# Five New Eremophilane Sesquiterpenes from *Ligularia przewalskii*

by **Ji-Qing Xu**[a]) and **Li-Hong Hu***[a])[b])

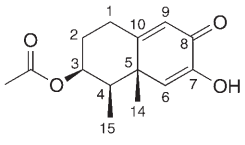
[a]) Shanghai Research Center for Modernization of Traditional Chinese Medicine, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai, 201203, P. R. China

[b]) School of Pharmacy, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China

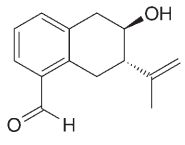
(phone: +86-21-50272221; fax: +86-21-50272221; e-mail: simmhulh@mail.shcnc.ac.cn)

Five new eremophilane-type sesquiterpenes, 3$\beta$-(acetyloxy)-7-hydroxynoreremophila-6,9-dien-8-one (**1**), 8$\beta$-hydroxy-2-dehydroxyliguhodgsonal (**2**), 3$\beta$-(acetyloxy)-11-methoxy-8-oxoeremophila-6,9-dien-12-oic acid (**3**), 3$\beta$-(acetyloxy)-11-(2′-methylbutanoyloxy)-8-oxoeremophila-6,9-dien-12-oic acid (**4**), and 3$\beta$-(acetyloxy)-6$\alpha$-hydroxyligularenolide (**5**), along with the three known compounds **6**–**8**, were isolated from the roots of *Ligularia przewalskii*. The structures of the new compounds were elucidated through spectral studies including HR-EI-MS, IR, and NMR data.

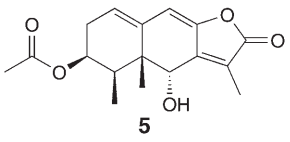
**Introduction.** – The genus *Ligularia* belongs to the tribe Senecioneae, family Compositae, and comprises more than 110 species native to China. Approximately 40 species have long been used as traditional Chinese herbal medicine for the purposes of invigorating the circulation of blood, clearing heat and toxins, and as diuretic and choleretic agents [1]. Previous phytochemical studies on the genus *Ligularia* have revealed that it is a rich source of eremophilane derivatives. So far, notable activities were reported for eremophilenolides, including antibacteria, cytotoxicity, and inhibition of production of NO and prostaglandin $E_2$ in Macrophage [2–4]. The roots of *Ligularia przewalskii* have been used for relieving cough and asthma in Northwest China. We report herein the investigation of the plant, which resulted in the isolation of five new (**1**–**5**) and three known eremophilane derivatives (**6**–**8**).



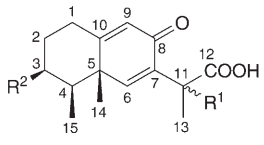
**1**

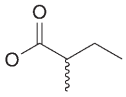


**2**



**5**



| | $R^1$ | $R^2$ |
|---|---|---|
| **3** | MeO | AcO |
| **4** |  | AcO |
| **6** | $\alpha$-H | AcO |
| **7** | $\beta$-H | AcO |
| **8** | H | H |

**Results and Discussion.** – Compound **1**, obtained as a colorless gum, has the molecular formula $C_{14}H_{18}O_4$, as determined by HR-EI-MS ($M^+$ at $m/z$ 250.1210; calc. 250.1205). The IR spectrum showed absorption bands for OH (3338 $cm^{-1}$) and C=O groups (1731, 1643 $cm^{-1}$). The $^1$H-NMR spectrum (*Table 1*) indicated three typical Me signals appearing at $\delta$(H) 1.04 (*d*, $J$ = 6.2 Hz), 1.34 (*s*), and 2.09 (*s*), and two olefinic signals at $\delta$(H) 6.20 (*s*) and 6.13 (*s*). Its $^{13}$C-NMR spectrum (*Table 2*) displayed 14 signals including two C=O groups ($\delta$(C) 181.5 (C=O), 170.1 (lactone C=O)), two C=C bonds ($\delta$(C) 122.6, 125.3, 146.8, 169.3), one oxygenated methine ($\delta$(C) 72.0), and three Me groups ($\delta$(C) 43.5, 43.3, 21.0). The $^1$H- and $^{13}$C-NMR signals of **1** were fully assigned by means of $^1$H,$^1$H-COSY, HMQC, and HMBC experiments.

