

Five New Sesquiterpenoids from *Parasenecio petasitoides*

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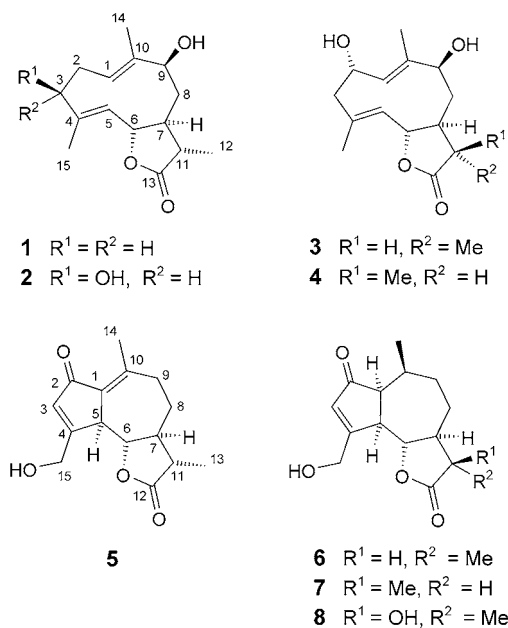
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From the whole plants of *Parasenecio petasitoides*, five new sesquiterpenoids were isolated, (*E,E*)-3 α ,9 β -dihydroxy-6 β H,11 β H-13-norgermacra-1(10),4-dien-11,6-carbolactone (**2**), (*E,E*)-2 α ,9 β -dihydroxy-6 β H,11 β H-13-norgermacra-1(10),4-dien-11,6-carbolactone (**3**), (*E,E*)-2 α ,9 β -dihydroxy-6 β H,11 α H-13-norgermacra-1(10),4-dien-11,6-carbolactone (**4**), (*E*)-15-hydroxy-2-oxo-6 β H,11 α H-13-norguaia-3-ene-11,6-carbolactone (**7**), and (*E*)-11 β ,15-dihydroxy-2-oxo-6 β H-13-norguaia-3-ene-11,6-carbolactone (**8**), together with three known compounds, deacetyl herbolide A (**1**), jacquilenin (**5**), and (*E*)-15-hydroxy-2-oxo-6 β H,11 β H-13-norguaia-3-ene-11,6-carbolactone (**6**). The structures of these natural products were elucidated spectroscopically, especially by 1D- and 2D-NMR techniques, in combination with high-resolution mass spectroscopy.

1. Introduction. – The genus *Parasenecio*, belonging to the family of Compositae, comprises more than 60 species [1]. There are 51 species occurring in China, and they are distributed mainly over the mountain areas in south-west China [1]. The genus *Parasenecio* had been formally misidentified as the genus *Cacalia* in China, and was recently revised as the genus *Parasenecio* in the Flora of China [1]. The *Parasenecio* species is an important source of Chinese traditional folklore medicine, with *ca.* 26 species being used as Chinese traditional folklore herbs for invigorating the circulation of blood, curing rheumatismal aches, and injuries from falls, *etc.* [2]. Recently, a number of new eremophilane-type sesquiterpenoids were isolated from several plants of this genus in China, and some of the compounds were found to exhibit antibacterial activity [3].

Parasenecio petasitoides, a perennial herbaceous plant, has, so far, not been investigated chemically. In the present work, we will describe the isolation and structure elucidation of the sesquiterpenoids **1**–**8**, which were obtained from the whole plants of *P. petasitoides* collected from the Shanxi province in the Qinling Mountains, Peoples Republic of China. The isolated compounds include the five new sesquiterpenoids **2**–**4**, **7**, and **8**, as well as three known compounds, deacetyl herbolide A (**1**), jacquilenin (**5**), and (*E*)-15-hydroxy-2-oxo-6 β H,11 β H-13-norguaia-3-ene-11,6-carbolactone (**6**).

