Diterpenes and Disulfides from the Marine Mangrove Plant *Bruguiera sexangula* var. *rhynchopetala*

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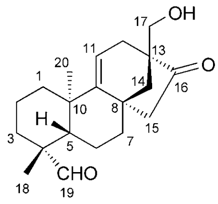
Phytochemical investigation of the stems of *Bruguiera sexangula* var. *rhynchopetala* resulted in the isolation and characterization of four new and seven known secondary metabolites. The new compounds were spectroscopically identified as 17-hydroxy-16-oxobeyer-9(11)-en-19-al (**1**), 16,17-dihydroxy-19-nor-*ent*-kaur-9(11)-en-3-one (**2**), (16*R*)-13,17-epoxy-16-hydroxy-*ent*-kaur-9(11)-en-19-al (**3**), and (−)-3,4-dihydro-3-hydroxy-7-methoxy-2*H*-1,5-benzodithiepine-6,9-dione (**10**). The configurations of the known compounds brugierol (**11**) and isobrugierol (**12**) were re-investigated. Compounds **11** and **12**, together with 2,6-dimethoxy-1,4-benzoquinone (**13**), are proposed to be degradation products of the novel, unusual disulfide **10** (*Scheme*).

Introduction. – The genus *Bruguiera* (Rhizophoraceae) represents evergreen trees widely distributed in tropical Africa, Australia, and South and Southeast Asia, as well as in the tropical Pacific [1]. Previous chemical investigation mainly focused on *B. gymnorrhiza* from India, showing a variety of triterpenes, diterpenes, and flavonoids in its leaves, roots, and bark [2–5]. Recently, our investigation of the stem of the same plant from South China yielded 13 diterpenes, including four new compounds [6]; and from the leaves, a novel macrocyclic polydisulfide was isolated [7]. Whereas *B. sexangula* was found to contain mainly tropane derivatives such as brugine and 3-hydroxytropane [8], *B. conjugate* was shown to contain disulfides [9].

In continuation of our investigation of Chinese mangrove plants, the EtOH extract of the stem of *B. sexangula* var. *rhynchopetala* was examined. Herein, we describe the isolation and characterization of 13 compounds from this plant: *1*) three new diterpenes (**1**–**3**); *2*) six known diterpenes (**4**–**9**), *i.e.*, 17-hydroxy-16-oxobeyeran-19-al (**4**) [6], 16,17-dihydroxy-*ent*-kaur-9(11)-en-19-al (**5**) [6], methyl 16,17-dihydroxy-*ent*-kaur-9(11)-en-19-oate (**6**) [10][11], methyl (16*R*)-13,17-epoxy-16-hydroxy-*ent*-kaur-9(11)-en-19-oate (**7**) [1], ceriopsin F (**8**) [10], and (1*β*,15*R*)-*ent*-pimar-8(14)-ene-1,15,16-triol (**9**); *3*) a new dithiobenzoquinone (**10**); *4*) two cyclic disulfides, *i.e.*, brugierol (**11**) and isobrugierol (**12**); and *5*) 2,6-dimethoxy-1,4-benzoquinone (**13**) [12].

Results and Discussion. – Compound **1**, obtained as a colorless, amorphous powder, was identified as 17-hydroxy-16-oxobeyer-9(11)-en-19-al. Its molecular formula was determined as $C_{20}H_{28}O_3$ by means of HR-FAB-MS (*m/z* 317.2114 ($[M+H]^+$, calc. 317.2111)) and ^1H- and ^{13}C-NMR data. The IR spectrum suggested the presence of C=O (1716, 1742), C=C (1671), and OH (3317 cm^{-1}) groups. The ^1H- and ^{13}C-NMR



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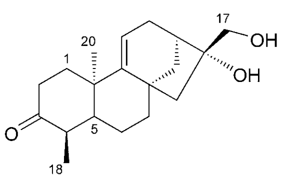

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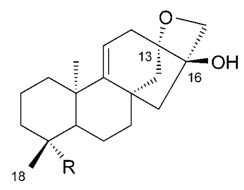

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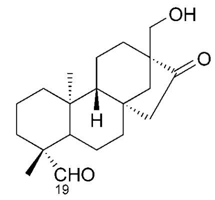

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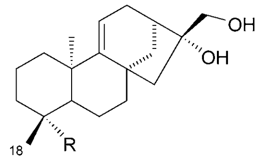

