Sesquiterpenoids and Phenylpropane Derivatives from *Sonchus uliginosus*

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Six new compounds were isolated from the whole plant of *Sonchus uliginosus*, including three eudesmane-type sesquiterpenoids (1β,6α)-1,6,14-trihydroxyeudesm-3-en-12-oic acid γ-lactone (**1**), (1β,6α)-1,6,14-trihydroxyeudesma-3,11(13)-dien-12-oic acid γ-lactone (**2**), and (1β,6α)-1,6-dihydroxy-14-*O*-[(4-hydroxyphenyl)acetyl]eudesma-3,11(13)-dien-12-oic acid γ-lactone (**3**), and three phenylpropane derivatives, 4-hydroxy-γ,3,5-trimethoxybenzenepropanol (**6**), γ,3,4,5-tetramethoxybenzenepropanol (**7**), and γ,3,4,5-tetramethoxybenzenepropanol acetate (**8**), together with the two known compounds **4** and **5**. The new structures were elucidated by means of spectroscopic methods, such as IR, EI-MS, HR-ESI-MS, 1D- and 2D-NMR, and by comparison of the spectroscopic data with those reported for structurally related compounds.

Introduction. – The genus *Sonchus*, representing 8 species in China, has long been used as folk medicine for the treatment of fever, stasis, and inflammation, as well as for detoxication and mobilization of blood circulation [1]. In some species, eudesmanolides [2][3], sesquiterpane glycosides [4][5][6], and ionone glycoside derivatives [5] have been found. Up to now, the chemical constituents of *S. uliginosus* have not been investigated. In continuation of our studies aimed at finding new chemical constituents from the Compositae plant family, we now report six new, *i.e.*, **1**–**3** and **6**–**8**, and two known compounds, *i.e.*, **4** and **5** [6], isolated from the whole plant of *S. uliginosus*.[1])

Results and Discussion. – Compound **1** was obtained as a white amorphous powder. The molecular formula of **1** was determined as $C_{15}H_{22}O_4$ based on HR-ESI-MS (*m*/*z* 284.1861 ($[M+NH_4]^+$)). The IR spectrum showed absorption bands for OH groups (3289 cm^{-1}) and a γ-lactone carbonyl group (1763 cm^{-1}). Comparing the data and features of the ^{1}H- and ^{13}C-NMR spectra of **1** (*Table 1*) with those of known compounds [3][7], a structure based on a (6α)-6,14-dihydroxyeudesman-12-oic acid γ-lactone with an additional OH group and a C=C bond was inferred and confirmed by the HMBC data (see *Fig.*). The relative configuration of **1** was determined on the basis of the analysis of coupling constants and NOE experiments. From all these data, the structure of compound **1** was deduced as (1β,6α)-1,6,14-trihydroxyeudesm-3-en-12-oic acid γ-lactone.