2. Results and Discussion. – Compound **2** showed strong IR absorption bands at 3396 and 1751 cm⁻¹ for OH and lactone groups, respectively. Comparison of the ¹H- and ¹³C-NMR data of **1** and **2** indicated that both compounds had the same skeleton. A molecular formula of C₁₅H₂₂O₄ was derived for **2** by HR-EI-MS (*m/z* 266.1498 (*M*⁺; calc. 266.1518)), which is 16 mass units higher than the *M*⁺ signal for **1** [4], indicating



the presence of an additional OH group in **2**. In the 1H -NMR spectra, the only difference between **1** and **2** was the presence of an additional OH group at C(3) in compound **2**, as deduced from the *multiplet* at δ_H 4.19 (H–C(3); in $CDCl_3$) and the *singlet* at δ_C 78.9 in the ^{13}C -NMR (DEPT) spectrum. The NMR chemical shift and coupling constants for H–C(3) (*dd*, $J = 10.1, 5.7$), when recorded in $CDCl_3/CD_3OD$ instead of $CDCl_3$, and the chemical shift of C(3) suggested that the 3-OH group was likely to be β -oriented (see *Table 1*) [5]. The connectivity and the coupling patterns of each H-bearing fragment were determined by a $^1H, ^1H$ -COSY experiment (*Fig. 1*), in which two H-atom signals at δ_H 2.22–2.29 (*m*), attributable to H–C(2), showed correlations with H–C(3) at δ_H 4.19 and H–C(1) at 5.07 (*ddq*, $J = 11.8, 4.7, 1.4$), confirming the presence of a 3-OH function. The ‘ γ -*gauche*’ effect (*Fig. 2*) of the 3β -OH group of **2** caused a remarkable high-field chemical shift for C(15) (δ_C 11.4) relative to that of **1** (δ_C 17.5) and to those of compounds with 3α -OH groups, in which

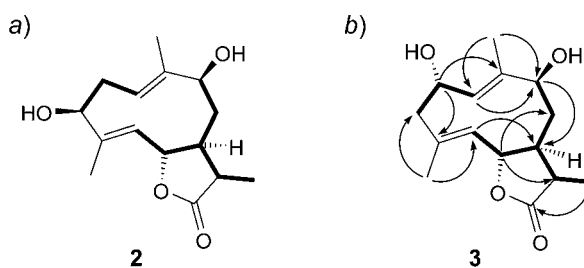


Fig. 1. $^1H, ^1H$ -COSY Correlations (bold) and selected HMBC (H \rightarrow C) correlations observed for compounds **2** and **3**

Table 1. ¹H-NMR Spectral Data of the Sesquiterpenoids 1–8. Chemical shifts δ in ppm, coupling constants J in Hz. Asterisks (*) denote overlapping signals.