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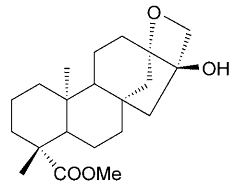
6 R = MeOOC



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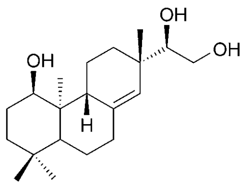

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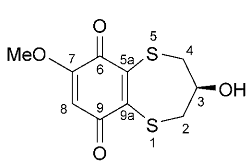

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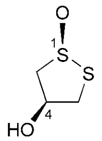

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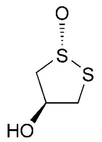

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data were in good agreement with a 16-oxobeyeran diterpene of type **4** [6], with the exception of an additional C(9)=C(11) bond in **1**. A detailed 2D-NMR analysis, and comparison of the NMR data with those of **4**, previously isolated from *B. gymnorrhiza*, confirmed the structure of **1**.

The ^{13}C-NMR (DEPT) spectrum of **1** (*Table 1*) showed 20 resonances: two Me, nine CH$_2$, and three CH groups, and six quaternary C-atoms, with an aldehyde function at δ(C) 205.6 (C(19)), a C=O group at 222.7 (C(16)), and a trisubstituted C=C bond at 153.7 and 115.9. The C=C bond was deduced to be at C(9) and C(11) based on COSY correlations between H−C(11) at δ(H) 5.44 (*dd*, *J* = 2.3, 3.9 Hz) and the geminal H-atoms of CH$_2$(12) [δ(H) 2.16 (*dd*, *J* = 3.8, 17.8); 2.24 (*dd*, *J* = 2.3, 17.8 Hz)], as well as based on HMBC correlations from CH$_2$(12) to C(9), C(17) at δ(C) 65.5 (*t*), C(16), and C(14) at δ(C) 45.8 (*t*). Further HMBC correlations between H−C(11) and C(13) at δ(C) 53.1 (*s*), C(12) at 34.8 (*t*), C(10) at 39.7 (*s*), and C(8) at 39.3 (*s*) supported the proposed position of the C=C bond.

The relative configuration of **1** was determined by a NOESY experiment and by comparison of its NMR data with those of **4**. Crucial NOE correlations were observed between H−C(19) at δ(H) 9.78 and Me(20) at 0.97, between Me(18) at δ(H) 1.07 (*s*) and H−C(5) at 1.38 (br. *d*), and between H$_\alpha$−C(15) at δ(H) 2.87 (*dd*) and Me(20), indicating that **1** possesses a beyerane skeleton, with *trans*-fused *A*/*B* rings like in the kauranes, but with an α-oriented, *cis*-fused ring *D*. Since the absolute configuration of **4**, occurring in the same plant, has been determined by circular dichroism [6], the configuration of the 9,11-didehydro analogue **1** is most likely the same as that in **4**.

The structure of compound **2** was identified as 16,17-dihydroxy-19-nor-*ent*-kaur-9(11)-en-3-one. Its molecular formula was established as C$_{19}$H$_{28}$O$_3$ through HR-FAB-

Table 1. *^{1}H- and ^{13}C-NMR Data of Compounds* **1**–**3**. At 500/125 MHz, resp., in $CDCl_3$; δ in ppm, *J* in Hz.