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

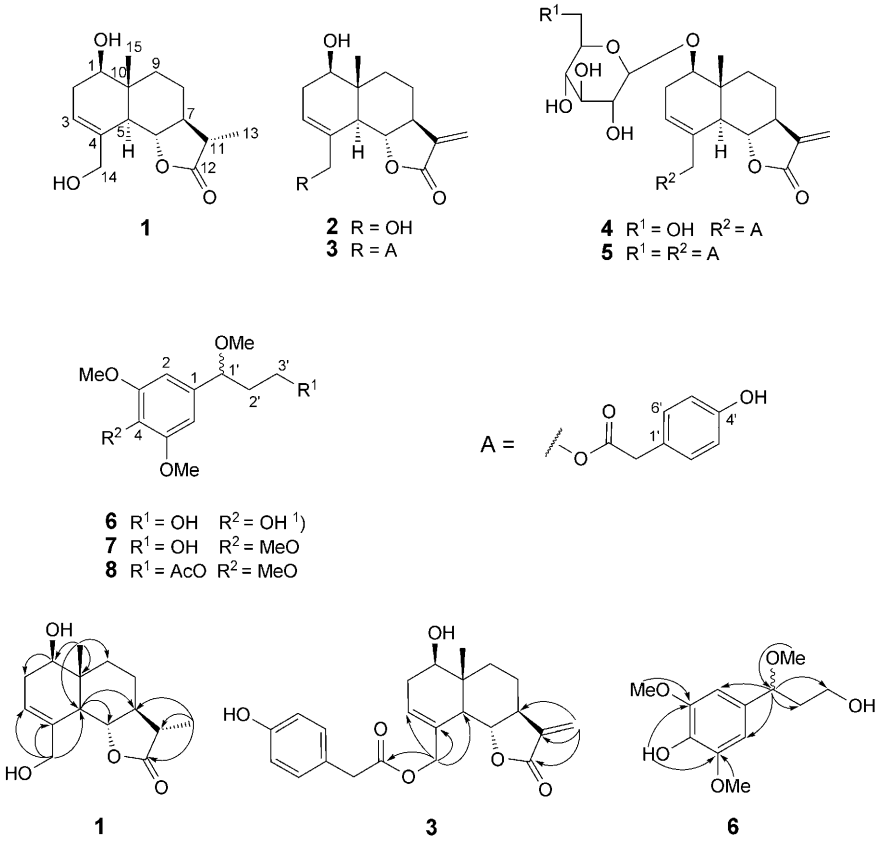

Figure. *Key HMBC correlations* (H → C) *for* **1**, **3**, *and* **6**

The ^{1}H- and ^{13}C-NMR (DEPT) spectra (*Table 1*) indicated the presence of 15 C-atoms, *i.e.*, two Me, four CH_2 (one for a CH_2OH), and six CH groups and three quaternary C-atoms. In the ^{1}H-NMR spectrum, there were typical signals for two Me groups at δ(H) 1.15 (*d*, $J = 7.2$ Hz) and 1.10 (*s*), as well as a signal for a C=CH moiety at δ(H) 6.14 (br. *s*, 1 H). In the ^{13}C-NMR spectrum, there were resonances for an ester carbonyl at δ(C) 178.74, and three oxygenated C-atoms at δ(C) 80.73, 74.19, and 64.02. The HMBC cross-peaks between Me(15) at δ(H) 1.10 and C(1) at δ(C) 74.19, C(5) at δ(C) 48.89, C(9) at δ(C) 34.94, and C(10) at δ(C) 40.92, and between H–C(1) at δ(H) 3.88 and C(2) at δ(C) 32.91 indicated that the OH group was attached at C(1) (*Fig.*). The HMBC cross-peaks between CH_2(14) at δ(H) 4.60 and C(3) at δ(C) 120.63, C(4) at δ(C) 137.69, and C(5) at δ(C) 48.89 indicated that the C=C bond was between C(3) and C(4). The HMBC cross-peaks between H–C(5) at δ(H) 2.39 and C(6) at δ(C) 80.73 and C(7) at δ(C) 53.02 revealed that the γ-lactone moiety was at C(6) and C(7).

The large coupling constants observed for H–C(1) with H–C(2) ($J(1\alpha,2\beta) = 9.6$ Hz) and for H–C(6) with H–C(5) ($J(6\beta,5\alpha) = 10.4$ Hz) and H–C(7) ($J(6\beta,7\alpha) = 10.4$ Hz) allowed the assignment of the relative configuration at the stereogenic centers C(1), C(6), and C(7), *i.e.*, of the α-position of H–C(1) and the $6\alpha,7\beta$-orientation the γ-lactone moiety. In addition, in the NOE difference spectrum of **1**, the signal of H–C(6) was enhanced (2.85%) on irradiation of Me(15), indicating the β-orientation of H–C(6), whereas the signals of H–C(1), H–C(5), and H–C(7) were not affected, indicating their α-orientation. Further NOEs were observed for H–C(1)/H–C(5) and H–C(7) (3.61 and 1.81%, resp.), which also confirmed the relative configuration at C(1), C(5), C(6), and C(7). The configuration at C(11) was deter-

Table 1. *^{1}H- and ^{13}C-NMR Data of* **1–3**. At 400 and 100 MHz, resp., in (D_5) pyridine (**1** and **2**) or D_2O (**3**); δ in ppm, J in Hz; trivial atom numbering.