	1 ^{a)}	2 ^{b)}	2 ^{c)}	3 ^{b)}	3 ^{c)}
H–C(1)	4.95 (<i>m</i>)	5.07 (<i>ddq</i> , <i>J</i> = 11.8, 4.7, 1.4)	4.99 (<i>ddq</i> , 11.8, 4.5, 1.2)	5.09 (<i>dq</i> , <i>J</i> = 9.7, 1.4)	5.04 (<i>dq</i> , <i>J</i> = 9.8, 1.2)
H–C(2)		2.22–2.29 (<i>m</i>)	2.36, 2.19 (<i>m</i>)	4.69*	4.61 (<i>ddd</i> , <i>J</i> = 9.8, 9.8, 5.6)
H _β –C(3)		4.19 (<i>m</i>)	4.10 (<i>dd</i> , <i>J</i> = 10.1, 5.7)	2.58 (<i>dd</i> , <i>J</i> = 11.0, 5.6)	2.58 (<i>dd</i> , <i>J</i> = 11.1, 5.6)
H _α –C(3)				1.97 (<i>dd</i> , <i>J</i> = 11.0, 10.0)	1.96 (<i>dd</i> , <i>J</i> = 11.1, 9.8)
H–C(5)	4.47*	4.64 (br. <i>d</i> , <i>J</i> = 9.9)	4.49 (br. <i>d</i> , <i>J</i> = 9.8)	4.78 (br. <i>d</i> , <i>J</i> = 10.2)	4.70 (br. <i>d</i> , <i>J</i> = 10.0)
H–C(6)	4.47*	4.76 (<i>dd</i> , <i>J</i> = 9.9, 9.1)	4.56 (<i>dd</i> , <i>J</i> = 9.8, 9.8)	4.69*	4.58 (<i>dd</i> , <i>J</i> = 10.0, 9.8)
H–C(7)		1.79 (<i>m</i>)	1.67 (<i>m</i>)	1.82 (<i>m</i>)	1.75 (<i>m</i>)
H–C(8)		1.89–1.97 (<i>m</i>)	1.74–1.84 (<i>m</i>)	1.91 (<i>m</i>)	1.85 (<i>m</i>)
H–C(9)	4.03 (<i>dd</i> , <i>J</i> = 10, 3)	4.03 (<i>m</i>)	3.95 (<i>dd</i> , <i>J</i> = 9.8, 3.3)	4.06 (<i>m</i>)	3.99 (<i>dd</i> , <i>J</i> = 9.1, 3.8)
H–C(11)		2.36 (<i>dq</i> , 12.3, 7.0)	2.26 (<i>dq</i> , <i>J</i> = 12.3, 7.1)	2.35 (<i>dq</i> , <i>J</i> = 12.3, 7.0)	2.31 (<i>dq</i> , <i>J</i> = 12.0, 7.0)
H–C(13)	1.25 (<i>d</i> , <i>J</i> = 7)	1.19 (<i>d</i> , 7.0)	1.21 (<i>d</i> , <i>J</i> = 7.1)	1.19 (<i>d</i> , <i>J</i> = 7.0)	1.27 (<i>d</i> , <i>J</i> = 7.0)
H–C(14)	1.43 (<i>d</i> , <i>J</i> = 1.4)	1.49 (<i>d</i> , 1.4)	1.40 (<i>d</i> , <i>J</i> = 1.2)	1.51 (<i>d</i> , <i>J</i> = 1.4)	1.45 (<i>d</i> , <i>J</i> = 1.2)
H–C(15)	1.69 (<i>s</i>)	1.71 (<i>d</i> , 1.7)	1.65 (<i>d</i> , <i>J</i> = 1.3)	1.74 (<i>d</i> , <i>J</i> = 1.4)	1.71 (<i>d</i> , <i>J</i> = 1.2)
	4 ^{b)}	5 ^{a)}	6 ^{d)}	7 ^{b)}	8 ^{b)}
H–C(1)	5.09 (<i>dq</i> , <i>J</i> = 9.7, 1.4)		2.81 (<i>dd</i> , <i>J</i> = 7.0, 4.0)	2.76 (<i>dd</i> , <i>J</i> = 7.2, 3.9)	2.74 (<i>dd</i> , <i>J</i> = 7.2, 3.9)
H–C(2)	4.69 (<i>m</i>)				
H–C(3)	2.57 (<i>dd</i> , <i>J</i> = 11.0, 5.6, β-H); 1.97 (<i>dd</i> , <i>J</i> = 11.0, 9.7, α-H)	6.43 (<i>s</i>)	6.30 (<i>dt</i> , <i>J</i> = 2.0, 2.0)	6.24 (<i>dt</i> , <i>J</i> = 2.0, 2.0)	6.26 (<i>dt</i> , <i>J</i> = 2.0, 2.0)
H–C(5)	4.79 (br. <i>d</i> , <i>J</i> = 10.2)	3.59 (<i>d</i> , <i>J</i> = 10)	3.25 (<i>m</i>)	3.26 (<i>m</i>)	3.24 (<i>m</i>)
H–C(6)	4.91 (<i>dd</i> , <i>J</i> = 10.2, 9.8)	3.61 (<i>dd</i> , <i>J</i> = 10, 10)	4.49 (<i>dd</i> , <i>J</i> = 10.5, 9.5)	4.69 (<i>dd</i> , <i>J</i> = 10.4, 10.2)	4.65*
H–C(7)	2.36 (<i>m</i>)	1.98 (<i>m</i>)	1.83 (<i>ddd</i> , <i>J</i> = 11.5, 10.5, 2.5)	2.37 (<i>m</i>)	1.93 (<i>m</i>)
H–C(8)	1.81–1.92 (<i>m</i>)	1.99, 1.39 (<i>m</i>)	1.86, 1.51 (<i>m</i>)	1.74, 1.60 (<i>m</i>)	1.75 (<i>m</i>)
H–C(9)	4.06 (<i>m</i>)	2.42, 2.40 (<i>m</i>)	1.94, 1.69 (<i>m</i>)	1.95, 1.67 (<i>m</i>)	1.97, 1.69 (<i>m</i>)
H–C(10)			2.56 (<i>m</i>)	2.52 (<i>m</i>)	2.54 (<i>m</i>)
H–C(11)	2.64 (<i>dq</i> , <i>J</i> = 7.8, 7.6)	2.28 (<i>dq</i> , <i>J</i> = 12.4, 7.0)	2.39 (<i>dq</i> , <i>J</i> = 11.5, 7.0)	2.40 (<i>dq</i> , <i>J</i> = 7.8, 7.0)	
H–C(13)	1.18 (<i>d</i> , <i>J</i> = 7.6)	1.25 (<i>d</i> , <i>J</i> = 7.0)	1.18 (<i>d</i> , <i>J</i> = 7.0)	1.19 (<i>d</i> , <i>J</i> = 7.8)	1.37 (<i>s</i>)
H–C(14)	1.49 (<i>d</i> , <i>J</i> = 1.4)	2.43 (<i>s</i>)	0.78 (<i>d</i> , <i>J</i> = 7.0)	0.73 (<i>d</i> , <i>J</i> = 7.4)	0.74 (<i>d</i> , <i>J</i> = 7.4)
H–C(15)	1.75 (<i>d</i> , <i>J</i> = 1.6)	4.85, 4.48 (2 <i>d</i> , <i>J</i> = 17.7 each)	4.46, 4.60 (2 br. <i>d</i> , <i>J</i> = 19.0 each)	4.45, 4.62 (2 br. <i>d</i> , <i>J</i> = 19.4 each)	4.48 (br. <i>d</i> , <i>J</i> = 19.3), 4.65*