Table 1. *$^1$H-NMR Data* (400 MHz) *of Compounds* **1**–**5**. $\delta$ in ppm, $J$ in Hz.

| | **1**[a]) | **2**[a]) | **3**[b]) | **4**[b])[c]) | **5**[b]) |
|---|---|---|---|---|---|
| $CH_2$(1) | 2.57–2.61 (*m*), | 7.34 (*dd*, *J* = 6.5, 1.9) | 2.75–2.87 (*m*), | 2.76–2.80 (*m*), | 5.83 (*s*) |
| or H–C(1) | 2.30–2.34 (*m*) | | 2.35–2.37 (*m*) | 2.34–2.36 (*m*) | |
| $CH_2$(2) | 2.03–2.05 (*m*), | 7.33 (*t*, *J* = 6.5) | 2.17–2.20 (*m*), | 1.62–1.66 (*m*), | 2.37–2.40 (*m*) |
| or H–C(2) | 1.63–1.65 (*m*) | | 1.67–1.70 (*m*) | 2.17–2.19 (*m*) | |
| H–C(3) | 4.89 (br. *d*, | 7.65 (*dd*, | 5.07 (br. *d*, | 5.07 (br. *d*, | 5.03 (br. *s*) |
| | *J* = 3.0) | *J* = 6.7, 2.0) | *J* = 2.7) | *J* = 3.0) | |
| H–C(4) | 1.64–1.68 (*m*) | – | 1.76–1.77 (*m*) | 2.10–2.12 (*m*) | 2.16 (*q*, *J* = 6.8) |
| H–C(6) | 6.20 (*s*) | 3.10 (*d*, *J* = 17.7), | 7.33 (*s*) | 7.38 (*s*) | 4.68 (*s*) |
| or $CH_2$(6) | | 3.35 (*dd*, *J* = 17.7, 4.5) | | | |
| H–C(7) | – | 2.37 (br. *d*, *J* = 4.5) | – | – | – |
| H–C(8) | – | 3.82 (br. *d*, *J* = 4.5) | – | – | – |
| H–C(9) | 6.13 (*s*) | 3.02 (*d*, *J* = 17.4), | 6.10 (*s*) | 6.09 (*s*) | 6.05 (*s*) |
| or $CH_2$(9) | | 2.69 (*dd*, *J* = 17.4, 8.7) | | | |
| $CH_2$(12) | – | 4.74 (*s*), 4.77 (*s*) | – | – | – |
| Me(13) | – | 1.76 (*s*) | 1.53 (*s*) | 1.82 (*s*) | 2.05 (*s*) |
| Me(14) | 1.34 (*s*) | – | 1.42 (*s*) | 1.39 (*s*) | 1.18 (*s*) |
| Me(15) | 1.04 (*d*, | 10.17 (*s*) | 1.20 (*d*, | 1.21 (*d*, | 1.27 (*d*, |
| or H–C(15) | *J* = 6.2) | | *J* = 6.9) | *J* = 7.1) | *J* = 6.9) |
| AcO | 2.09 (*s*) | – | 2.14 (*s*) | 2.14 (*s*) | 2.04 (*s*) |
| MeO | – | – | 3.24 (*s*) | – | – |
| OH | 8.49 (*s*) | – | – | – | – |

[a]) Measured in ($D_6$)DMSO. [b]) Measured in $CD_3OD$. [c]) (2-Methyl-1-oxobutoxy) moiety: 2.41–2.44 (*m*, H–C(2′)); 1.32–1.34, 1.26–1.29 (2*m*, $CH_2$(3′)); 0.93 (*t*, *J* = 7.2, Me(4′)); 1.13 (*d*, *J* = 7.2, Me(5′)).