Atom	**1**		**2**		**3**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
H_α–C(1)	1.31 (*ddd*, *J* = 4.5, 13.0, 14.0)	37.4 (*t*)	2.32 (*ddd*, *J* = 2.5, 3.0, 14.4)	39.8 (*t*)	1.20 (*ddd*, *J* = 4.5, 13.5, 13.5)	39.9 (*t*)
H_β–C(1)	1.92–1.94 (*m*)		2.51 (*ddd*, *J* = 5.9, 14.4, 14.4)		1.97–2.00 (*m*)	
H_α–C(2)	1.59–1.62 (*m*)	18.6 (*t*)	1.57–1.61 (*m*)	38.0 (*t*)	1.55–1.58 (*m*)	19.1 (*t*)
H_β–C(2)	1.66–1.68 (*m*)		2.20–2.22 (*m*)		1.59–1.62 (*m*)	
H_α–C(3)	1.05 (*ddd*, *J* = 4.5, 13.5, 13.5)	34.0 (*t*)		212.9 (*s*)	1.00–1.03 (*m*)	35.0 (*t*)
H_β–C(3)	2.16–2.19 (*m*)				2.07–2.09 (*m*)	
H–C(4)		48.6 (*s*)	2.27–2.30 (*m*)	46.8 (*d*)		49.3 (*s*)
H–C(5)	1.38 (br. *d*, *J* = 12.4)	53.6 (*d*)	1.62–1.64 (*m*)	44.6 (*d*)	1.68 (br. *d*, *J* = 10.2)	45.8 (*d*)
H_α–C(6)	1.87 (*dddd*, *J* = 3.0, 12.4, 13.0, 13.0)	19.5 (*t*)	1.42 (*ddd*, *J* = 10.6, 10.6, 14.0)	23.6 (*t*)	1.52–1.55 (*m*)	17.0 (*t*)
H_β–C(6)	2.01–2.03 (*m*)		1.90–1.93 (*m*)		2.00–2.03 (*m*)	
H_α–C(7)	1.70–1.72 (*m*)	39.3 (*t*)	1.57–1.59 (*m*)	29.5 (*t*)	1.53–1.55 (*m*)	29.6 (*t*)
H_β–C(7)	1.98–2.00 (*m*)		2.04 (*ddd*, *J* = 10.0, 10.5,13.5)		1.97–2.00 (*m*)	
C(8)		39.3 (*s*)		42.8 (*s*)		40.9 (*s*)
C(9)		153.7 (*s*)		154.8 (*s*)		156.5 (*s*)
C(10)		39.7 (*s*)		37.3 (*s*)		38.3 (*s*)
H–C(11)	5.44 (*dd*, *J* = 2.3, 3.9)	115.9 (*d*)	5.24 (br. *s*)	114.5 (*d*)	5.36 (br.)	114.8 (*d*)
H_α–C(12)	2.16 (*dd*, *J* = 3.8, 17.8)	34.8 (*t*)	2.18 (*dd*, *J* = 3.9, 14.5)	30.2 (*t*)	2.42 (br. *d*, *J* = 15.5)	37.2 (*t*)
H_β–C(12)	2.24 (*dd*, *J* = 2.3, 17.8)		2.26–2.28 (*m*)		2.53 (br. *d*, *J* = 15.5)	
H–C(13)		53.1 (*s*)	2.23–2.25 (*m*)	44.0 (*d*)		80.0 (*s*)
H_α–C(14)	1.73 (*dd*, *J* = 3.8, 11.0)	45.8 (*t*)	1.55–1.58 (*m*)	42.7 (*t*)	1.58 (*d*, *J* = 14.2)	49.0 (*t*)
H_β–C(14)	2.00 (*d*, *J* = 11.0)		2.09 (*dd*, *J* = 5.0, 11.0)		2.07 (*d*, *J* = 14.2)	
H_α–C(15)	2.12 (*d*, *J* = 17.6)	57.4 (*t*)	1.58 (*d*, *J* = 13.5)	55.5 (*t*)	1.79 (*d*, *J* = 13.5)	52.9 (*t*)
H_β–C(15)	2.87 (*dd*, *J* = 3.6, 17.6)		1.92 (*d*, *J* = 13.5)		1.91 (*d*, *J* = 13.5)	
C(16)		222.7 (*s*)		84.7 (*s*)		79.0 (*s*)
H_a–C(17)	3.63 (*d*, *J* = 11.3)	65.5 (*t*)	3.50 (*d*, *J* = 10.8)	68.2 (*t*)	3.63 (*d*, *J* = 12.1)	67.9 (*t*)
H_b–C(17)	3.78 (*d*, *J* = 11.3)		3.63 (*d*, *J* = 10.8)		3.67 (*d*, *J* = 12.1)	
Me(18)	1.07 (*s*)	24.4 (*q*)	1.00 (*d*, *J* = 6.5)	11.0 (*q*)	1.02 (*s*)	24.2 (*q*)
H–C(19)	9.78 (*s*)	205.6 (*d*)			10.0 (*s*)	206.4 (*d*)
Me(20)	0.97 (*s*)	23.4 (*q*)	1.28 (*s*)	21.2 (*q*)	0.96 (*s*)	23.7 (*q*)

MS data (*m/z* 327.1927 ($[M+\mathrm{Na}]^+$, calc. 327.1931)). IR Absorptions at 3394 and 1710 cm^{-1} suggested the presence of OH and C=O groups, and the ^{1}H- and ^{13}C-NMR data (*Table 1*) pointed to an *ent*-kaurane diterpene.

