaO_4^+$; calc. 359.2198).

6β-Acetoxyrhizomucronol A (= *(3*R*,4a*S*,6*R*,6a*R*,11a*S*,11b*S*)-3-Ethenyldodecahydro-3,4a,7,7,11a-pentamethyl-9-oxo-1*H*-oxepino[4,3-f]chromen-6-yl Acetate*; **1a**). Colorless oil. R_f (hexane/acetone 8:2) 0.5. ^{1}H-NMR: see *Table 1*.

Rhizomucronol B (= *(1*S*,3*R*,4a*S*,6*R*,6a*S*,10a*R*,10b*R*)-3-Ethenyldecahydro-1,6-dihydroxy-3,4a,7,7,10a-pentamethyl-1*H*-benzo[f]chromen-8(4a*H*)-one*; **2**). Amorphous solid. R_f (hexane/acetone 6:4) 0.5. $[\alpha]_D^{27} = -105$ (*c* = 0.13, $CHCl_3$). IR (KBr): 3413, 2925, 2854, 1716, 1605, 1461, 1378, 1329, 1219, 1115, 1036, 920, 772. ^{1}H-, ^{13}C-, and 2D-NMR: see *Tables 1* and *2*, and *Figs. 2* and *3*); HR-ESI-MS: 359.2199 ($[M+Na]^+$; $C_{20}H_{32}NaO_4^+$; calc. 359.2198).

6β,11β-Diacetoxyrhizomucronol B (= *(1*S*,3*R*,4a*S*,6*R*,6a*S*,10a*R*,10b*R*)-3-Ethenyldodecahydro-3,4a,7,7,10a-pentamethyl-8-oxo-1*H*-benzo[f]chromene-1,6-diyl Diacetate*; **2a**). Colorless oil. R_f (hexane/acetone 8:2) 0.5. IR (KBr): 2923, 2853, 1737, 1459, 1370, 1236, 1139, 1076, 1026, 974, 768. ^{1}H-NMR: see *Table 1*.

Supplementary Material. Supplementary data (spectral data of compounds **1**–**4**; ^{1}H-, ^{13}C-NMR, DEPT, and all 2D-NMR spectra for **1** to **2**; ^{1}H- and ^{13}C-NMR spectra of **3** and **4**; IR and ^{1}H-NMR spectra of acetylated derivatives of **1** and **2** associated with this article) can be obtained from the corresponding author.

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