Sesquiterpenoids from the Aerial Parts of *Inula japonica*

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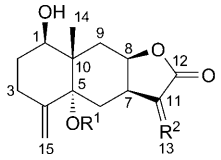
Fourteen sesquiterpenoids with an eudesmane C-atom skeleton, including four new ones, (1*β*,5*α*,7*β*,8*β*,11*β*)-5-hydroperoxy-1-hydroxyeudesm-4(15)-eno-12,8-lactone (**1**), (1*β*,5*α*,7*β*,8*β*)-8-(acetyloxy)-5-hydroperoxy-1-hydroxycostic acid methyl ester (**12**), and a mixture of (1*β*,3*β*,4*β*,7*β*,8*β*)-1,3-dihydroxyeudesma-5,11(13)-dieno-12,8-lactone (**7**) and (1*β*,3*β*,4*β*,7*β*,8*β*,11*β*)-1,3-dihydroxyeudesm-5-eno-12,8-lactone (**8**), were isolated from the aerial parts of *Inula japonica* (Asteraceae). Their structures were determined by extensive spectroscopic methods, and those of **7** and **12** confirmed by means of single-crystal X-ray diffraction analysis.

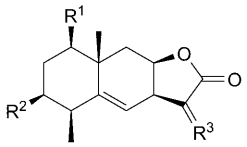
Introduction. – The Asteraceae family is a rich resource of sesquiterpenoids [1]. Some novel sesquiterpenoids have been found from the Asteraceae in recent years [2–8]. The genus *Inula* belonging to the Asteraceae contains *ca.* 100 species, distributed predominantly in Europe, Africa, Asia, and the Mediterranean region [9]. *Inula japonica* is mainly distributed in Northern China, and its aerial parts have been used for a long time as traditional Chinese medicine in the Chinese Pharmacopoeia (called Jin-Fei-Cao) to treat furunculosis, cough, digestive disorders, bronchitis, and inflammation [10]. Recently, extracts of the plant have been reported to possess diverse biological activities, such as antifungal, antibacterial, antidiabetic, and hypolipidemic properties [3][11–13]. Previous phytochemical investigations of *I. japonica* revealed that sesquiterpenoids were the main active constituents [11][14–16]. To search for biologically active compounds, we investigated the chemical constituents of the aerial parts of the plant, and fourteen eudesmane sesquiterpenoids were isolated, including four new ones, (1*β*,5*α*,7*β*,8*β*,11*β*)-5-hydroperoxy-1-hydroxyeudesm-4(15)-eno-12,8-lactone[1]) (**1**) [17], (1*β*,5*α*,7*β*,8*β*)-8-(acetyloxy)-5-hydroperoxy-1-hydroxycostic acid methyl ester[1]) (**12**) [11], (1*β*,3*β*,4*β*,7*β*,8*β*)-1,3-dihydroxyeudesma-5,11(13)-dieno-12,8-lactone[1]) (**7**) [18], (1*β*,3*β*,4*β*,7*β*,8*β*,11*β*)-1,3-dihydroxyeudesm-5-eno-12,8-lactone[1]) (**8**) [18], and ten known compounds (5*α*)-5-hydroperoxyasperilin (**2**) [17], (5*α*)-5-hydroxyasperilin (**3**) [19], alantolactone (**4**) [11], (1*β*)-1-hydroxyalantolactone (**5**) [11][20], (1*β*,11*β*)-11,13-dihydro-1-hydroxyalantolactone (**6**) [11][21], ivangustin (**9**) [11], (8*β*)-8-hydroxysantamarin (**10**) [15], (1*β*,7*β*,8*β*)-8-(acetyloxy)-1-hydroxycostic

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

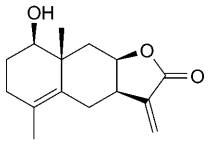
acid methyl ester (**11**) [11], britannilactone (**13**) [22], and 1-*O*-acetylbritannilactone (**14**) [22]. To the best of our knowledge, among these known sesquiterpenoids, compounds **2**–**4** were reported from *I. japonica* for the first time. We also recorded the ^{13}C-NMR spectra of compounds **2**, **3**, and **10** (*cf.* below, *Table 3*), which have not yet been reported.