The $^{13}$C-NMR data of **1** were nearly superimposable with those of 3$\beta$-(acetyloxy)-1$\beta$,7-dihydroxynoreremophila-6,9-dien-8-one [5], indicating that they share the same eremophilane sesquiterpene skeleton, except for the substitution pattern at C(1). The low chemical shift values of the two H-atoms ($\delta$(H) 2.57–1.61, 2.30–2.34) attached to C(1) and their HMQC correlation with C(1), along with their COSY correlation with H–C(2), suggested that C(1) was an unfunctionalized methylene group. The low coupling constant ($J$ = 3.0 Hz) of H–C(3) indicated that it occupied an equatorial $\alpha$-

Table 2. *$^{13}$C-NMR Data* (100 MHz) *of Compounds* **1–5**. $\delta$ in ppm.

| | **1**[a]) | **2**[a]) | **3**[b]) | **4**[b])[c]) | **5**[b]) |
|---|---|---|---|---|---|
| C(1) | 27.2 | 134.0 | 29.0 | 28.8 | 128.6 |
| C(2) | 32.4 | 126.0 | 33.8 | 33.6 | 31.7 |
| C(3) | 72.0 | 130.4 | 74.7 | 74.6 | 74.7 |
| C(4) | 43.5 | 133.1 | 44.2 | 44.1 | 40.9 |
| C(5) | 43.3 | 137.8 | 45.2 | 45.0 | 46.3 |
| C(6) | 125.3 | 30.2 | 153.9 | 154.1 | 77.8 |
| C(7) | 146.8 | 48.3 | 138.0 | 136.9 | 151.3 |
| C(8) | 181.5 | 65.9 | 186.6 | 185.7 | 148.9 |
| C(9) | 122.6 | 37.9 | 125.2 | 125.5 | 110.8 |
| C(10) | 169.3 | 136.8 | 170.9 | 170.1 | 139.9 |
| C(11) | – | 147.3 | 79.6 | 81.5 | 124.2 |
| C(12) | – | 111.7 | 175.9 | 173.9 | 173.1 |
| C(13) | – | 19.1 | 20.7 | 22.3 | 9.4 |
| C(14) | 21.1 | – | 20.9 | 20.6 | 15.1 |
| C(15) | 12.2 | 193.4 | 12.8 | 12.8 | 15.3 |
| AcO | 21.0, 170.1 | – | 21.3, 172.4 | 21.3, 172.3 | 21.3, 172.7 |
| MeO | – | – | 51.7 | – | – |

[a]) Measured in ($D_6$)DMSO. [b]) Measured in $CD_3OD$. [c]) (2-Methyl-1-oxobutoxy) moiety: 176.5 (C(1′)); 42.8 (C(2′)); 28.0 (C(3′)); 12.0 (C(4′)); 17.3 (C(5′)).

position. From the above data, the structure of compound **1** was, therefore, elucidated as 3$\beta$-(acetyloxy)-7-hydroxynoreremophila-6,9-dien-8-one[1]).

Compound **2**, isolated as a colorless gum, was assigned to have the molecular formula $C_{14}H_{16}O_2$ from its HR-EI-MS analysis ($M^+$ at $m/z$ 216.1154; calc. 216.1150). The IR spectrum (KBr) showed absorption bands for OH (3396 cm$^{-1}$), C=O (1624 cm$^{-1}$), and aromatic (1384 cm$^{-1}$) groups. Its $^1$H-NMR spectrum (*Table 1*) displayed a Me *singlet* at $\delta$(H) 1.76 (*s*), two resonances of a terminal olefinic bond at $\delta$(H) 4.74 and 4.77, and of three aromatic H-atoms ($\delta$(H) 7.34 (*dd*, $J$ = 6.5, 1.9 Hz); 7.33 (*t*, $J$ = 6.5 Hz); 7.65 (*dd*, $J$ = 6.7, 2.0 Hz)), and an aldehyde group at $\delta$(H) 10.17 (*s*). The $^{13}$C-NMR spectrum (*Table 2*) of **2** exhibited 14 signals including one Me group, three $CH_2$ (one belonging to the C-atom of the terminal olefinic bond; $\delta$(C) 111.7), two methines (one oxygenated; $\delta$(C) 65.9), three sp$^2$ aromatic CH ($\delta$(C) 134.0, 126.0, 130.4), and an aldehyde C=O group ($\delta$(C) 193.4).

The $^{13}$C-NMR data of **2** were nearly superimposable with those of 2-dehydroxy-liguhodgsonal [6]; the only difference was, that **2** has an additional OH group, located at C(8) ($\delta$(C) 65.9), which was evident from the chemical shift value of H–C(8) ($\delta$(H) 3.82), the HMBC correlations H–C(6)/C(8), and the COSY correlations H–C(7)/H–C(8) and H–C(8)/H–C(9) (*Fig. 1*).