	1		**2**		**3**[a]	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
H–C(1)	3.88 (*dd*, J=6.8, 9.6)	74.19 (*d*)	3.88 (*dd*, J=6.8, 9.6)	74.08 (*d*)	4.10 (*dd*, J=7.2, 9.2)	82.72 (*d*)
CH_2(2)	2.64, 2.39 (2*m*)	32.91 (*t*)	2.64, 2.59 (2*m*)	32.91 (*t*)	2.16, 2.08 (2*m*)	30.50 (*t*)
H–C(3)	6.14 (br. *s*)	120.63 (*d*)	6.14 (br. *s*)	120.75 (*d*)	5.61 (br. *s*)	130.34 (*d*)
C(4)	–	137.69 (*s*)	–	137.53 (*s*)	–	131.04 (*s*)
H–C(5)	2.39 (*d*, J=10.4)	48.89 (*d*)	2.39 (*d*, J=10.4)	49.37 (*d*)	2.51 (*d*, J=10.8)	48.46 (*d*)
H–C(6)	4.16 (*dd*, J=10.4, 10.4)	80.73 (*d*)	4.11 (*dd*, J=10.4, 10.4)	81.13 (*d*)	2.65 (*dd*, J=10.8, 10.8)	81.92 (*d*)
H–C(7)	1.47 (*m*)	53.02 (*d*)	2.50 (*m*)	50.50 (*d*)	2.08 (*m*)	49.76 (*d*)
CH_2(8)	1.68, 1.47 (2*m*)	22.50 (*t*)	1.81, 1.51 (2*m*)	20.87 (*t*)	2.03, 1.76 (2*m*)	20.47 (*t*)
CH_2(9)	1.47, 1.33 (2*m*)	34.94 (*t*)	1.47, 1.33 (2*m*)	34.60 (*t*)	1.68, 1.08 (2*m*)	34.16 (*t*)
C(10)	–	40.92 (*s*)	–	40.99 (*s*)	–	39.87 (*s*)
H–C(11) or C(11)	2.32 (*m*)	40.07 (*d*)	–	139.57 (*s*)	–	138.11 (*s*)
C(12)	–	178.74 (*s*)	–	170.07 (*s*)	–	173.83 (*s*)
Me(13) or CH_2(13)	1.15 (*d*, J=7.2)	12.12 (*q*)	6.10, 5.31 (2*d*, J=2.4)	115.63 (*t*)	5.76, 5.34 (2*d*, J=2.8)	118.70 (*t*)
CH_2(14)	4.60 (*dd*, J=14.4, 6.8)	64.02 (*t*)	4.60 (*dd*, J=14.4, 6.8)	64.02 (*t*)	4.43, 4.15 (2*d*, J=10.8)	68.71 (*t*)
Me(15)	1.10 (*s*)	10.93 (*q*)	1.07 (*s*)	10.93 (*q*)	0.54 (*s*)	11.67 (*q*)

[a]) Ester group A–C(14): δ(H) 6.85 (*d*, J=8.4, H–C(2′,6′)), 6.48 (*d*, J=8.4, H–C(3′,5′)), 3.31 (*d*, J=14.8, CH_2–C(1′)); δ(C) 125.83 (*s*, C(1′)), 131.12 (*d*, C(2′,6′)), 115.85 (*d*, C(3′,5′)), 154.70 (*s*, C(4′)), 40.99 (*t*, CH_2–C(1′)), 173.99 (*s*, COO).

mined by means of empirical rules [8]. In the ^{13}C-NMR spectrum, the δ(C) 12.12 of Me(13) is typical for 6-hydroxyeudesman-12-oic acid γ-lactones having an α-methyl group at C(11). This was confirmed by an NOE at the signal of H–C(11) (2.74%) on irradiation of H–C(6), indicating the β-orientation of H–C(11).

Compound **2** was obtained as a white amorphous powder with the molecular formula $C_{15}H_{20}O_4$ as deduced by HR-ESI-MS (*m*/*z* 282.1707 ($[M+NH_4]^+$)). The IR spectrum showed typical absorption bands for OH groups (3290 cm^{-1}) and an α-methylene-substituted γ-lactone moiety (1753 cm^{-1}). From further data (see *Table 1*), the structure of **2** was elucidated as (1β,6α)-1,6,14-trihydroxyeudesma-3,11(13)-dien-12-oic acid γ-lactone.

Comparing the NMR data of **2** with those of **1**, the main difference was that the α-methyl-substituted γ-lactone moiety of **1** (δ(H) 1.15 (*d*, J=7.2 Hz, Me(13)) and 2.32 (*m*, H–C(11)); δ(C) 12.12 (C(13)), 40.07 (C(11)), and 178.74 (C(12)) was replaced in **2** by an α-methylene-substituted γ-lactone moiety (δ(H) 6.10 and 5.31 (2*d*, J=2.4 Hz, CH_2(13)); δ(C) at 115.63 (C(13)), 139.57 (C(11)), and 170.07 (C(12)). The HMBC cross-peaks between CH_2(13) at δ(H) 6.10 and 5.31 and C(7) at δ(C) 50.50, C(11) at δ(C) 139.57, and C(12) at δ(C) 170.07 confirmed the presence of an α-methylene-substituted γ-lactone unit. The remaining signals were similar to the ones of **1**.

