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Sesquiterpenes from roots of *Lingularia veitchiana*

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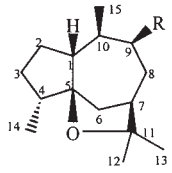
Together with seven known sesquiterpenes, a new guaiane, a new furanoeremophilane, and a new eudesmane were isolated from the roots of *Ligularia veitchiana*. Their structures were elucidated by spectroscopic methods. The bioactivities of three known guaiane sesquiterpenes were determined.

1. Introduction

The roots of *Lingularia veitchiana* (Hemsl.) Greenm. (Compositea), has long been used as a Chinese folk medicine for the treatment of influenza, cough, ulcer, and tuberculosis [1], and has therefore been investigated by our group. Several eremophilane derivatives [2–5] have been isolated from the whole plant material collected from northwest China having a dry and cool climate. However, a phytochemical investigation on the roots of this plant collected from Shen-Nong-Jia wilderness area (which has a wet and warm growing condition in south China with both climate and altitude significantly different from those of northwest China), we isolated a series of guaiane components and other sesquiterpenes. This paper reports the isolation and structure elucidation of three new sesquiterpenes 9β-methoxyliguloxide (**4**), 1,10β-epoxy-6β-isobutanoyloxy-9-oxo-furanoeremophilane (**6**) and 8α-hydroxy-4(15),11-eudesmadiene (**7**), as well as seven known sesquiterpenes liguloxidol acetate (**1**), liguloxidol (**2**), liguloxide (**3**), 6β-angeloyloxy-1,10β-epoxy-9-oxo-furanoeremophilane (**5**), liguhodgsonal (**8**), spathulenol (**9**), and β-oplopenone (**10**). In addition, the anti-tumor activities of three guaianes were tested against human hepatoma (SMMC-7721) and ovaria carcinoma (HO-8910) cell lines with vincristin sulphate as a standard.



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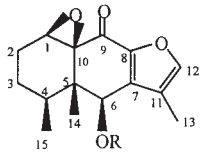
3 R=H
4 R=OCH_3



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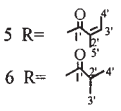

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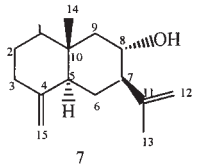

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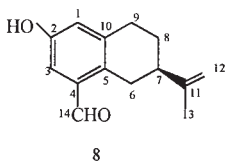

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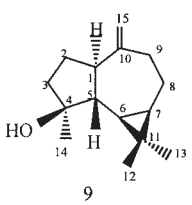

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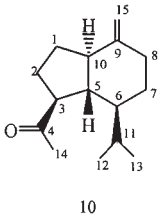

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2. Investigations, results and discussion

Compound **1** was obtained as colorless prisms, m.p. 78–80 °C (petroleum ether–acetyl acetate). Its EIMS gave a molecular ion peak at *m/z* 280, combined with the results of HR-ESIMS ($[M + H]^+$ at *m/z* 281.21144, calcd. for $C_{17}H_{29}O_3$, 281.2109), the molecular formula of **1** was deduced to be $C_{17}H_{28}O_3$. The structure of compound **1** was established to be a known guaiane liguloxidol acetate [6] by its spectroscopic data (^1H, ^{13}C NMR, ^1H-^1H COSY, HMQC, HMBC and ^1H-^1H NOESY) (Tables 1, 2) and single crystal X-ray analysis (Fig.).

Comparisons of the ^1H and ^{13}C NMR spectra data with those of **1**, compound **2** and **3** were elucidated as liguloxidol and liguloxide [6] respectively. Since **1**, **2**, **3** were reported previously [6] without ^{13}C NMR data, the assignments of their ^{13}C NMR data were reported in this paper. Compound **4** was obtained as a pale yellow oil. The ^{13}H NMR spectrum showed sixteen ^{13}C resonance and DEPT experiments differentiate these signals as $5 \times CH_3$, $4 \times CH_2$, $5 \times CH$, and $2 \times C$ (Table 2). The molecular formula of **4** was deduced to be $C_{16}H_{28}O_2$ combined with the result of its EIMS spectrum in which showed a mole-