	R^1	R^2
1[1])	OH	β-Me, H
2[1])	OH	CH_2
3[1])	H	CH_2



	R^1	R^2	R^3
4	H	H	CH_2
5	OH	H	CH_2
6	OH	H	β-Me, H
7	OH	OH	CH_2
8	OH	OH	β-Me, H



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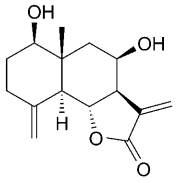

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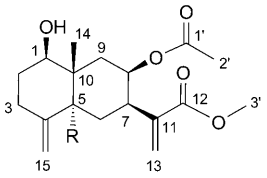
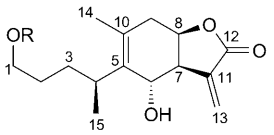


11[1]) R = H
12[1]) R = OOH



13[1]) R = H
14[1]) R = Ac

Results and Discussion. – Compound **1** was obtained as a colorless oil. Its molecular formula, $C_{15}H_{22}O_5$, was deduced by HR-ESI-MS (*m/z* 300.1800 ($[M+NH_4]^+$)). The IR spectrum exhibited the presence of OH (3371 cm^{-1}) and γ-lactone (1753 cm^{-1}) groups. The ^{1}H-NMR spectrum (*Table 1*) showed two Me groups (δ(H) 0.92 (*s*) and 1.23 (*d*, *J* = 7.2 Hz)), two olefinic H-atoms (δ(H) 4.90 and 5.16 (2 br. *s*)), two O-bearing CH groups (δ(H) 3.90 (*dd*, *J* = 4.8,11.6 Hz) and 4.60–4.62 (*m*)), and one OOH group (δ(H) 7.56 (br. *s*)). The ^{13}C-NMR and DEPT spectra (*Table 1*) exhibited signals of fifteen C-atoms, including two Me, five CH_2, and four CH groups (two O-bearing, at δ(C) and 72.7 (C(1)) and 77.3 (C(8)), and four quaternary C-atoms (one O-bearing, at δ(C) 86.6 (C(5)), and one olefinic, at δ(C) 145.3 (C(4)). The NMR data of **1** were similar to those of the known compound **2**, except for the absence of a C=C bond between C(11) and C(13). In the HMBC experiment (*Fig. 1*), the O-bearing H-atom at δ(H) 3.90 gave a ^2J correlation to C(10) (δ(C) 42.3) and ^3J correlations to C(14) (δ(C) 15.0) and C(9) (δ(C) 32.7), which suggested that the OH group was attached to C(1). Similarly, the HMBCs from CH_2(3), CH_2(15), CH_2(6), and Me(14) to C(5) indicated that the OOH group must be at C(5). The relative configuration of compound **1** was determined by *J* values and the NOESY experiment (*Fig. 1*). If Me(14) was β-oriented, the characteristic coupling constants *J* = 11.6 and 4.8 Hz of H–C(1) suggested that OH–C(1) was also β-oriented. Similarly, the *J* (H–C(7), H–C(11)) was 7.0 Hz, in accord with a β-orientation of Me(13) [11]. In the NOESY plot, the correlations of

Table 1. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$; 400 and 100 MHz, resp.) *of* **1**[1]) *and* **12**[1]). δ in ppm, J in Hz.