^{a)} Literature values; in CDCl₃ [4][11]. ^{b)} Exper. values (400 MHz); in (D₆)acetone. ^{c)} Exper. values (400 MHz); in CDCl₃/CD₃OD 1:1. ^{d)} Literature values; in CD₃OD [10].

C(15) normally appears at a δ_C value of *ca.* 17 to 18 [6]. The relative configuration of **2** was settled by NOESY experiments (Fig. 3). The chemical shifts of all H- and C-atom signals were fully determined by ^1H , ^1H -COSY and HMQC experiments. Thus, the structure of **2** was elucidated as (*E,E*)-3 α ,9 β -dihydroxy-6 β H,11 β H-13-norgermacra-1(10),4-dien-11,6-carbolactone.

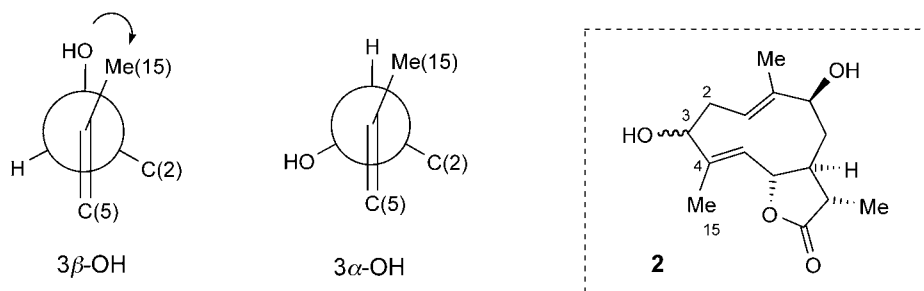


Fig. 2. View along the C(4)–C(3) bond of **2** to illustrate the ‘ γ -gauche’ effect between the 3-OH and the Me(15) groups