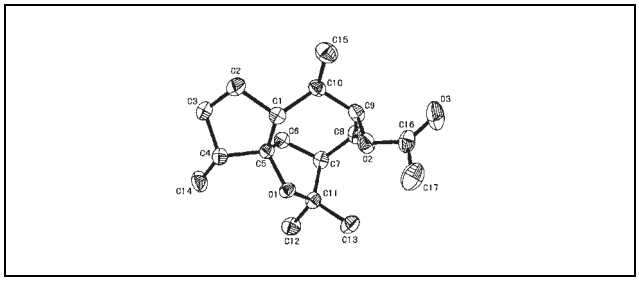

Fig: ORTEP diagram of the crystal structure of **1**

Table 1: ^{1}H NMR data of compounds 1–7 (400 MHz, $CDCl_3$, TMS, δ/ppm)

H	1**	2***	3***	4***	5	6	7
1	1.93 m*	1.92 m*	1.93 m*	1.93 m*	3.38 d 4.6	3.31 d 4.8	1.3–1.6 m*
2	1.11 m*	1.09 m*	0.98 m*	1.05 m*	1.2–2.4 m*	1.4–2.1 m*	1.3–1.6 m*
	1.99 m*	1.94 m*	1.98 m*	1.96 m*			
3	1.66 m*	1.66 m*	1.68 m*	1.64 m*	1.2–2.4 m*	1.4–2.1 m*	1.7–1.9 m*
	1.07 m*	1.04 m*	0.95 m*	1.03 m*			
4	2.12 m*	2.06 dd m*	2.01 m*	2.08 m*	1.2–2.4 m*	1.4–2.1 m*	–
5	–	–	–	–	–	–	1.82 brd 11.2
6	1.69 m*	1.61 dd 15.5, 3.2	1.61 m*	1.62 m*	6.74 s	6.60 s	1.57 dt 12.0, 5.6
	2.17 m*	2.07 m*	1.96 m*	2.06 m*			1.23 dt 12.0, 11.2
7	2.10 m*	2.08 m*	2.00 m*	2.08 m*	–	–	2.67 dt 5.0, 11.2
8	1.67 m*	1.78 m*	1.58 m*	1.89 m*	–	–	3.89 dt 5.0, 11.2
	2.16 m*	2.21 m*	1.88 m*	2.23 ddd			
9	5.11 ddd	3.56 ddd	1.69 m*	3.17 ddd	–	–	1.98 dd 12.0, 11.2
	4.2, 2.0, 1.0	4.2, 2.0, 1.0	1.42 m*	4.2, 2.0, 1.0			1.63 dd 12.0, 5.0
10	1.73 m*	2.03 m*	1.76 m*	2.04 m*	–	–	–
12	1.31 s	1.44 s	1.21 s	1.33 s	7.47 brs	7.44 brs	4.71 brs; 4.72 brs
13	1.19 s	1.15 s	1.06 s	1.12 s	1.92 brs	1.91 brs	1.75 brs
14	0.96 d 6.8	0.94 d 6.7	0.84 d 6.7	0.97 d 6.7	1.26 s	1.20 s	0.73 s
15	0.90 d 6.6	0.90 d 6.7	0.78 d 6.7	0.88 d 6.7	1.03 d 7.2	1.00 d 7.3	4.54 brs; 4.82 brs
2′	–	–	–	–	–	2.69 qq 7.2, 6.8	–
3′	–	–	–	–	6.29 qq 7.2, 1.0	1.25 d 7.2	–
4′	–	–	–	–	2.08 dq 7.2, 1.0	1.23 d 6.8	
5′	–	–	–	–	1.98 dq 1.0, 1.0	–	–
OMe	2.09 s	–	–	3.26 s	–	–	–
OH	–	3.20 brs	–	–	–	–	–

* Overlapping signals
** Assigned by HMBC and HMQC
*** Assigned by comparison with compound **1**

cular ion peak at *m/z* 252. The ^{1}H and ^{13}C NMR spectra of **4** closely resemble those of **1** (Table 1, 2) except the presence of a methoxyl group instead of the acetyloxyl group in **1**. The multiplet due to H-9 appeared at δ 3.17 (1 H, ddd, J = 4.2, 2.0, 1.0 Hz) that significantly shifted to high field relative to the corresponding resonance of **1** (Table 1). Thus, a 9-methoxyl group was indicated in compound **4**. The stereochemistry of **4** was identical with that of **1** because of the same splitting pattern and coupling constants of H-9 (ddd, J = 4.2, 2.0, 1.0 Hz) (Table 1). Compound **4** could then be described as a new guaiane 9β-methoxyliguloxide.