The ^{13}C-NMR (DEPT) spectrum of **2** showed 19 resonances: two Me, eight $\mathrm{CH_2}$, and four CH groups, and five quaternary C-atoms. The ^{1}H-NMR spectrum exhibited a *singlet* at δ(H) 1.28 (Me(20)), a *doublet* at 1.00 ($J=6.5$ Hz, Me(18)), a vinylic resonance at 5.24 (br. *s*, H−C(11)), and an isolated, oxygenated $\mathrm{CH_2}$ resonance at 3.50/3.63 (2*d*, $J=10.8$ each, $\mathrm{CH_2}$(17)). The ^{1}H- and ^{13}C-NMR spectra of **2** closely resembled those of 16,17-dihydroxy-*ent*-kaur-9(11)-en-19-al (**5**) [6], except for the signals in ring *A*, where a Me *doublet* (Me(18)) and a C=O function at δ(C) 212.9 (*s*) were observed. The HMBC spectrum exhibited long-range correlations between Me(18) and C(3), C(4) (δ(C) 46.8 (*d*)), and C(5) (δ(C) 44.6 (*d*)); further HMBC correlations were found between Me(20) and C(1) (δ(C) 39.8 (*t*)), C(10) (δ(C) 37.3 (*s*)), C(5), and C(9) (δ(C) 154.8 (*s*)), which indicated a C=O group in 3-position and the replacement of a 4-Me group by a H-atom. NOESY Correlations between Me(20) and H−C(4) at δ(H) 2.29 (*m*), and between Me(18) and H−C(5) at δ(H) 1.64 (*m*) indicated a *trans*-junction of rings *A* and *B*, and β-orientation of Me(18).

Compound **3** corresponds to (16*R*)-13,17-epoxy-16-hydroxy-*ent*-kaur-9(11)-en-19-al. Its molecular formula was established as $\mathrm{C_{20}H_{28}O_3}$ from HR-FAB-MS data (*m/z* 317.2112 ($[M+\mathrm{H}]^+$, calc. 317.2111)). IR Absorptions at 3259, 2722, and 1712 cm^{-1} were due to OH and CHO groups. The ^{1}H- and ^{13}C-NMR data of **3** nearly matched those of methyl 13,17-epoxy-16-hydroxy-*ent*-kaur-9(11)-en-19-oate (**7**), previously isolated from *B. gymnorrhiza* [6], except for an aldehyde instead of an ester function at C(4).

HMBC Correlations of H−C(19) with C(3) (δ(C) 35.0 (*t*)), C(4) (49.3 (*s*)), C(5) (45.8 (*d*)), and C(18) (24.2 (*q*)) confirmed the location of the formyl group. The configurations at rings *A*/*B* and the fusion geometries of rings *C*/*D*/*E* were found to be the same as in compounds **1** and **7**, respectively, based on the key NOESY correlations between H−C(19) and Me(20) (δ(H) 0.96 (*s*)), between Me(18) (δ(H) 1.02 (*s*)) and H−C(5) (δ(H) 1.68 (br. *d*, $J=10.2$ Hz)), and between $\mathrm{H_a}$−C(15) (δ(H) 1.79 (*d*, $J=13.5$ Hz)) and both $\mathrm{H_b}$−C(14) (δ(H) 2.07 (*d*, $J=14.2$ Hz)) and $\mathrm{H_a}$−C(17) (δ(H) 3.63 (*d*, $J=12.1$ Hz)).

The structure of compound **10** was elucidated as (−)-3,4-dihydro-3-hydroxy-7-methoxy-2*H*-1,5-benzodithiepine-6,9-dione. This compound was isolated as a violet, amorphous solid, and its molecular formula was determined as $\mathrm{C_{10}H_{10}O_4S_2}$ from HR-FAB-MS data (*m/z* 259.0097 ($[M+\mathrm{H}]^+$, calc. 259.0093), indicating six degrees of unsaturation. UV Absorptions at 241, 320, 541 nm, and IR absorptions at 3423, 1662, and 1640 cm^{-1} were characteristic an OH group and a quinone moiety, as further confirmed by ^{13}C-NMR analysis. A COSY experiment established a 2-hydroxypropyl unit, which was suggested to form a 1,4-dithiacycloheptane ring attached to a 1,4-benzoquinone. The HMBC spectrum pointed to the presence of a MeO group at C(6).