Compound **3** was obtained as a yellow gum. The molecular formula $C_{23}H_{26}O_6$ was deduced from HR-ESI-MS which gave an $[M+Na]^+$ ion peak at m/z 421.4446. Comparing with compound **2**, the IR spectrum of **3** showed extra absorption bands for a benzyl group (1611, 1516, and 1445 cm^{-1}) and another ester carbonyl (1710 cm^{-1}), besides the absorption bands for an OH group (3404 cm^{-1}), and an α-methylene-substituted γ-lactone unit (1759 cm^{-1}). From the spectral data (see *Table 1*), compound **3** was identified as (1β,6α)-1,6-dihydroxy-14-*O*-[(4-hydroxyphenyl)acetyl]eudesma-3,11(13)-dien-12-oic acid γ-lactone.

The ^{1}H-NMR spectrum of **3** was similar to that of **2**, except for the appearance of signals due to a (4-hydroxyphenyl)acetate moiety at δ(H) 6.85 (*d*, J=8.4 Hz, H–C(2′), H–C(6′)), 6.48 (*d*, J=8.4 Hz, H–C(3′), H–C(5′)), and 3.31 (*d*, J=14.8 Hz, CH_2–C(1′) [6] [9], which was confirmed by the ^{13}C-NMR chemical shifts δ(C) 125.83 (C(1′)), 131.12 (C(2′), C(6′)), 115.85 (C(3′), C(5′)), 154.70 (C(4′)), 40.99 (CH_2–C(1′)), and 173.99 (COO). The EI-MS of **3**, with a fragment ion at m/z 151.9 ($C_8H_8O_3^+$), which was higher than other peaks, also indicated the presence of a (4-hydroxyphenyl)acetate group. The HMBC cross-peaks (*Fig.*) between CH_2(14) at δ(H) 4.43 and 4.15 and an ester C=O at δ(C) 173.99 indicated that the (4-hydroxyphenyl)acetate group was attached at C(14).

Compound **6** was obtained as a colorless gum. The HR-ESI-MS experiment showed the $[M+Na]^+$ signal at m/z 265.1049, in accord with the molecular formula $C_{12}H_{18}O_5$. In the IR spectrum, absorption bands for OH groups (3361 cm^{-1}) and a benzyl group (1610, 1516, 1459 cm^{-1}) were present. Careful comparison of the ^{1}H- and ^{13}C-NMR data of **6** (*Table 2*) with those of related compounds [10–12], led to the conclusion that **6** had a phenylpropane skeleton. From further data (see *Table 2*), the structure of compound **6** was deduced as 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-methoxypropane[1]).

Table 2. *^{1}H- and ^{13}C-NMR Data of* **4**–**6**. At 300 and 75 MHz, resp., in $CDCl_3$; δ in ppm, J in Hz; arbitrary atom numbering[1]).

	6		**7**		**8**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
C(1)	–	132.63 (*s*)	–	137.31 (*s*)	–	137.26 (*s*)
H–C(2,6)	6.54 (br. *s*)	102.82 (*d*)	6.53 (br. *s*)	102.89 (*d*)	6.51 (br. *s*)	102.96 (*d*)
C(3,5)	–	147.08 (*d*)	–	153.32 (*d*)	–	153.34 (*s*)
C(4)	–	134.02 (*s*)	–	137.31 (*s*)	–	137.26 (*s*)
H–C(1′)	4.30 (*dd*, J=4.2, 9.3)	84.08 (*d*)	4.32 (*dd*, J=3.9, 9.3)	83.98 (*d*)	4.15 (*m*)	80.77 (*d*)
CH_2(2′)	2.03, 1.85 (2*m*)	40.50 (*t*)	2.02, 1.85 (2*m*)	40.44 (*t*)	2.11, 1.94 (2*m*)	37.17 (*t*)
CH_2(3′)	3.78 (*t*, J=5.7)	61.22 (*t*)	3.79 (*t*, J=5.4)	61.16 (*t*)	4.15 (*m*)	61.44 (*t*)
MeO–C(1′)	3.24 (*s*)	56.50 (*q*)	3.26 (*s*)	56.72 (*q*)	3.23 (*s*)	56.75 (*q*)
MeO–C(3,5)	3.90 (*s*)	56.25 (*q*)	3.88 (*s*)	56.03 (*q*)	3.87 (*s*)	56.04 (*q*)
OH–C(4) or MeO–C(4)	5.59 (*s*)	–	3.86 (*s*)	60.81 (*q*)	3.85 (*s*)	60.83 (*q*)
AcO	–	–	–	–	2.02 (*s*)	21.03 (*q*), 171.12 (*s*)