The structure of compound **5** was identified as a known furanoeremophilane 6β-angeloyloxy-1,10β-epoxy-9-oxofuranoeremophilane for its ^{1}H and ^{13}C NMR spectral data was completely the same as those reported in the literature [7, 8].

The molecular formula of **6** was deduced to be $C_{19}H_{24}O_5$ by its EIMS which gave a molecular ion peak at *m/z* 332, combined with the ^{13}C NMR and DEPT spectra which showed the presence of five CH_3, two CH_2, five CH, and seven C. The IR absorption bands indicated the presence of an ester carbonyl at 1738 cm^{-1} and a conjugated carbonyl at 1690 cm^{-1}. The ^{1}H NMR spectrum showed the

Table 2: ^{13}C NMR data of compounds 1–10 (100.16 MHz, $CDCl_3$, TMS, δ/ppm)

C	1*	2	3	4	5	6	7	8	9	10
1	50.6 d	50.5 d	55.8 d	50.0 d	62.5 d	62.4 d	46.4 t	121.5 d	53.4 d	27.3 t
2	28.5 t	26.9 t	28.0 t	28.5 t	24.9 t	24.7 t	26.3 t	153.4 s	26.7 t	28.4 t
3	29.4 t	29.0 t	29.6 t	29.3 t	19.2 t	18.8 t	40.7 t	115.8 d	41.7 t	56.0 d
4	42.7 d	42.3 d	42.3 d	42.4 d	31.9 d	31.5 d	147.7 s	134.9 s	80.9 s	211.6 s
5	92.4 s	92.7 s	92.5 s	92.1 s	45.2 s	45.2 s	49.1 d	131.7 s	54.3 d	52.0 d
6	29.2 t	28.9 t	29.0 t	29.3 t	68.6 d	68.6 d	29.0 t	29.9 t	29.9 d	49.2 d
7	46.2 d	45.7 d	45.4 d	46.6 d	137.2 s	136.8 s	45.6 d	41.4 d	27.5 d	26.5 t
8	33.4 t	36.1 t	33.4 t	30.9 t	146.4 s	146.4 s	68.0 d	27.1 t	24.8 t	35.2 t
9	76.4 d	75.3 d	30.8 t	85.6 d	181.2 s	181.0 s	51.0 t	30.8 t	38.8 t	150.8 s
10	40.6 d	42.0 d	39.3 d	41.7 d	65.5 s	65.4 s	35.3 s	139.9 s	153.4 s	51.7 d
11	80.1 s	81.1 s	80.5 s	79.8 s	121.6 s	121.5 s	150.5 s	149.0 s	20.2 s	29.5 d
12	24.2 q	24.0 q	22.9 q	24.1 q	146.6 d	146.6 d	108.0 t	109.6 t	16.3 q	21.7 q
13	31.5 q	30.6 q	31.4 q	31.5 q	8.2 q	8.4 q	21.0 q	20.7 q	28.6 q	15.6 q
14	13.7 q	14.1 q	13.4 q	13.8 q	16.3 q	16.1 q	17.2 q	192.2 d	26.0 q	28.8 q
15	19.4 q	19.5 q	22.8 q	19.5 q	15.4 q	15.2 q	108.3 t	–	106.2 t	103.4 r
1′	171.2 s	–	–	57.9 q	167.1 s	176.5 s	–	–	–	
2′	21.4 q	–	–	–	126.6 s	34.1 d	–	–	–	
3′	–	–	–	–	141.5 d	19.3 q	–	–	–	
4′	–	–	–	–	20.6 q	18.5 q	–	–	–	
5′	–	–	–	–	16.0 q	–	–	–	–	