Regarding the relative configuration of **2**, due to the resonance of $H_\alpha$–C(6) overlapping with that of $H_\alpha$–C(9) in ($D_6$)DMSO, $CDCl_3$ was selected as NMR solvent to obtain the $^1$H-NMR and NOESY spectra, in which the NOESY correlation (*Fig. 2*)

[1]) For systematic names, see *Exper. Part.*

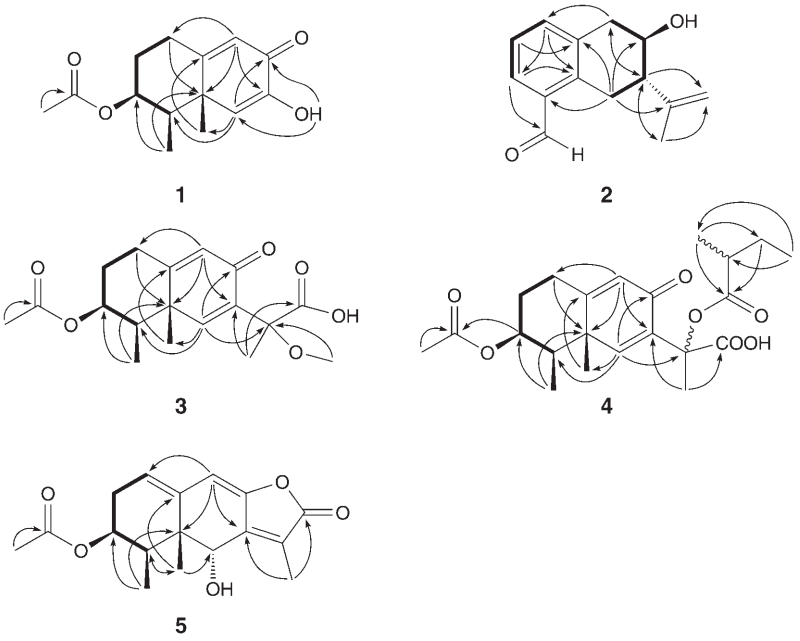



Fig. 1. *$^1H,^1H$-COSY* (—) *and key HMBC* (H → C) *Correlations of* **1**–**5**

of $H_\beta$–C(9) ($\delta$(H) 2.69) and H–C(7) ($\delta$(H) 2.37) demonstrated that H–C(7) is $\beta$-axially oriented, whereas the correlation of $H_\alpha$–C(6) ($\delta$(H) 3.10) and H–C(8) ($\delta$(H) 3.82) showed the $\alpha$-axially oriented H–C(8). Thus, **2** was established as 8$\beta$-hydroxy-2-dehydroxyliguhodgsonal[1]), with its absolute configuration not determined.

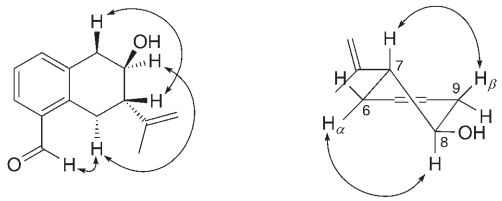


Fig. 2. *Key NOESY correlations of* **2** (measured in $CDCl_3$)

Compound **3**, obtained as a colorless oil, was assigned to have the molecular formula $C_{18}H_{24}O_6$ by HR-EI-MS analysis ($M^+$ at $m/z$ 336.1570; calc. 336.1573). The IR spectrum showed the strong signals of three C=O groups (1733, 1666, 1633 $cm^{-1}$). The $^1$H-NMR spectrum (*Table 1*) exhibited resonances of two olefinic H-atoms at $\delta$(H) 7.33 and 6.10, a Me *singlet* at $\delta$(H) 3.24 probably linked to an O-atom, and three other Me *singlet*s at $\delta$(H) 2.14, 1.53, and 1.42, in addition to a Me *doublet* at $\delta$(H) 1.20. The $^{13}$C-NMR (DEPT) spectrum (*Table 2*) showed signals for four Me groups, two $CH_2$ groups, one pair of olefinic C-atoms at $\delta$(C) 153.9, 138.0, 170.9 and 125.2, three CH groups including one oxygenated methine at $\delta$(C) 74.7, an $\alpha,\beta$ unsaturated C=O group

at $\delta$(C) 186.6, and two other C=O groups at $\delta$(C) 175.9 and 172.4 probably due to a carboxylic acid or a carboxylic acid ester.