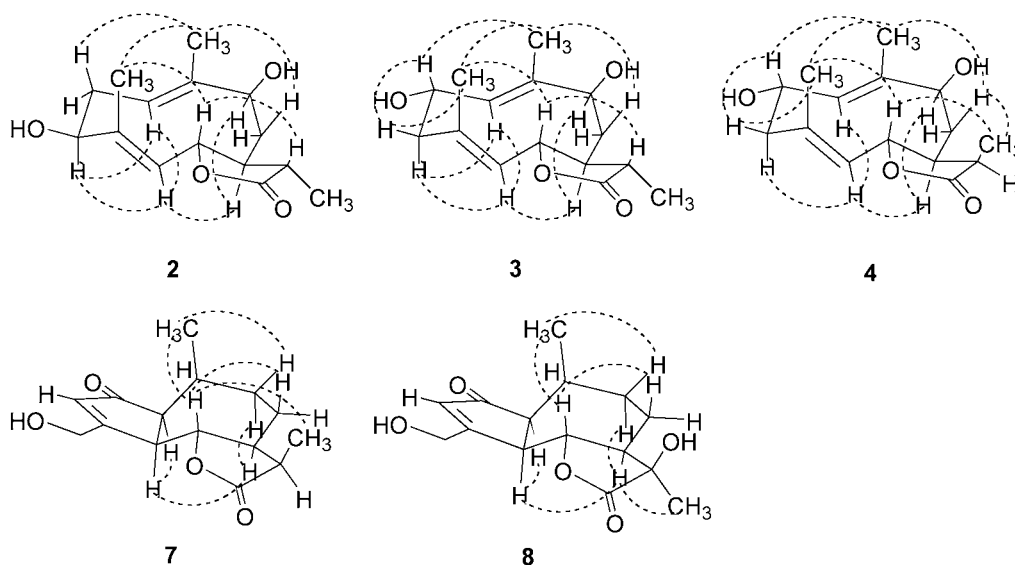


Fig. 3. Key NOESY correlations (dashed lines) observed in compounds **2**, **3**, **4**, **7**, and **8**

Compound **3** was assigned a molecular formula of $\text{C}_{15}\text{H}_{22}\text{O}_4$ by HR-EI-MS (m/z 266.1514 (M^+ ; calc. 266.1518)). The IR absorption bands of **3** indicated the presence of OH and lactone groups (3417 and 1755 cm^{-1} , resp.). The ^1H - and ^{13}C -NMR data indicated that **3** was also a typical germacranolide-type sesquiterpenoid [5]. Comparison of the ^1H - and ^{13}C -NMR data of **3** with those of **2** indicated that these two compounds were isomers, the only difference being the position of one of the OH functions. An OH group was allotted to C(2) by ^1H , ^1H -COSY correlation (Fig. 1): the H–C(2) signal at δ_{H} 4.69 correlated with the signals at δ_{H} 5.09 (*dq*, $J=9.7, 1.4$,

H–C(1)), 2.58 (*dd*, $J = 11.0, 5.6$, H $_{\beta}$ –C(3)), and 1.97 (*dd*, $J = 11.0, 10.0$, H $_{\alpha}$ –C(3)). The presence of a 2 α –OH group was confirmed by a HMBC experiment (*Fig. 1*), the configuration being assigned based on the coupling constants between H–C(2) and H $_{\beta}$ –C(3) ($J = 5.6$ Hz), and between H–C(2) and H $_{\alpha}$ –C(3) (10.0 Hz) [7]. The 2 α –configuration was further confirmed by a NOESY experiment (*Fig. 3*): a strong correlation was observed between H–C(2) and H $_{\beta}$ –C(3), and a correlation was also observed between H–C(2) and H–C(14) (δ_{H} 1.51). The structure of **3** was, therefore, assigned as (*E,E*)-2 $\alpha,9\beta$ -dihydroxy-6 β H,11 β H-13-norgermacra-1(10),4-dien-11,6-carbolactone.