The ^{1}H NMR spectrum of **10** exhibited signals attributable to a MeO group at δ(H) 3.83 (*s*), an aromatic *singlet* at 5.92, an oxygenated CH at 4.35 (*dddd*), and four $\mathrm{CH_2}$ at 3.37–3.42 ppm. The ^{13}C-NMR (DEPT) spectrum showed a MeO group at δ(C) 56.6 (*q*), two C=O groups at 176.9 (*s*) and 182.3 (*s*), respectively, four aromatic carbons at 138.3 (*s*), 142.9 (*s*), 159.0 (*s*), and 107.8 (*d*), an oxygenated CH at 66.0 (*d*), as well as two $\mathrm{CH_2}$ at 36.2 (*t*) and 36.6 (*t*), respectively. The HMQC spectrum allowed the assignment of all H-atoms, and of all C-atoms bearing H-atoms. HMBC Correlations between H−C(8) at δ(H) 5.92 (*s*) and C(9) at δ(C) 182.3 (*s*), C(6) at 176.9 (*s*), C(7) at 159.0 (*s*), and C(9a) at 142.9 (*s*), and a correlation between the MeO H-atoms at δ(H) 3.84 and C(7), in association with the extremely high-field ^{13}C-NMR signal for C(8) (107.1 ppm), indicated that the MeO group and the aromatic H-atom were located next to each other on a trisubstituted benzoquinone.

The COSY spectrum showed cross-peaks from δ(H) 4.35 (*dddd*, H−C(3)) to 3.37 (*dd*, J=6.1, 15.0, H_a−C(4)), 3.66 (*dd*, J=3.1, 15.0, H_b−C(4), H_b−C(2)), and 3.42 (*dd*, J=6.5, 15.0 Hz, H_a−C(2)), pointing to the presence of a propan-2-ol-1,3-diyl moiety. Further HMBC correlations traced from CH_2(4) to C(5a) at δ(C) 138.3 (*s*), and from CH_2(2) to C(9a) at δ(C) 142.9 (*s*) indicated an 1,4-dithiepane ring. MM2 Calculations postulated the seven-membered ring to be in a 'semi-chair' conformation, and the small J values for H−C(3) indicated an axial OH group. However, the absolute configuration at C(3) remains unclear.

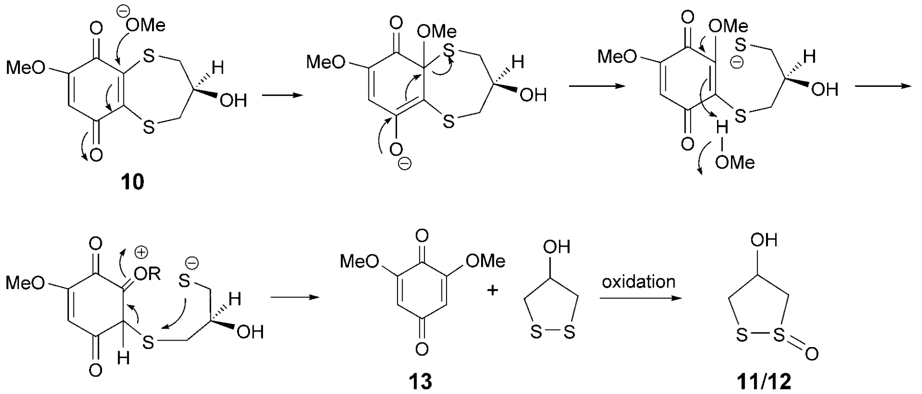
Brugierol (**11**) and isobrugierol (**12**) have been isolated before from the plant *B. conjugate* [9]. Re-investigation of the coupling constants of **11** and **12** (see *Table 2*) and consideration of the *Karplus* rule indicated that the H−C(4) H-atoms in both compounds had been placed erroneously in axial positions [9]. The small coupling constants for H−C(4) rather point to equatorial positions in the five-membered 'semi-chair' rings, as calculated by MM2. The sulfinyl O-atoms have to be *cis* and *trans* to the 4-OH groups in **11** and **12**, respectively, as evident from the more-downfield chemical shift of H−C(4) in **11** (relative to that in **12**) due to the intramolecular H-bond C(4)−H···O−S.