With the exception of the MeO signal ($\delta$(H) 3.24; $\delta$(C) 51.7), the $^1$H- and $^{13}$C-NMR spectra of **3** were nearly identical with those of 3$\beta$-(acetyloxy)-8-oxoeremophila-6,9-dien-12-oic acid [7], suggesting that **3** was an analogue with the same sesquiterpene skeleton, which was also supported by the HMBC correlations (*Fig. 1*) Me(15)/C(3) and C(5), H–C(6)/C(4), C(14), and C(11), H–C(9)/C(1), C(5), and C(7), as well as the COSY correlation signals H–C(1)/H–C(2), H–C(2)/H–C(3), and H–C(3)/H–C(4). The oxygenated Me group ($\delta$(H) 3.24) was correlated with C(11) ($\delta$(C) 79.6) in the HMBC spectrum, revealing that the MeO group was linked to C(11). Thus, **3** was determined as 3$\beta$-(acetyloxy)-11-methoxy-8-oxoeremophila-6,9-dien-12-oic acid[1]). The relative configuration at C(11), and the absolute configuration of **3**, however, remain to be established.

Compound **4**, isolated as a colorless oil, was assigned to have the molecular formula $C_{22}H_{30}O_7$ on the basis of the HR-EI-MS molecular-ion peak ($M^+$ at $m/z$ 406.1995; calc. 406.1992). The IR spectrum of **4** showed strong absorption peaks of an OH group (3446 cm$^{-1}$) and three C=O groups (1738, 1664, and 1616 cm$^{-1}$). Its $^1$H-NMR spectrum (*Table 1*) exhibited three Me *singlet*s at $\delta$(H) 2.14, 1.82, and 1.39, two Me *doublet*s at $\delta$(H) 1.21 (*d*, $J$ = 7.1 Hz) and 1.13 (*d*, $J$ = 7.2 Hz), a Me *triplet* at $\delta$(H) 0.93 (*t*, $J$ = 7.2 Hz), an oxygenated methine at $\delta$(H) 5.07 (br. *d*, $J$ = 3.0 Hz), and two olefinic resonances at $\delta$(H) 7.38 and 6.09. In the $^{13}$C-NMR spectrum (*Table 2*), the 22 signals were resolved into an $\alpha,\beta$-unsaturated C=O group at $\delta$(C) 185.7, and three signals at $\delta$(C) 176.5, 173.9, and 172.3 probably due to carboxylic acid or carboxylic acid ester groups, two pairs of C=C bonds at $\delta$(C) 154.1, 136.9, 125.5, and 170.1, three sp$^3$ CH groups (one being oxygenated; $\delta$(C) 74.6), two sp$^3$ C-atoms (one being oxygenated; $\delta$(C) 81.5), three $CH_2$, and six Me groups.

With the exception for the five signals of the (2-methyl-1-oxobutoxy) moiety ($\delta$(C) 176.5, 42.8, 28.0, 12.0, and 17.3), the $^{13}$C-NMR spectrum of **4** was nearly identical to that of **3**, indicating that they shared the same eremophilane skeleton, which was confirmed by very similar cross-peaks in the HMBC plot (*Fig. 1*). The AcO group was attached to C(3), which was deduced through the chemical shift value of H–C(3) ($\delta$(H) 5.07) and the HMBC correlations of H–C(3) with the C=O group. The (2-methyl-1-butoxy) moiety was evidently linked to the remaining oxygenated C(11) ($\delta$(C) 81.5). In analogy to **1**, H–C(3) ($\delta$(H) 5.07) of **4** was $\alpha$-oriented due to its low coupling constant ($J$ = 3.0 Hz). Therefore, **4** was determined as 3$\beta$-(acetyloxy)-11-[(2-methylbutanoyl)oxy]-8-oxoeremophila-6,9-dien-12-oic acid[1]).