Compound **4** had a molecular formula of C₁₅H₂₂O₄, as determined by HR-EI-MS (m/z 266.1515 (M^+ ; calc. 266.1518)). The ¹H- and ¹³C-NMR data revealed that **4** was a stereoisomer of **3**. The relative configuration of **4** was elucidated by a detailed NOESY experiment (*Fig. 3*): H–C(13) at δ_{H} 1.18 showed strong interactions with H–C(6) (δ_{H} 4.91) and H $_{\beta}$ –C(8), indicative of a β -configured Me(13) group. For germacranolide-type sesquiterpenoids, the coupling constant between H $_{\beta}$ –C(11) and H–C(7) is usually *ca.* 12–13 Hz [8], whereas that between H $_{\alpha}$ –C(11) and H–C(7) is normally 7–8 Hz [9]. In the case of **4**, the latter was 7.8 Hz, indicating that H–C(11) was α -oriented. Compared with compound **3**, the C(8) resonance of compound **4** was shifted upfield ($\Delta\delta_{\text{C}} = -2.8$) due to the '*\gamma-gauche*' effect of the Me(13 β) group. The structure of compound **4** was, thus, derived as (*E,E*)-2 $\alpha,9\beta$ -dihydroxy-6 β H,11 α H-13-norgermacra-1(10),4-dien-11,6-carbolactone.

Compound **7** was assigned the molecular formula C₁₅H₂₀O₄ by HR-EI-MS (m/z 264.1354 (M^+ ; calc. 264.1362)). The IR bands at 3408, 1768, and 1672 cm⁻¹ indicated the presence of OH, lactone, and α,β -unsaturated C=O groups, respectively. Comparison of the ¹H- and ¹³C-NMR spectral data of **7** and **6** [10] revealed that both compounds had the same structural backbone and functional patterns, and that they were stereoisomers, the only difference being the orientation of the Me(13) group. A NOESY experiment (*Fig. 3*) indicated β -configuration for the Me(13) group (correlation between H–C(13) at δ_{H} 1.19 and H–C(6) at δ_{H} 4.69). The configuration of **7** was also fully assigned by a NOESY experiment (*Fig. 3*), and the compound was identified as (*E*)-15-hydroxy-2-oxo-6 β H,11 α H-13-norguaia-3-ene-11,6-carbolactone.

Compound **8** had the molecular formula C₁₅H₂₀O₅, as determined by HR-EI-MS (m/z 280.1317 (M^+ ; calc. 280.1311)). The similarity of IR absorptions as compared to those of **7** suggested the presence of OH, lactone, and α,β -unsaturated C=O groups. The ¹H- and ¹³C-NMR data of **7** and **8** were very similar. The molecular weight of **8** was 16 mass units higher than that of **7**, suggesting the presence of an additional OH group. The absence of the H–C(11) signal in the ¹H NMR spectrum of **8** and an additional signal for a quaternary C-atom at δ_{C} 74.3 in its ¹³C-NMR spectrum indicated that the OH group was located at C(11). The β -orientation was assigned to the 11-OH group by a NOESY experiment (H–C(13) at δ_{H} 1.37 was strongly correlated with H–C(7) at δ_{H} 1.93). The configuration of **8** was also corroborated by a NOESY experiment (*Fig. 3*), and the compound was identified as (*E*)-11 $\beta,15$ -dihydroxy-2-oxo-6 β H-13-norguaia-3-ene-11,6-carbolactone.

The three known compounds were identified as deacetylherbolide A (**1**), jacquilenin (**5**) [11], and (*E*)-15-hydroxy-2-oxo-6 β H,11 β H-13-norguaia-3-ene-11,6-carbolactone (**6**) [10] on the basis of their spectral data (¹H-NMR, ¹³C-NMR, EI-MS).

Experimental Part

General. All solvents were of anal. grade (*Shanghai Chemical Plant*). The petroleum ether used for plant extractions had a b.p. of 60–90°. Silica gel (200–300 mesh) was used for column chromatography (CC), and precoated SiO₂ GF₂₅₄ plates (*Qingdao Haiyang Chemical Plant*) were used for TLC. *MCI Gel CHP20P* (75–150 µm; *Mitsubishi Chemical Industries Ltd.*) and *C₁₈* reverse-phased silica gel (150–200 mesh, *Merck*) were also used for CC. Melting points (m.p.) were measured on a *Fisher-Johns* melting-point apparatus and are uncorrected. Optical rotations were determined on a *Perkin-Elmer 341* polarimeter. IR Spectra were recorded on a *Perkin-Elmer 577* spectrometer; in cm⁻¹. NMR Spectra were recorded on *Bruker AM-400* or *Varian Mercury-400* spectrometers; chemical shifts δ in ppm are given rel. to SiMe₄ as internal standard, coupling constants *J* in Hz. Mass spectra (EI-MS; 70 eV) were recorded on a *Finnigan MAT-95* mass spectrometer; in *m/z* (rel. %).