The ^{1}H- and ^{13}C-NMR (DEPT) spectra indicated that **6** contained three MeO, two CH_2, three CH, and four quaternary C-atoms. The ^{1}H-NMR spectrum showed two overlapped C=CH moieties at δ(H) 6.54 (br. *s*, 2 H), an OH proton at δ(H) 5.59 (br. *s*, 1 H), and three MeO groups at δ(H) 3.90 (*s*, 6 H) and 3.24 (*s*, 3 H). In the ^{13}C-NMR spectrum, typical signals for an oxygenated CH_2 at δ(C) 61.22 and an oxygenated CH at δ(C) 84.08 were present. The EI-MS of **6** with the molecular ion M^+ at *m*/*z* 242 and the base peak at *m*/*z* 197 (loss of C_2H_5O), confirmed the presence of a CH_2CH_2OH moiety. The HMBC cross-peaks (*Fig.*) between the upfield MeO signal at δ(H) 3.24 and C(1′) at δ(C) 84.08 indicated that this MeO group was attached at C(1′)[1]). The HMBC cross-peaks between H–C(1′) at δ(H) 4.30 and C(2′) at δ(C) 40.50 and C(3′) at δ(C) 61.22 suggested the existence of a $CH(OMe)CH_2CH_2OH$ side chain. In addition, the HMBC cross-peaks between H–C(1′) at δ(H) 4.30 and C(2) and C(6) at δ(C) 102.82 indicated that this $CH(OMe)CH_2CH_2OH$ side chain was attached at C(1) of the aromatic ring.

Compound **7** was obtained as a colorless gum. The molecular formula was established as $C_{13}H_{20}O_5$ on the basis of the HR-ESI-MS (*m*/*z* 279.1206 ($[M+Na]^+$)). The ^{1}H- and ^{13}C-NMR spectral data (*Table 2*) of **7** were very similar to those of **6**, except for the signals of OH–C(4) which were replaced by those of a MeO–C(4)[1]). This could be confirmed by the HMBC cross-peaks between MeO–C(4) at δ(H) 3.86 and C(4) at δ(C) 137.31. The above data allowed us to assign **7** as 3-hydroxy-1-methoxy-1-(3,4,5-trimethoxyphenyl)propane[1]).

Compound **8** was characterized as the acetate of **7**. The IR spectrum revealed absorption bands for a C=O group (1737 cm^{-1}). The ^{1}H- and ^{13}C-NMR spectra (*Table 2*) also suggested the presence of an AcO group (δ(H) 2.02 and δ(C) 21.03 and 171.12). These data, together with the molecular formula $C_{15}H_{22}O_6$, assigned by the HR-ESI-MS (*m*/*z* 321.1308 ($[M+Na]^+$)), suggested for **8** the structure of 3-(acetyloxy)-1-methoxy-1-(3,4,5-trimethoxyphenyl)propane[1]).

Compounds **6**–**8** are chiral and were isolated in optically active form. The absolute configuration at the asymmetric center C(1′) was not determined.

The known compounds **4** [6] and **5** [6] were identified by comparison of their physical and spectral data with those reported in the literature.

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Experimental Part

General. Column chromatography (CC): silica gel (200–300 mesh; *Qingdao Marine Chemical Factory*, Qingdao, P. R. China). TLC: silica GF_{254} (10–40 μ; *Qingdao Marine Chemical Factory*); detection at 254 nm or by heating after spraying with 5% H_2SO_4 in EtOH (*v*/*v*). $[\alpha]_D$: *Perkin-Elmer-341* polarimeter. IR Spectra: *Nicolet-NEXUS-670* FT-IR spectrometer; in cm^{-1}. UV Spectra: *Shimadzu-UV-260* spectrometer. NMR Spectra: *Bruker-AM-400* FT-NMR spectrometer and *Varian-Mercury-300BB* spectrometer (^{1}H at 400 or 300 MHz; ^{13}C at 100 or 75 MHz); $SiMe_4$ as internal standard. MS: *VG-ZABHS* instrument at 70 eV for EI, and *Bruker-APEX-II* instrument with glycerol as the matrix for HR-ESI; in *m*/*z* (rel. %).