* Assigned by HMBC and HMQc

presence of a β-methyl furan ring at δ 7.44 (1 H, brs, α-proton of furan ring) and δ 1.91 (3 H, brs, β-methyl). Comparison of NMR data with those of compound **5** (Table 1, 2) showed a very close similarity except the presence of an isobutanoyl instead of the angeloyl in **5**. The above observations suggested that the 6β-ester group in the case of **6** to be an isobutanoyl. The stereochemistry of **6** was identical with that of **5** by comparing their ^{1}H NMR data and coupling constants (Table 1). Thus, the structure of compound **6** was identified as 1,10β-epoxy-6β-isobutanoyloxy-9-oxo-furanoeremophilane.

Compound **7** has a molecular formula $C_{15}H_{24}O$ deduced by its EIMS spectrum ($[M]^+$ *m/z* 220) supported by the ^{13}C NMR and DEPT spectra ($2 \times CH_3$, $7 \times CH_2$, $3 \times CH$, and $3 \times C$). A hydroxyl group was indicated by the IR absorption band at 3420 cm^{-1} and the fragment of *m/z* 202 $[M\text{-}H_2O]^+$ in the EIMS spectrum. Its ^{1}H NMR spectrum showed the presence of two tertiary methyl groups (δ 0.73 and δ 1.75 s), of which the latter being attached with olefinic carbon, and two vinylidene groups at δ 4.71, 4.72 (1 H each, brs), and δ 4.54, 4.82 (1 H each, brs). Combined with the presence of significant fragment *m/z* 41 $[C_3H_5]^+$ in EIMS, an isoallyl group could be indicated. The above information and the ^{13}C NMR data of compound **7** (Table 2) suggested a 4(15),11-eudesmadiene framework [9]. The configuration of isoallyl group would be 7β (an equatorial position for large group) according to the biogenetic consideration. An oxygen-bearing methine proton was observed at δ 3.89 (1 H, dt, $J = 5.0$, 11.2 Hz), therefore, the hydroxyl group would be 8α which is the only position to compatible the 7,9-diaxial relationship of H-8β with the two large and one small J values: $J_{8,9\alpha} = J_{8,7\alpha} = 11.2$ Hz, $J_{8,9\alpha} = 5.0$ Hz. The hydrogen at C-5 must occupy the axial position by its large coupling constants: $J_{5,6\beta} = 11.2$ Hz. The 10-Me would also be β-configuration because of its relative high field signal at δ 0.73 [10]. Thus, the structure of compound **7** was elucidated as 8α-hydroxy-4(15),11-eudesmadiene. Its ^{13}C NMR spectrum also supported the structure.

Compounds **8**, **9**, **10** were identified as liguhodgsonal [11], spathulenol [12], and β-oplopenone [13] respectively by comparison of their spectral data (EIMS, ^{1}H NMR and ^{13}N NMR) with those reported in the literature.

Using MTT method, the anti-tumor activities of compounds **1**, **2**, **3** against human hepatoma (SMMC-7721) and human ovaria carcinoma (HO-8910) cell lines were studied comparison with standard – vincristin sulphate. The half inhibitory concentration (IC_{50}) against the two cell lines were listed in Table 3. Among the three compounds tested, compound **1** exhibited the most effective anti-tumor activity especially against the human ovaria carcinoma (HO-8910) cell line.

Table 3: Half inhibition concentrations (IC_{50}) of compounds 1–3 (μg/ml)

Tumor cell lines	Vincristin sulphate	1	2	3
Hepatoma (SMMC-7721)	67.37	102.38	165.11	400.45
Ovarian carcinoma (HO-8910)	67.44	81.29	178.09	508.80

3. Experimental

3.1. Equipment

Optical rotations were recorded on a Perkin-Elmer 341 Polarimeter; UV spectra were obtained on a TU-1901 UV-VIS spectrophotometer; IR spectra were taken on a Nicolet Avatar 360 FT-IR spectrometer; The NMR spectra were obtained on a Bruker AM 400 FT-NMR spectrometer with chemical shifts reported in δ (ppm) using TMS as an internal standard; MS data were obtained on a VG-ZAB-HS instrument (70 eV); Silica gel (200–300 mesh) used for column chromatography and silica GF_{254} (10–40 μ) for TLC supplied by Qingdao Marine Chemical Factory, Qingdao, P.R. China; Spots were detected on TLC under UV or by heating after spraying with 5% H_2SO_4 in C_2H_5OH; Melting points are uncorrected.