Plant Material. The whole plants of *P. petasitoides* were collected in July 2002 in the area of Shanxi province in the Qinling Mountains, P.R. China. The plants were identified by Prof. *Xiao-An Wang*, School of Biology, Shanxi Normal University, China. A voucher specimen has been deposited at Shanghai Institute of Materia Medica (Accession number: Paras-2002-3Y).

Extraction and Isolation. The air-dried powder of the whole plants of *P. petasitoides* (1.5 kg) was extracted with petroleum ether/acetone 1:1 (3 × 10 l) at r.t. The resulting crude extract was concentrated under reduced pressure. The crude extract (46.0 g) was fractionated on a *MCI-gel* column (100 g), eluting with 95% aq. EtOH to give a major fraction of 29.0 g, which was subjected to CC (SiO₂ (500 g); petroleum ether/acetone 50:1, 30:1, 20:1, 10:1, 7:1, 4:1, 2:1, 1:1, 0:1; using 2 l of solvent each) to furnish nine fractions. *Fraction 5* was purified chromatographically on 1) a *Sephadex LH-20* column (CHCl₃/MeOH 1:1), 2) a reverse-phased *C₁₈* silica-gel column (MeOH/H₂O 3:7), and 3) a silica-gel column (petroleum ether/acetone 5:1) to afford **1** (24 mg). *Fraction 6* was purified on a *MCI-gel* column (MeOH/H₂O 1:1) to afford several major subfractions, which were purified by CC (SiO₂; petroleum ether/AcOEt 4:1) to yield **5** (4.6 mg), **6** (45.0 mg), **7** (3.5 mg), and **8** (18.4 mg). *Fraction 7* was first decolorized on a *MCI-gel* column (MeOH/H₂O 2:3) to obtain one major fraction, which was purified on a *Sephadex LH-20* column (CHCl₃/MeOH 1:1) to afford three fractions. Each was further purified by CC (SiO₂; petroleum ether/acetone 2:1) to yield **2** (11.2 mg), **3** (6.0 mg), and **4** (3.2 mg).

(*E,E*)-3 α ,9 β -Dihydroxy-6 β H,11 β H-13-norgermacra-1(10),4-dien-11,6-carbolactone (**2**). White solid. $[\alpha]_D^{20} = +134.6$ (*c* = 0.17, CHCl₃). IR (Film): 3396, 2926, 1751, 1668, 1456, 1379, 1335, 1240, 1215, 1188, 1142, 1049, 962, 868, 581. ¹H- and ¹³C-NMR: see *Tables 1* and *2*, resp. EI-MS: 266 (18, *M*⁺), 248 (19), 175 (31), 167 (39), 149 (30), 139 (37), 121 (34), 107 (41), 87 (100), 81 (93). HR-EI-MS: 266.1498 (*M*⁺, C₁₅H₂₂O₄⁺; calc.: 266.1518).