Possibly, compounds **11**–**13** are, indeed, artifacts arising from oxidative degradation of **10**, as proposed in the *Scheme*.

Table 2. *^{1}H-NMR Data of Compounds* **11** *and* **12**. At 500 MHz in $CDCl_3$; δ in ppm, J in Hz.

	12	**11**
H_a–C(3)	2.97 (*dd*, J=3.5, 14.0)	3.47 (*dd*, J=6.5, 13.0)
H_b–C(3)	4.05 (*dd*, J=1.0, 14.0)	3.35 (*dd*, J=2.5, 13.0)
H–C(4)	4.54 (*dddd*, J=1.0, 1.0, 3.5, 4.0)	5.14 (*dddd*, J=2.5, 2.5, 6.5, 6.6)
H_a–C(5)	3.59 (*dd*, J=4.0, 10.5)	3.29 (*dd*, J=6.6, 11.6)
H_b–C(5)	4.07 (*dd*, J=1.0, 10.5)	3.70 (*dd*, J=2.5, 11.6)

Scheme



Experimental Part

General. Column chromatography (CC): silica gel (200–300 mesh, *Qingdao Marine Chemistry*) or *Sephadex LH-20* (18–110 μm, *Pharmacia*). TLC: *GF-254* silica gel (*Qingdao Marine Chemistry*). Semi-prep. RP-HPLC: *Kromasil* prepacked *ODS* column (10×250 mm; *Pharmacia*) and *Alltech-426* apparatus. UV/VIS Spectra: *Lengguang 756-MC* spectrophotometer; in $CHCl_3$, λ_{max} (log ε) in nm. Optional rotation: *Perkin-Elmer 243B* polarimeter. IR Spectra: *Thermo Nicolet Nexus 470* FT-IR spectrometer; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker Avance-500* spectrometer; chemical shifts δ in ppm rel. to $MeSi_4$, coupling constants J in Hz. EI-MS: *Bruker APEX-II* mass spectrometer; HR-FAB-MS: *Bruker Daltonics APEX-II* FT-ICR mass spectrometer; in m/z (rel. %).

Plant Material. The stems of *B. sexangula* var. *rhynchopetala* were collected at mangrove garden in Haikou, Hainan Island, P. R. China, in June 2002. The plant was authenticated by Prof. *Peng Lin*, Xiamen University. A voucher specimen (M-007) was deposited at the State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Beijing, P. R. China.

Extraction and Isolation. The air-dried and pulverized stems (4.9 kg) were extracted with 85% aq. EtOH (20 l) at r.t. The crude extract was concentrated under reduced pressure, and the residue (218 g) was partitioned between H_2O and *a*) petroleum ether (PE), *b*) AcOEt, and *c*) BuOH to afford 13.2, 8.3, and 47 g of org. extracts, resp., together with an aqueous residue. The PE fraction (13.2 g) was subjected to CC (SiO_2; PE/AcOEt 40 : 1 → 1 : 1): ten fractions (*Fr. 1–10*) according to TLC. *Fr. 8* (80 mg, eluted with PE/AcOEt 40 : 1 2 : 1) was further separated by semi-prep. HPLC (*ODS*; MeOH/H_2O 7 : 3) to yield compounds **3** (1.9 mg), **7** (7.0 mg), **8** (6.0 mg), and **9** (1.6 mg). *Fr. 4* (150 mg, eluted with PE/AcOEt 10 : 1) was re-subjected to CC (SiO_2; PE/AcOEt 4 : 1) to afford compounds **13** (1.7 mg), **1** (3.2 mg), and **4** (4.8 mg); the remaining fractions were combined, and passed through a *Sephadex LH-20* column (MeOH) to afford compound **10** (11.5 mg). *Fr. 5* (70 mg, eluted with PE/AcOEt 5 : 1) was re-subjected to CC (SiO_2; $CHCl_3$/MeOH 40 : 1) to yield compounds **12** (30 mg) and **11** (20 mg). *Fr. 7* (60 mg, eluted with PE/AcOEt 3 : 1) was purified by semi-prep. HPLC (*ODS*; MeOH/H_2O 7 : 3) to afford compounds **2** (1.2 mg), **5** (8 mg), **6** (3.0 mg), and **7** (5 mg).