3.2. Plant material

The roots of *Ligularia veitchiana* (Hemsl.) Greenm. were collected in Shen-Nong-Jia wilderness area, Hubei Province, P.R. China. And was identified by Prof. Pu-Song Peng, Wuhan Institute of Botany, Chinese Academy of Science, Hubei Province, P.R. China. A voucher specimen has been deposited in the same institute.

3.3. Extraction and isolation

Air-dried and powdered roots of *L. veitchiana* (1.1 kg) were exhaustively extracted with a micture of petroleum ether (60–90 °C)–Et_2O–MeOH (1 : 1 : 1) at RT. The extract was concentrated under reduced pressure, to give a residue (84 g), which was chromatographed on a silica gel column (200–300 mesh, 700 g) with a gradient of petroleum ether–acetone (50 : 1–1 : 1, 500 ml each fluent). Combination of the appropriate fractions (monitored by TLC analysis) led to seven fractions (A–G). The fr.B (petroleum ether–acetone 40 : 1, 10 g) was chromatographed on a silica gel column (200–300 mesh, 150 g) eluting with a gradient of petroleum ether–EtOAc (50 : 1–30 : 1, 100 ml each eluate). Eluates B_9 and B_{10} were combined and re-chromatographed on silica gel (10 g) eluting with petroleum ether–acetone (100 : 1) to afford **9** (12 mg). Eluate B_{15} was re-chromatographed on silica gel (10 g) eluting with benzene–acetone (100 : 1) to afford **10** (15 mg). The fr.C (petroleum ether–acetone 30 : 1, 10 g) was chromatographed on silica gel (150 g) eluting with petroleum ether–EtOAc (30 : 1, 100 ml each eluate). Eluate C_8 was purified on a silica gel column (20 g) eluting with petroleum ether–benzene (80 : 1) to afford **3** (28 mg). Eluates C_{12} and C_{13} was combined and re-chromatographed on silica gel (20 g) eluting with $CHCl_3$–EtOAc (30 : 1) to afford **2** (22 mg); Compound **1** (60 mg) was obtained as colorless prisms from fr.D and recrystallized from a mixture of petroleum ether–EtOAc at RT. The remaining fr.D was further chromatographed on silica gel (10 g) eluting with $CHCl_3$–EtOAc (40 : 1) to afford **4** (30 mg); The fr.E (2 g) was chromatographed on silica gel (20 g) eluting with petroleum ether–EtOAc (20 : 1, 20 ml each eluate). Eluate E_3 was purified on silica gel (5 g) eluting with petroleum ether–acetone (20 : 1) to afford **7** (11mg). Compound **5** (5 mg) was obtained by preparative TLC of eluate E_2 developed with $CHCl_3$–EtOAc (40 : 1); The fr.F (3 g) was separated on silica gel (30 g) with elution of petroleum ether–EtOAc (20 : 1, 20 ml each eluate). Eluate F_4 and F_5 was separated respectively by silica gel (10 g) with elution of $CHCl_3$–acetone (100 : 1) to afford **6** (26 mg) and **8** (14 mg).

3.4. *Liguloxidol acetate* (**1**)

Colorless prisms, m.p. 78–80 °C (petroleum ether–acetyl acetate), IR (ν_{max}^{KBr}, cm^{-1}): 2970, 2927, 1731, 1239, 1013, 969, 875; EIMS *m/z* (rel int): 280 $[M]^+$ (0.7), 265 (5), 205 (15), 105 (12), 95 (12), 81 (19), 69 (24), 55 (51), 43 (100); HR-ESIMS *m/z*: 281.21144 $[M + H]^+$; ^{1}H and ^{13}C NMR data see Tables 1, 2.