Table 2. ¹³C-NMR Spectral Data of the Sesquiterpenoids **1–8**

	1 ^{a)}	2 ^{b)}	3 ^{b)}	4 ^{b)}	5 ^{a)}	6 ^{c)}	6 ^{b)}	7 ^{b)}	8 ^{b)}
C(1)	129.3	126.6	132.1	131.8	131.1	55.3	53.8	53.8	53.9
C(2)	25.5	38.3	68.4	68.2	195.1	211.6	207.2	207.2	207.3
C(3)	39.4	78.9	49.6	49.6	133.2	129.3	128.8	128.4	128.5
C(4)	140.1	141.4	140.5	139.7	171.6	186.3	183.4	183.1	183.2
C(5)	127.2	125.2	129.9	130.0	49.5	52.1	51.2	51.1	51.0
C(6)	80.9	81.5	80.9	80.3	83.7	83.4	82.2	82.1	81.5
C(7)	51.5	52.3	51.4	46.3	56.1	52.2	51.5	46.1	53.2
C(8)	36.5	35.9	37.6	34.8	25.8	26.2	25.7	22.4	21.2
C(9)	79.6	80.2	79.0	79.2	37.7	35.7	34.9	34.8	34.4
C(10)	138.9	143.1	139.1	138.9	153.5	36.2	34.7	34.5	34.6
C(11)	42.0	42.8	42.0	41.2	41.3	42.9	41.6	39.9	74.3
C(12)	178.2	178.8	178.1	178.8	177.2	180.8	177.8	178.5	176.4
C(13)	13.3	13.9	13.1	10.8	12.2	13.0	12.8	10.9	19.8
C(14)	10.7	12.4	11.3	11.4	21.8	15.1	14.9	14.7	14.7
C(15)	17.3	11.4	18.2	18.2	62.5	63.0	62.4	62.2	62.3

^{a)} Literature data; in CDCl₃ [4][11]. ^{b)} Exper. data (100 MHz); in (D₆)acetone. ^{c)} Literature data; in CD₃OD [10].

(*E,E*)-2 α ,9 β -Dihydroxy-6 β H,11 β H-13-norgermacra-1(10),4-dien-11,6-carbolactone (**3**). White solid. $[\alpha]_D^{20} = +121.4$ ($c = 0.10$, CHCl₃). IR (KBr): 3417, 2929, 1755, 1668, 1456, 1319, 1236, 1186, 1049, 1020, 962, 575. ¹H- and ¹³C-NMR: see *Tables 1* and 2, resp. EI-MS: 266 (8, M^+), 248 (22), 175 (31), 149 (21), 135 (29), 121 (40), 109 (39), 107 (68), 100 (84), 95 (61), 71 (100). HR-EI-MS: 266.1514 (M^+ , C₁₅H₂₂O₄⁺; calc.: 266.1518).

(*E,E*)-2 α ,9 β -Dihydroxy-6 β H,11 α H-13-norgermacra-1(10),4-dien-11,6-carbolactone (**4**). White solid. $[\alpha]_D^{20} = +112.0$ ($c = 0.18$, CHCl₃). IR (Film): 3383, 2924, 1747, 1668, 1456, 1378, 1288, 1211, 1018, 962. ¹H- and ¹³C-NMR: see *Tables 1* and 2, resp. EI-MS: 266 (12, M^+), 248 (17), 175, (29), 149 (47), 135 (31), 121 (43), 109 (37), 107 (69), 100 (89), 95 (63), 71 (100). HR-EI-MS: 266.1515 (M^+ , C₁₅H₂₂O₄⁺; calc.: 266.1518).

(*E*)-15-Hydroxy-2-oxo-6 β H,11 α H-13-norguaia-3-ene-11,6-carbolactone (**7**). White solid. $[\alpha]_D^{20} = +404.5$ ($c = 0.10$, CHCl₃). IR (KBr): 3408, 2931, 1768, 1672, 1608, 1385, 1265, 1219, 1198, 1049, 986, 852, 611. ¹H- and ¹³C-NMR: see *Tables 1* and 2, resp. EI-MS: 264 (100, M^+), 246 (25), 233 (47), 218 (19), 191 (29), 149 (55). HR-EI-MS: 264.1354 (M^+ , C₁₅H₂₀O₄⁺; calc.: 264.1362).

(*E*)-11 β ,15-Dihydroxy-2-oxo-6 β H-13-norguaia-3-ene-11,6-carbolactone (**8**). Colorless crystals (acetone). M.p. 212–214°. $[\alpha]_D^{20} = +5.0$ ($c = 0.10$, CHCl₃). IR (KBr): 3508, 3369, 2928, 1770, 1676, 1612, 1441, 1329, 1269, 1246, 1136, 1045, 993, 922, 860, 630. ¹H- and ¹³C-NMR: see *Tables 1* and 2, resp. EI-MS: 280 (100, M^+), 262 (7), 249 (17), 234 (22), 191 (35), 175 (30), 139 (28). HR-EI-MS: 280.1317 (M^+ , C₁₅H₂₀O₅⁺; calc.: 280.1311).

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