17-Hydroxy-16-oxobeyer-9(11)-en-19-al (**1**). Colorless, amorphous solid. $[\alpha]_D^{20} = -77.4$ ($c = 0.14$, $CHCl_3$). IR (KBr): 3317, 2926, 2872, 2729, 2711, 1742, 1716, 1671, 1459, 1375, 1038, 754. ^1H- and ^{13}C-NMR: see *Table 1*. EI-MS: 316 (22, M^+), 288 (6), 285 (17), 256 (49), 241 (17), 227 (24), 213 (35), 185 (17), 171 (24), 157 (45), 131 (62), 105 (61), 91 (89). HR-FAB-MS: 317.2114 ($[M+H]^+$, $C_{20}H_{29}O_3^+$; 317.2117).

*16,17-Dihydroxy-19-nor-*ent*-kaur-9(11)-en-3-one* (**2**). Colorless, amorphous solid. $[\alpha]_D^{20} = +52.3$ ($c = 0.15$, $CHCl_3$). IR (KBr): 3394, 2934, 2865, 1710, 1577, 1431, 1377, 1195, 1139, 1063, 878. ^1H- and ^{13}C-NMR: see *Table 1*. EI-MS: 304 (3, M^+), 286 (90), 271 (59), 268 (27), 255 (51), 211 (30), 159 (36), 145 (56), 131 (85), 105 (69), 91 (100), 55 (55). HR-FAB-MS: 327.1927 ($[M+Na]^+$, $C_{19}H_{28}NaO_3^+$; calc. 327.1936).

*(16*R*)-13,17-Epoxy-16-hydroxy-*ent*-kaur-9(11)-en-19-al.* (**3**). Colorless, amorphous solid. $[\alpha]_D^{20} = +123.75$ ($c = 0.17$, $CHCl_3$). IR (KBr): 3259, 2959, 2922, 1712, 2722, 1591, 1459, 1377. ^1H- and ^{13}C-NMR: see *Table 1*. EI-MS: 316 (32, M^+), 285 (37), 267 (15), 259 (34), 241 (47), 231 (20), 215 (51), 199 (25), 171 (33), 159 (45). HR-FAB-MS: 317.2112 ($[M+H]^+$, $C_{20}H_{29}O_3^+$; calc. 317.2117).

*(−)-3,4-Dihydro-3-hydroxy-7-methoxy-2*H*-1,5-benzodithiepine-6,9-dione* (**10**). Violet, amorphous solid. UV ($CHCl_3$): 241 (3.59), 320 (3.49), 541 (2.68). $[\alpha]_D^{20} = -45$ ($c = 0.08$, $CHCl_3$). IR (KBr): 3423, 2995, 2914, 1662, 1640, 1437, 1408, 1031, 956, 704. ^1H-NMR (500 MHz, $CDCl_3$): 5.92 (*s*, H−C(8)); 4.35 (*dddd*, $J = 3.1$, 3.5, 6.1, 6.5, H−C(3)); 3.83 (*s*, 7-MeO); 3.66 (*dd*, $J = 3.1$, 15.0, H_b−C(4), H_b−C(2)); 3.42 (*dd*, $J = 6.5$, 15.0, H_a−C(2)); 3.37 (*dd*, $J = 6.1$, 15.0, H_a−C(4)). ^{13}C-NMR (125 MHz, $CDCl_3$): 176.9 (*s*, C(6)); 138.3 (*s*, C(5a)); 142.9 (*s*, C(9a)); 182.3 (*s*, C(9)); 107.8 (*d*, C(8)); 159.0 (*s*, C(7)); 36.6 (*t*, C(4)); 66.0 (*d*, C(3)); 36.2 (*t*, C(2)), 56.6 (*q*, MeO). EI-MS: 258 (33, M^+), 260 (3), 259 (6), 213 (11), 186 (20), 158 (13), 112 (12), 84 (20), 69 (100). HR-FAB-MS: 259.0097 ($[M+H]^+$, $C_{10}H_{11}O_4S_2^+$; calc. 259.0093).

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