3.5. *Liguloxidol* (**2**)

Pale yellow oil; EIMS *m/z* (rel int): 238 $[M]^+$ (2), 223 (53), 205 (45), 161 (22), 105 (34), 81 (53), 69 (71), 55 (100); ^{1}H and ^{13}C NMR data see Tables 1, 2.

3.6. *Liguloxide* (**3**)

Pale yellow oil; EIMS *m/z* (rel int): 222 $[M]^+$ (9), 207 (100), 189 (53), 164 (16), 149 (37), 137 (41), 109 (43), 81 (40), 55 (43), 41 (44); ^{1}H and ^{13}C NMR data see Tables 1, 2.

3.7. *9β-Methoxyliguloxide* (**4**)

Pale yellow oil, $[\alpha]_D^{21}$ −30.0 (c, 0.30, $CHCl_3$); EIMS *m/z* (rel int): 252 $[M]^+$ (0.5), 237 (45), 205 (37), 187 (16), 161 (12), 147 (10), 123 (20), 95 (22), 69 (46), 55 (96), 41 (100); ^{1}H and ^{13}C NMR data see Tables 1, 2.

3.8. *6β-Angeloyloxy1,10β-epoxy-9-oxo-furanoeremophilane* (**5**)

Colorless needles; UV (λ_{max}, nm, $CHCl_3$): 284; EIMS *m/z* (rel int): 344 $[M]^+$ (4), 262 $[M\text{-}COC(CH_3)CH(CH_3)]^+$ (17), 244 $[M\text{-}OAng]^+$ (3), 189

(7), 151 (18), 137 (11), 83 (100), 55 (29); ^{1}H and ^{13}C NMR data see Tables 1, 2.

3.9. 1,10β-Epoxy-6β-isobutanoyloxy-furanoeremophil-9-one (6)

Pale yellow gum, $[\alpha]_D^{20}$ −17.6 (c, 0.50, $CHCl_3$), IR (ν_{max}^{film}, cm^{-1}): 2974, 2938, 1738, 1690, 1534, 1462, 1414, 1385, 1146, 983, 914, 754; UV (λ_{max}, nm, $CHCl_3$): 286; EIMS *m/z* (rel int): 332 $[M]^+$ (0.5), 262 $[M\text{-}COCH(CH_3)_2]^+$ (55), 228 (71), 213 (43), 178 (99), 151 (46), 137 (53), 83 (100), 71 (67), 55 (49), 43 (82); ^{1}H and ^{13}C NMR data see Tables 1, 2.

3.10. 8α-Hydroxy-4(15),11-eudesmadiene (7)

Colorless oil, $[\alpha]_D^{20}$ +14.8 (c, 1.19, $CHCl_3$); EIMS *m/z* (rel int): 220 $[M]^+$ (12), 202 $[M\text{-}H_2O]^+$ (35), 187 (56), 159 (100), 145 (53), 131 (58), 107 (83), 91 (88), 55 (67), 41 (96); ^{1}H and ^{13}C NMR data see Tables 1, 2.

3.11. Liguhodgsonal (8)

Colorless needles; EIMS *m/z* (rel int): 216 $[M]^+$ (92), 201 $[M\text{-}CH_3]^+$ (100), 173 (40), 145 (24), 120 (21), 91 (17), 77 (6); ^{1}H NMR δ ppm ($CDCl_3$, 400 MHz): 6.85 (1 H, d, 2.6 Hz, H-1), 7.14 (1 H, d, 2.6 Hz, H-3), 3.41 (1 H, dd, 17.5 Hz, 4.6 Hz, H-6α), 2.85 (3 H, m, H-6β, 9), 2.34 (1 H, m, H-7α), 1.96 (1 H, m, H-8α), 1.65 (1 H, m, H-8β), 4.79 (1 H, brs, H-12), 4.81 (1 H, brs, H-12), 1.82 3 H, s, H-13), 10.26 (1 H, s, CHO), 4.93 (1 H, brs, −OH); ^{13}C NMR data see Table 2.