	1		**12**	
	δ(H)	δ(C) (DEPT)	δ(H)	δ(C) (DEPT)
H–C(1)	3.90 (*dd*, *J* = 4.8, 11.6)	72.7 (*d*)	3.99 (*dd*, *J* = 5.2, 11.4)	72.1 (*d*)
CH_2(2)	1.49 – 1.60, 1.79 – 1.86 (2*m*)	29.7 (*t*)	1.56 – 1.67, 1.80 – 1.91 (2*m*)	29.7 (*t*)
CH_2(3)	2.22 – 2.26, 2.47 – 2.55 (2*m*)	30.3 (*t*)	2.20 – 2.28, 2.57 – 2.65 (2*m*)	30.1 (*t*)
C(4)		145.3 (*s*)		146.2 (*s*)
C(5)		86.6 (*s*)		87.8 (*s*)
CH_2(6)	1.29 – 1.36, 2.15 – 2.20 (2*m*)	21.9 (*t*)	2.00 – 2.03, 2.03 – 2.05 (2*m*)	24.8 (*t*)
H–C(7)	2.78 (*dddd*, *J* = 6.0, 6.8, 7.0, 14.0)	36.4 (*d*)	3.38 – 3.41 (*m*)	36.1 (*d*)
H–C(8)	4.60 – 4.62 (*m*)	77.3 (*d*)	5.34 – 5.35 (*m*)	69.8 (*d*)
CH_2(9)	2.28 – 2.32 (*m*), 1.89 (*dd*, *J* = 4.8, 15.5)	32.7 (*t*)	1.85 – 1.87, 1.87 – 1.90 (2*m*)	35.5 (*t*)
C(10)		42.3 (*s*)		42.9 (*s*)
H–C(11) or C(11)	2.87 (*dq*, *J* = 7.0, 7.2)	41.2 (*d*)		140.7 (*s*)
C(12)		179.4 (*s*)		167.5 (*s*)
Me(13) or CH_2(13)	1.23 (*d*, *J* = 7.2)	9.4 (*q*)	5.64, 6.31 (2 br. *s*)	125.3 (*t*)
Me(14)	0.92 (*s*)	15.0 (*q*)	1.01 (*s*)	15.7 (*q*)
CH_2(15)	4.90, 5.16 (2 br. *s*)	114.0 (*t*)	4.90, 5.12 (2 br. *s*)	112.4 (*t*)
C(1′)				170.1 (*s*)
Me(2′)			1.97 (*s*)	21.3 (*q*)
Me(3′)			3.78 (*s*)	52.2 (*q*)
OOH	7.56 (br. *s*)		7.82 (br. *s*)	

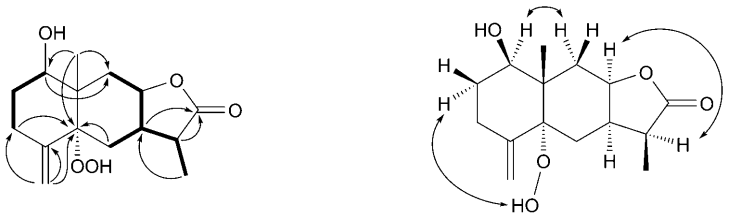


Fig. 1. *Key ^{1}H,^{1}H-COSY* (—), *Key gHMBC* (H → C), *and NOESY* (H ↔ H) *features of* **1**

HOO–C(5) with H_α–C(2) and of H–C(8) with H–C(11) suggested that HOO–C(5) and H–C(11) were α-oriented. Therefore, compound **1** was determined as (1β,5α,7β,8β,11β)-5-hydroperoxy-1-hydroxyeudesm-4(15)-eno-12,8-lactone[1]).

Compounds **7** and **8** were isolated as a colorless, crystalline mixture (ratio nearly 1:1). The molecular formula of **7** was determined as $C_{15}H_{20}O_4$ from its HR-ESI-MS (*m*/*z* 282.1705 ($[M + NH_4]^+$)). The ^{13}C-NMR spectrum (*Table 2*), together with the DEPT experiment of **7** showed signals of fifteen C-atoms, including two Me, three CH_2, and six CH groups, and four quaternary C-atoms. The NMR data of **7** (*Table 2*) were similar to those of compounds **5** and **6**, except for the fact that the δ(C) of C(3) of **5** was downfield shifted from δ(C) 29.4 to 70.0, suggesting the presence of an OH at C(3) of **7**. The observed HMBCs from H–C(3) (δ(H) 3.71 – 3.77) to C(15) (δ(C) 16.5), C(2)

Table 2. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$; 400 and 100 MHz, resp.) *of* **7**[1]) *and* **8**[1]). δ in ppm, J in Hz.