Plant Material. The whole plant of *Sonchus uliginosus* was collected in Heyang County, Shanxi province, P. R. China, in August 2005, and identified by Prof. *Guoliang Zhang* from the School of Life Science, Lanzhou University. A voucher specimen (No. 2005-C008) was deposited at the College of Chemistry and Chemical Engineering, Lanzhou University.

Extraction and Isolation. The air-dried whole plant of *S. uliginosus* (7.5 kg) was pulverized and extracted with MeOH (7 days × 3 times) at r.t. The solvent was evaporated giving an extract (600.0 g)

which was suspended in H_2O (1.5 l) and successively partitioned with petroleum ether (60–90°) (1.5 l), AcOEt (1.5 l), and BuOH (1.5 l). The AcOEt portion afforded, on concentration, a residue (7.8 g) which was subjected to CC (silica gel (100 g), $CHCl_3$/MeOH 20:1, 15:1, 10:1, 5:1, 3:1, 1:1, and 0:1): Fractions F_1 ($CHCl_3$/MeOH 20:1, 800–1000 ml), F_2 ($CHCl_3$/MeOH 15:1, 1000–1200 ml), F_3 ($CHCl_3$/MeOH 10:1, 1000–1200 ml), F_4 ($CHCl_3$/MeOH 5:1, 2600–2800 ml), F_5 ($CHCl_3$/MeOH 3:1, 2800–2900 ml), F_6 ($CHCl_3$/MeOH 3:1, 1000–1200 ml), and F_7 ($CHCl_3$/MeOH 1:1 to 0:1, 3300–3500 ml). F_1 (185 mg) was subjected to repeated CC (silica gel, petroleum ether/AcOEt 2:1 to 1:1): pure **6** (6 mg), **7** (4 mg), and **8** (3 mg). F_2 (600 mg) was subjected to CC (silica gel, $CHCl_3$/acetone 8:1) to afford $F_{2.1}$, $F_{2.2}$, $F_{2.3}$, and $F_{2.4}$. $F_{2.3}$ (68 mg) was further purified by repeated CC (silica gel, petroleum ether/acetone 2:1): **1** (18 mg) and **2** (12 mg). F_4 (2.0 g) was subjected to CC (silica gel, $CHCl_3$/MeOH 15:1) to afford a crude fraction which was further separated by prep. TLC (silica gel GF_{254} (10–40 μ), 25×25 cm, AcOEt/MeOH/H_2O 10:1:0.5): **5** (8 mg, R_f 0.476). F_5 (1.8 g) was subjected to CC (silica gel, $CHCl_3$/MeOH 10:1): $F_{5.1}$, $F_{5.2}$, $F_{5.3}$, $F_{5.4}$, and $F_{5.5}$. $F_{5.2}$ (800 mg) was further purified by repeated CC (silica gel, $CHCl_3$/MeOH 8:1) to afford crude 4 (96 mg) which was subjected to prep. TLC (silica gel GF_{254} (10–40 μ), 25×25 cm, $CHCl_3$/MeOH 4:1): **4** (56 mg, R_f 0.434). F_6 (600 mg) was subjected to CC (silica gel, $CHCl_3$/MeOH 5:1) to afford a crude fraction containing **3** (32 mg) which was further separated by prep. TLC (silica gel GF_{254} (10–40 μ), 25×25 cm, AcOEt/MeOH/H_2O 5:1:0.5): **3** (12 mg, R_f 0.515).