3.12. Spathulenol (9)

Colorless oil; EIMS *m/z* (rel int): 220 $[M]^+$ (0.3), 205 $[M\text{-}CH_3]^+$ (11), 159 (10), 119 (18), 91 (37), 79 (33), 43 (100); ^{1}H NMR δ ppm ($CDCl_3$, 400 MHz): 1.04 (3 H, s, H-12), 1.06 (3 H, s, H-13), 1.28 (1 H, s, H-15), 4.66 (1 H, brs, H-14), 4.69 (1 H, brs, H-14); ^{13}C NMR data see Table 2.

3.13. β-Oplopenone (10)

Colorless needles; IR (ν_{max}^{KBr}, cm^{-1}): 2953, 2871, 1709, 1357, 1157, 885; EIMS *m/z* (rel int): 220 $[M]^+$ (7), 177 (43), 135 (14), 121 (13), 107 (21), 91 (28), 43 (100); ^{1}H NMR δ ppm ($CDCl_3$, 400 MHz): 0.65 (3 H, d, 6.7 Hz, H-12), 0.90 (3 H, d, 7.0 Hz, H-13), 2.19 (3 H, s, H-14), 4.56 (1 H, d, 1.6 Hz, H-15), 4.67 (1 H, d, 1.6 Hz, H-15); ^{13}C NMR data see Table 2.

3.14. X-ray crystal structure of compound 1

Crystal data: $C_{17}H_{28}O_3$, formula wt 280.39, crystal size 0.56 × 0.46 × 0.42 mm, tetragonal, space group $P4_3$, a = 10.1050 (10) Å, b = 10.1050 (10) Å, c = 15.884 (2) Å, V = 1621.9 (3) $Å^3$, Z = 4, D_c = 1.148 g/cm^3, F(000) = 616, MoK_α (λ = 0.71073 Å), μ = 0.077 mm^{-1}. The reflection data were collected on a Siemens P4, using graphite-monochromated radiation. A total of 2259 reflections were collected in the range $2.02° \leq \theta \leq 26.98°$, of which 1961 unique reflections with $I > 2\sigma(I)$ were used for refinement. The final R and R_w were 0.0361 and 0.0801, respectively. The structure was solved by the direct method using the program SHELXS-97. Non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were included at calculated positions and not refined.

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References

1 Hou, K. Z.; A Dictionary of the Families and Genera of Chinese Seed Plants, 2. Ed., p. 276, Science Press, Beijing 1982
2 Zao, Y.; Jia, Z. J.; Tan, R. X.; Yang, L.: Phytochemistry **31**, 2785 (1992)
3 Jia, Z. J.; Zhao, Y.; Tan, R. X.; Yang, L.: Phytochemistry **31**, 199 (1992)
4 Jia, Z. J.; Zhao, Y.; Tan, R. X.:J. Nat. Prod. **56**, 494 (1993)
5 Zhao, Y.; Jia, Z. J.; Yang, L.: Planta Med. **60**, 91 (1994)
6 Ishii, H.; Tozyo, T.; Nakamura, M.; Minato, H.: Tetrahedron **26**, 2911 (1970)
7 Cheng, D. L.; Gao, J. J.; Yang, L.: Chem. J. Chin. Univ. **13**, 781 (1992)
8 Fu, B.; Zhu, Q. X.; Yang, X. P.; Jia, Z. J.: Pharmazie **57**, 275 (2002)
9 Masakazu, I.; Tomoyaki, T.; Minoru, S.; Kenji, U.: Phytochemistry **30**, 563 (1991)
10 Zdero, C.; Bohlmann, F.: Phytochemistry **28**, 3105 (1989)
11 Naya, K.; Okayama, T.; Fujiwara, M.; Nakata, M.; Ohtsuka, T.; Kurio, S.: Bull. Chem. Soc. Jpn. **63**, 2239 (1990)
12 Xu, R. S.: Chemistry of Natural Product, p. 296, Science Press, Beijing 1993
13 Wayerstahl, P.; Marschall-Weyerstahl, H.; Manteuffel, E.; Kaul, V. K.: Planta Med. **54**, 259 (1988)