	7		**8**	
	δ(H)	δ(C) (DEPT)	δ(H)	δ(C) (DEPT)
H–C(1)	3.27 (*dd*, J = 4.0, 11.6)	78.5 (*d*)	3.31 (*dd*, J = 4.4, 12.8)	78.9 (*d*)
CH_2(2)	1.76–1.80, 1.84–1.87 (2*m*)	36.1 (*t*)	1.76–1.80, 1.90–1.93 (2*m*)	36.7 (*t*)
H–C(3)	3.71–3.73 (*m*)	70.0 (*d*)	3.71–3.73 (*m*)	70.0 (*d*)
H–C(4)	2.56–2.63 (*m*)	46.5 (*d*)	2.56–2.63 (*m*)	47.3 (*d*)
C(5)		147.8 (*s*)		149.2 (*s*)
H–C(6)	5.39 (*d*, J = 4.0)	124.4 (*d*)	5.42 (*d*, J = 3.2)	121.3 (*d*)
H–C(7)	3.68–3.70 (*m*)	41.0 (*d*)	3.08–3.12 (*m*)	40.2 (*d*)
H–C(8)	4.86–4.89 (*m*)	76.9 (*d*)	4.77–4.79 (*m*)	77.2 (*d*)
CH_2(9)	1.54, 2.49 (2*dd*, each J = 2.8, 14.8)	41.0 (*t*)	1.50 (*dd*, J = 2.8, 14.8), 2.53 (*dd*, J = 3.2, 14.8)	41.4 (*t*)
C(10)		38.9 (*s*)		39.3 (*s*)
C(11) or H–C(11)		142.0 (*s*)	3.00 (*dq*, J = 7.2, 6.8)	41.3 (*d*)
C(12)		170.7 (*s*)		179.4 (*s*)
CH_2(13) or Me(13)	6.06, 5.74 (2*d*, each J = 1.6)	121.9 (*t*)	1.62 (*d*, J = 7.2)	11.5 (*q*)
Me(14)	1.13 (*s*)	23.3 (*q*)	1.16 (*s*)	23.3 (*q*)
Me(15)	1.04 (*d*, J = 7.2)	16.5 (*q*)	1.07 (*d*, J = 7.6)	17.0 (*q*)

(δ(C) 36.1), and C(4) (δ(C) 46.5) further confirmed that the OH group was bonded to C(3). The large coupling constant between H–C(1) and H–C(2) (J = 11.6 Hz) suggested that OH–C(1) was β-oriented. Fortunately, we could obtain a single crystal of **7** from the mixture **7**/**8** in MeOH, so the relative configuration of **7** was further determined by an X-ray crystal-structure analysis[2]) (*Fig. 2*). Finally, compound **7** was determined as (1β,3β,4β,7β,8β)-1,3-dihydroxyeudesma-5,11(13)-dieno-12,8-lactone[1]).

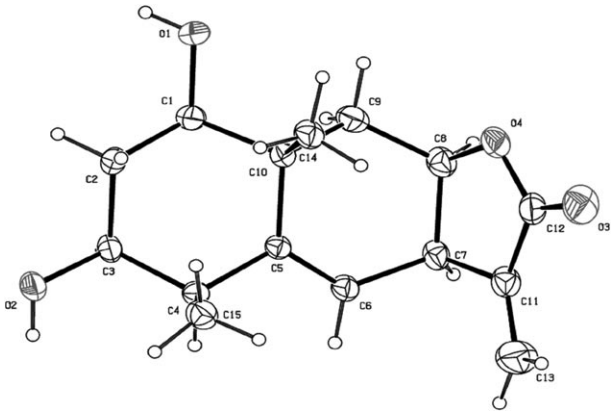


Fig. 2. *X-Ray crystal structure of* **7**

[2]) CCDC-798663 contains the supplementary crystallographic data for compound **7**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