Compound **5**, obtained as a colorless oil, had the molecular formula $C_{17}H_{20}O_5$ determined by HR-EI-MS analysis ($M^+$ at $m/z$ 304.1306; calc 304.1311). The IR spectrum showed absorption bands for OH (3444 cm$^{-1}$) and C=O (1740 cm$^{-1}$) groups. The $^1$H-NMR spectrum (*Table 1*) presented two olefinic H-atoms at $\delta$(H) 5.83 and 6.05, two oxygenated methines at $\delta$(H) 5.03 and 4.68, a Me *doublet* at $\delta$(H) 1.27, three Me *singlet*s at $\delta$(H) 2.05, 2.04, and 1.18. The $^{13}$C-NMR (DEPT) spectrum (*Table 2*) showed 17 signals, including four Me, one $CH_2$, and three sp$^3$ CH groups (two being oxygenated; $\delta$(C) 74.7, 77.8), three pairs of C=C bonds ($\delta$(C) 151.3, 148.9, 139.9, 128.6, 124.2, and 110.8), two ester CO groups ($\delta$(C) 172.7 and 173.1), and a quaternary sp$^3$ C-atom.

The $^{13}$C-NMR signals of **5**, nearly superpimposable with those of the skeleton C-atoms of 3$\beta$-(angeloyloxy)-6$\beta$-hydroxyligularenolide except for the absence of an (angeloyloxy) moiety [8], indicated that it has a ligularenolide skeleton. Similar to **3**, the only AcO group was attached at C(3) with $\beta$-equatorial orientation. The $\beta$-configuration of H–C(6) was deduced from the absence of a long-range coupling between the olefinic H-atoms of Me(13) and the allylic H-atom [9]. As a result, **5** was firmly established as 3$\beta$-(acetyloxy)-6$\alpha$-hydroxyligularenolide[1]).

## Experimental Part

*General*. All solvents used were of analytical grade (*Shanghai Chemical Plant*). Column chromatography (CC): silica gel ($SiO_2$) *H* (200–300 mesh; *Qingdao Marine Chemical Ltd.*), *Sephadex LH-20* (25–100 μm; *Pharmacia Fine Chemicals*), *MCI* gel *CHP 20P* (75–150 μm; *Mitsubishi Chemical Ind.*), *D-101* porous resin (*Chemical Factory of Tianjin University*), and *RP-18* (20–45 μm; *Fuji Silysia Chemical Ltd.*). Thin-layer chromatography (TLC): silica gel $GF_{254}$ (*Yantai Huiyou Inc.*). Optical rotations: $CHCl_3$ or MeOH solns.; *Perkin-Elmer 241* polarimeter. IR Spectra: *Perkin-Elmer 16-PC-FT-IR* spectrophotometer; in $cm^{-1}$. $^1$H- (400 MHz) and $^{13}$C-NMR (100 MHz) Spectra: *Bruker AMX-400* spectrometer; $\delta$ in ppm, *J* in Hz, with TMS as an internal standard. HR-EI-MS and EI-MS: *Finnigan MAT-90/95* sector-field mass spectrometer; in *m*/*z*.

*Plant Material*. The roots of *Ligularia przewalskii* were collected in Hefei City, Anhui Province, China, and identified by Prof. *Li-Hong Hu*. A voucher specimen was deposited in the Shanghai Research Center for Modernization of Traditional Chinese Medicine, Shanghai Institute of Materia Medica, Shanghai.

*Extraction and Isolation*. The air-dried and powdered roots of *L. przewalskii* (9.2 kg) were extracted with 95% EtOH (20 l × 3) at r.t. After removal of the solvent in vacuum, an extract of 783.4 g was obtained, suspended in $H_2O$, and then partitioned with $CHCl_3$ (2 l × 3). The evaporated $CHCl_3$ fraction (117.1 g) were subjected to CC (*MCI* gel; EtOH/$H_2O$ 20:80, 27:73, 35:65, 43:57, 50:50, 60:40, 80:20, and 100:0) to afford eight fractions (*Frs. A–H*). *Fr. C* (10.2 g) was further separated with CC ($SiO_2$; $CHCl_3$/MeOH 99:1, 98:2, 95:5, 9:1, 8:2) to give 8 subfractions (*Frs. C1–C8*). *Fr. C2* (142.5 mg) was separated by CC (*RP-18*; 65% aq. MeOH) to afford **1** (21 mg) and **3** (32 mg). *Fr. C4* (78.1 mg) was separated by CC (1. *RP-18*; 55% aq. MeOH; 2. *Sephadex LH-20*; MeOH) to yield **2** (30.2 mg), **4** (12.5 mg), and **8** (11.7 mg). *Fr. D* (14.3 g) was subjected to CC ($SiO_2$; $CHCl_3$/MeOH 99:1, 98:2, 95:5, 9:1, 8:2, 6:4) to afford 7 subfractions (*Frs. D1–D7*). *Fr. D3* (320 mg) was separated by CC (1. *Sephadex LH-20*; 30% aq. MeOH, 2. *RP-18*; 45% aq. MeOH) to provide **5** (40.1 mg). *Fr. D5* (451 mg) was separated by CC (1. *Sephadex LH-20*; MeOH; 2. *RP-18*; 50% aq. MeOH) to afford **6** (12.8 mg) and **7** (9.5 mg).