(1β,6α)-1,6,14-Trihydroxyeudesm-3-en-12-oic Acid γ-Lactone (=rel-*(3*R,*3a*R,*5a*S,*6*S,*9a*R,*9b*R*)-3a,4,5,5a,6,7,9a,9b-Octahydro-6-hydroxy-9-(hydroxymethyl)-3,5a-dimethylnaphtho[1,2-*b*]furan-2(3*H*)-one*; **1**): White amorphous powder. M.p. 208–210°. $[\alpha]_D^{20} = +104$ ($c = 0.2$, acetone). IR: 3289, 1763. ^{1}H- and ^{13}C-NMR: *Table 1*. EI-MS: 266 (48, M^+), 248 (100, $[M-H_2O]^+$). HR-ESI-MS: 284.1861 ($[M+NH_4]^+$, $C_{15}H_{26}NO_4^+$; calc. 284.1856).

(1β,6α)-1,6,14-Trihydroxyeudesma-3,11(13)-dien-12-oic Acid γ-Lactone (=rel-*(3a*R,*5a*S,*6*S,*9a*R,*9b*R*)-3a,4,5,5a,6,7,9a,9b-Octahydro-6-hydroxy-9-(hydroxymethyl)-5a-methyl-3-methylenenaphtho[1,2-*b*]furan-2(3*H*)-one*; **2**): White amorphous powder. M.p. 208–210°. $[\alpha]_D^{20} = +104$ ($c = 0.2$, acetone). IR: 3290, 1753. ^{1}H- and ^{13}C-NMR: *Table 1*. EI-MS: 264 (32, M^+), 246 (100, $[M-H_2O]^+$). HR-ESI-MS: 282.1707 ($[M+NH_4]^+$, $C_{15}H_{24}NO_4^+$; calc. 282.1700).

*(1β,6α)-1,6-Dihydroxy-14-*O*-[(4-hydroxyphenyl)acetyl]eudesma-3,11(13)-dien-12-oic Acid γ-Lactone* (=*4-Hydroxybenzeneacetic Acid* rel-*[(3a*R,*5a*S,*6*S,*9a*R,*9b*R*)-2,3,3a,4,5,5a,6,7,9a,9b-Decahydro-6-hydroxy-5a-methyl-3-methylene-2-oxonaphtho[1,2-*b*]furan-9-yl]methyl Ester*; **3**): Yellow gum. $[\alpha]_D^{20} = +53$ ($c = 1.0$, MeOH). IR: 3404, 1759, 1710, 1611, 1516, 1445. ^{1}H- and ^{13}C-NMR: *Table 1*. EI-MS: 398.1 (2, M^+), 380.1 (8, $[M-H_2O]^+$), 151.9 (45, [(4-hydroxyphenyl)acetic acid]$^+$). HR-ESI-MS: 421.4446 ($[M+Na]^+$, $C_{23}H_{26}NaO_6^+$; calc. 421.4445).

4-Hydroxy-γ,3,5-trimethoxybenzenepropanol (**6**): Colorless gum. $[\alpha]_D^{20} = -8$ ($c = 0.4$, $CHCl_3$). IR: 3361, 2920, 2851, 1610, 1516, 1459, 1419, 1212, 1112, 1046, 906, 836. ^{1}H- and ^{13}C-NMR: *Table 2*. EI-MS: 242 (1.5, M^+), 197 (100, $[M-C_2H_5O]^+$). HR-ESI-MS: 265.1049 ($[M+Na]^+$, $C_{12}H_{18}NaO_5^+$; calc. 265.1046).

γ,3,4,5-Tetramethoxybenzenepropanol (**7**): Colorless gum. $[\alpha]_D^{20} = -10$ ($c = 0.4$, $CHCl_3$). IR: 3382, 2922, 2852, 1592, 1505, 1459, 1420, 1233, 1125, 1102, 834. ^{1}H- and ^{13}C-NMR: *Table 2*. EI-MS: 256 (11.7, M^+), 211 (100, $[M-C_2H_5O]^+$). HR-ESI-MS: 279.1206 ($[M+Na]^+$, $C_{13}H_{20}NaO_5^+$; calc. 279.1203).

γ,3,4,5-Tetramethoxybenzenepropanol Acetate (**8**): Colorless gum. $[\alpha]_D^{20} = -14$ ($c = 0.3$, $CHCl_3$). IR: 3371, 2930, 2837, 1737, 1591, 1505, 1460, 1420, 1326, 1235, 1125, 1040, 835. ^{1}H- and ^{13}C-NMR: *Table 2*. EI-MS: 298 (71, M^+), 211 (100, $[M-C_4H_7O_2]^+$). HR-ESI-MS: 321.1308 ($[M+Na]^+$, $C_{15}H_{22}NaO_6^+$; calc. 321.1309).

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