The molecular formula of **8**, $C_{15}H_{22}O_4$ was deduced from its HR-ESI-MS (*m/z* 284.1864 ($[M+NH_4]^+$)). The ^{1}H- and ^{13}C-NMR spectra of **8** (*Table 2*) were closely similar to those of **7**, except for the absence of a C=C bond between C(11) and C(13). The ^{1}H,^{1}H-COSY experiment showed two spin systems (*Fig. 3*). The HMBCs from H–C(4) and H–C(6) to C(5) and from Me(14) to C(1), C(5), C(10), and C(9) (*Fig. 3*) helped us to connect the fragments together. Similarly, the observed HMBCs from H–C(1) to C(14), C(9), and C(10), and from H–C(3) to C(15), C(2), and C(4) suggested that OH groups were located at C(1) and C(3). The similarity of the NMR data of compounds **7** and **8** indicated that both OH groups of **8** should be also β-oriented, which can be expected from a biogenetic viewpoint. Thus, compound **8** was determined as (1β,3β,4β,7β,8β,11β)-1,3-dihydroxyeudesm-5-eno-12,8-lactone[1]).

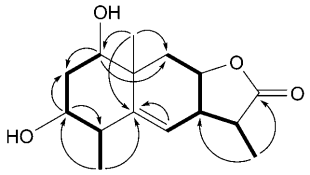


Fig. 3. *^{1}H,^{1}H-COSY* (—) *and Key gHMBC* (H → C) *features of* **8**

Compound **12** was isolated as colorless crystals. The molecular formula, $C_{18}H_{26}O_7$, was determined by its HR-ESI-MS (*m/z* 372.2027 ($[M+NH_4]^+$)) and implied six degrees of unsaturation. The ^{1}H-NMR spectrum (*Table 1*) showed an OOH signal at δ(H) 7.82 (br. *s*). The ^{13}C-NMR and DEPT spectra of **12** (*Table 1*) displayed signals of eighteen C-atoms, including three Me, six CH_2 (two olefinic, at δ(C) 125.3 and 112.4) and three CH groups (two O-bearing, at δ(C) 72.1 and 69.8), and six quaternary C-atoms. Intense inspection of the NMR data of **12** revealed the typical signals for an MeO (δ(H) 3.78; δ(C) 52.2), AcO (δ(H) 1.97; δ(C) 21.3), terminal double bond, and α-methylene γ-ester unit, which were similar to those of **11**. Comparison of the NMR data with those of **11** also indicated that an OOH group (δ(H) 7.82) was presented at C(5) (δ(C) 87.8) of **12**. Additionally, the simplified ^{1}H-NMR signal of CH_2(6) supported that the OOH group was at C(5). The HMBCs from H–C(3), CH_2(6), and Me(15) to C(5) further confirmed our assumption. The relative configuration of **12** could be determined by X-ray crystal-structure analysis[3]) (*Fig. 4*). Thus, the structure of compound **12** was determined as (1β,5α,7β,8β)-8-(acetyloxy)-5-hydroperoxy-7-hydroxycostic acid methyl ester[1]).

The ^{13}C-NMR data of the known endesmane derivatives **2**, **3**, and **10** are given in *Table 3*.

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[3]) CCDC-798664 contains the supplementary crystallographic data for compound **12**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

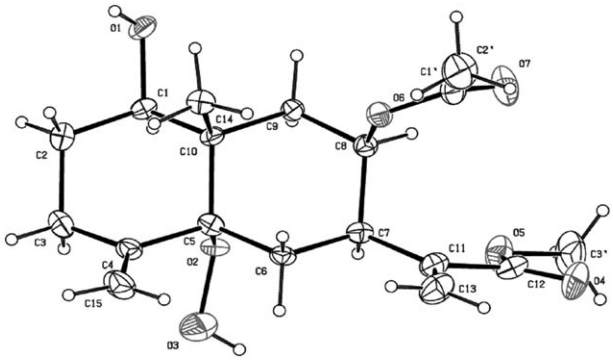

Fig. 4. *X-Ray crystal structure of* **12**

Table 3. *^{13}C-NMR Data* ($CDCl_3$, 100 MHz) *of* **2**[1]), **3**[1]), *and* **10**[1]). δ in ppm, *J* in Hz.