*3β-(Acetyloxy)-7-hydroxynoreremophila-6,9-dien-8-one* (=*(4a*S,5R,6S*)-6-(Acetyloxy)-5,6,7,8-tetrahydro-3-hydroxy-4a,5-dimethylnaphthalen-2(4a*H*)-one*; **1**). Colorless gum. $[\alpha]_D^{25} = +26$ ($c = 0.6$, MeOH). IR (KBr): 3338, 2942, 2879, 1731, 1643, 1421, 1257, 1209, 1178, 1118, 983, 906. $^1$H- and $^{13}$C-NMR: *Tables 1* and *2*. HR-EI-MS: 250.1210 ($M^+$, $C_{14}H_{18}O_4^+$; calc. 250.1205).

*8β-Hydroxy-2-dehydroxyliguhodgsonal* (=*(6*R,7S*)-5,6,7,8-Tetrahydro-6-hydroxy-7-(1-methylethenyl)naphthalene-1-carboxaldehyde*; **2**). Colorless gum. $[\alpha]_D^{25} = +4$ ($c = 0.25$, MeOH). IR (KBr): 3396, 2919, 1624, 1384, 1026. $^1$H- and $^{13}$C-NMR: *Tables 1* and *2*. HR-EI-MS: 216.1154 ($M^+$, $C_{14}H_{16}O_2^+$; calc. 216.1150).

*3β-(Acetyloxy)-11-methoxy-8-oxoeremophila-6,9-dien-12-oic Acid* (=*(7*S,8R,8a*R)-7-(Acetyloxy)-3,5,6,7,8,8a-hexahydro-α-methoxy-α,8,8a-trimethyl-3-oxo-2-naphthaleneacetic Acid*; **3**). Colorless oil. $[\alpha]_D^{25} = -33$ ($c = 0.2$, MeOH). IR (KBr): 2941, 2617, 1733, 1666, 1633, 1456, 1373, 1242, 1022, 979, 756, 667. $^1$H- and $^{13}$C-NMR: *Tables 1* and *2*. HR-EI-MS: 336.1570 ($M^+$, $C_{18}H_{24}O_6^+$; calc. 336.1573).

*3β-(Acetyloxy)-11-(2-methylbutanoyloxy)-8-oxoeremophila-6,9-dien-12-oic Acid* (=*(7*S,8R,8a*R)-7-(Acetyloxy)-3,5,6,7,8,8a-hexahydro-α,8,8a-trimethyl-α-(2-methyl-1-oxobutoxy)-3-oxonaphthalene-2-acetic Acid*; **4**). Colorless oil. $[\alpha]_D^{25} = -12$ ($c = 0.5$, MeOH). IR (KBr): 3446, 2968, 1738, 1664, 1616, 1456,

1375, 1242, 1024, 982, 754. $^1$H- and $^{13}$C-NMR: *Tables 1* and *2*. HR-EI-MS: 406.1995 ($M^+$, $C_{22}H_{30}O_7^+$; calc. 406.1992).

*3β-(Acetyloxy)-6α-hydroxyligularenolide* (=*(4*R*,4a*R*,5*R*,6*S*)-6-(Acetyloxy)-4a,5,6,7-tetrahydro-4-hydroxy-3,4a,5-trimethylnaphtho[2,3-*b*]furan-2(4*H*)-one*; **5**). Colorless oil. $[\alpha]_D^{25} = -24$ ($c = 0.5$, MeOH). IR (KBr): 3444, 2939, 1740, 1673, 1377, 1253, 1024. $^1$H- and $^{13}$C-NMR: *Tables 1* and *2*. HR-EI-MS: 304.1306 ($M^+$, $C_{17}H_{20}O_5^+$; calc. 304.1311).

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