	2	**3**	**10**
C(1)	72.7 (*d*)	72.9 (*d*)	78.8 (*d*)
C(2)	29.8 (*t*)	31.5 (*t*)	30.9 (*t*)
C(3)	30.3 (*t*)	33.2 (*t*)	33.4 (*t*)
C(4)	144.5 (*s*)	151.6 (*s*)	142.0 (*s*)
C(5)	86.7 (*s*)	74.7 (*s*)	54.0 (*d*)
C(6)	27.9 (*t*)	30.5 (*t*)	74.6 (*d*)
C(7)	37.1 (*d*)	38.2 (*d*)	53.5 (*d*)
C(8)	76.5 (*d*)	77.6 (*d*)	65.3 (*d*)
C(9)	32.4 (*t*)	34.6 (*t*)	42.9 (*t*)
C(10)	41.9 (*s*)	41.8 (*s*)	42.9 (*s*)
C(11)	141.6 (*s*)	144.3 (*s*)	135.7 (*s*)
C(12)	170.5 (*s*)	170.7 (*s*)	170.0 (*s*)
C(13)	120.9 (*t*)	119.5 (*t*)	118.3 (*t*)
C(14)	15.0 (*q*)	14.7 (*q*)	13.9 (*q*)
C(15)	114.5 (*t*)	108.9 (*t*)	110.7 (*t*)

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 200–300 mesh; *Qingdao Marine Chemical Factory*, Qingdao, P. R. China). TLC: SiO_2 *GF_{254}* (*Qingdao Marine Chemical Factory*). M.p.: *X-4* Digital-display micro-melting-point apparatus; uncorrected. X-Ray crystallographic analysis: *Bruker-Axs-Smart-Apex-II* imaging plate area detector with graphite monochromated MoK_α *radiation* (λ 0.71073 Å). Optical rotations: *Perkin-Elmer-341* polarimeter; in MeOH at 20°. IR Spectra: *Nicolet-Nexus-670* FT-IR spectrometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker-Avance-III-400* NMR spectrometer; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. HR-ESI-MS: *Bruker-Apex-II* instrument; in *m*/*z*.

Plant Material. The aerial parts of *Inula japonica* were purchased from *Lanzhou Fuxinghou Medical Materials Co., Ltd.*, in 2008 and identified by *Shi-Jie Xu*, School of Life Sciences, Lanzhou University. A voucher specimen (No. ZY2008I001) was deposited in the laboratory.

Extraction and Isolation. The air-dried plant material (9.5 kg) was extracted exhaustively with 95% aq. EtOH at 60°. The extract was concentrated and the residue (647 g) suspended in H_2O (1.1 l) and then extracted with petroleum ether (3 × 1.1 l), AcOEt (3 × 1.1 l), and BuOH (3 × 1.1 l), resp. The petroleum ether extract (327 g) was subjected to CC (SiO_2 (1500 g), gradient of petroleum ether/acetone 40:1, 20:1, 15:1, 10:1, 8:1, 5:1, 3:1, 2:1, 1:1, and 1:2): *Fractions 1–10* (by TLC). *Fr. 5* (5 g) was subjected to

CC) (SiO_2 (30 g), $CHCl_3$/AcOEt 40:1 → 1:1): *Fr. 5.1* (0.1 g) and *Fr. 5.2* (0.13 g), which were purified by prep. TLC ($CHCl_3$/AcOEt 3:1) to give **11** (11 mg) and **9** (15 mg). *Fr. 6* (6.5 g) was further separated by CC (SiO_2, $CHCl_3$/AcOEt 40:1 → 1:1): *Frs. 6.1–6.3. Fr. 6.1* was repeatly purified by CC (SiO_2, petroleum ether/AcOEt 20:1 → 5:1): **5** (50 mg) and **6** (3 mg). *Fr. 6.2* was purified by CC (SiO_2, petroleum ether/AcOEt 10:1): **2** (70 mg). CC (SiO_2, petroleum ether/AcOEt 7:1) of *Fr. 6.3* gave **1** (6 mg). The lactones **13** (50 mg) and **14** (50 mg) were obtained from *Fr. 7* (2 g) and *Fr. 8* (2.5 g) after CC (SiO_2, petroleum ether/actone 2.5:1 and 2:1, resp.), followed by recrystallization from acetone. The AcOEt extract (75 g) was subjected to CC (SiO_2, gradient of $CHCl_3$/MeOH 100:0, 100:1, 100:3, 100:5, 100:10, 100:15, 100:30, and 100:50): *Fr. 11–18* (by TLC). *Fr. 12* (2 g) was subjected to CC (SiO_2 (20 g), petroleum ether/AcOEt 10:1 → 3:1): **4** (3 mg). *Fr. 13* (3 g) was subjected to CC (SiO_2 (40 g), $CHCl_3$/AcOEt 10:1 → 1:1): **12** (2 mg) and **10** (5 mg). Lactones **7**/**8** (6 mg) were isolated as a mixture from *Fr. 14* (0.3 g), which was repeatly purified by CC (SiO_2, $CHCl_3$/MeOH 50:1 → 2:1. Lactone **3** (5 mg) was obtained from *Fr. 15* (0.2 g) after purification by CC (SiO_2, $CHCl_3$/MeOH 30:1 → 1:1).

(1β,5α,7β,8β,11β)-5-Hydroperoxy-1-hydroxyeudesm-4(15)-eno-12,8-lactone (= rel-*(3*R*,3a*S*,4a*S*,8*S*, 8a*R*,9a*S*)-Decahydro-4a-hydroperoxy-8-hydroxy-3,8a-dimethyl-5-methylenenaphtho[2,3-*b*]furan-2(3*H*)-one*; **1**): Colorless oil. $[\alpha]_D^{20} = -108$ ($c = 0.1$, MeOH). IR (KBr): 3371, 1752, 1706, 1651, 1357, 1186, 986, 961. ^{1}H- and ^{13}C-NMR: *Table 1*. HR-ESI-MS: 300.1800 ($[M+NH_4]^+$, $C_{15}H_{26}NO_5^+$; calc. 300.1805).

(1β,3β,4β,7β,8β)-1,3-Dihydroxyeudesma-5,11(13)-dieno-12,8-lactone (= rel-*(3a*R*,5*R*,6*S*,8*R*,8a*R*, 9a*R*)-3a,5,6,7,8,8a,9,9a-Octahydro-6,8-dihydroxy-5,8a-dimethyl-3-methylenenaphtho[2,3-*b*]furan-2(3*H*)-one*; **7**) *and (1β,3β,4β,7β,8β,11β)-Dihydroxyeudesm-5-eno-12,8-lactone* (= rel-*(3*R*,3a*S*,5*S*,6*R*,8*S*,8a*S*,9a*S*)-3a,6,7,8,8a,9,9a-Octahydro-6,8-dihydroxy-3,5,8a-trimethylnaphtho[2,3-*b*]furan-2(3*H*)-one*; **8**): Colorless crystals. IR (KBr): 3420, 1731, 1648, 1449, 1372, 1265, 1037, 978, 869. ^{1}H- and ^{13}C-NMR: *Table 2*. HR-ESI-MS: **7**: 282.1705 ($[M+NH_4]^+$, $C_{15}H_{24}NO_4^+$; calc. 282.1700); **8**: 284.1864 ($[M+NH_4]^+$, $C_{15}H_{26}NO_4^+$; calc. 284.1856).

(1β,5α,7β,8β)-8-(Acetyloxy)-5-hydroperoxy-1-hydroxycostic Acid Methyl Ester (= *Methyl* rel-*(2*R*,3*R*,4a*S*,5*R*,8a*R*)-3-(Acetyloxy)decahydro-8a-hydroperoxy-5-hydroxy-4a-methyl-α,8-bis(methylene)-naphthalene-2-acetate*; **12**): Colorless crystal. M.p. 202–204°. $[\alpha]_D^{20} = +17$ ($c = 0.1$, MeOH). UV (MeOH): 210 (4.1). IR (KBr): 3404, 2928, 2858, 1718, 1647, 1629, 1438, 1249, 1062, 1020, 987, 951. ^{1}H- and ^{13}C-NMR: *Table 3*. HR-ESI-MS: 372.2027 ($[M+NH_4]^+$, $C_{18}H_{30}NO_7^+$; calc. 372.2017).

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