Novel *ent*-Kaurane Diterpenoids from *Isodon xerophilus*

HOU, Ai-Jun[a](侯爱君) YANG, Hui[a](杨辉) LIU, Yan-Ze[b](刘延泽) ZHAO, Qin-Shi[a](赵勤实)
LIN, Zhong-Wen[a](林中文) SUN, Han-Dong*,[a](孙汉董)

[a] *Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming, Yunnan 650204, China*

[b] *Department of Phytochemistry, Henan College of Traditional Chinese Medicine, Zhengzhou, Henan 450003, China*

Further investigation on the leaves of *Isodon xerophilus* afforded three novel *ent*-kaurane diterpenoids, xerophilusins D—F (1—3), together with seven known compounds, phyllostachysin A (4), oleanolic acid, caffeic acid, rosmarinic acid, rutin, quercetin-3-*O*-β-*D*-glucopyranoside, and quercetin. Structures of 1—3 were elucidated on the basis of their spectral properties and X-ray crystallographic analysis. Compound 1 showed broad spectra inhibiting human tumor cells and significant cytotoxicity.

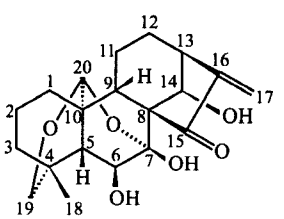
Keywords *Isodon xerophilus*, Labiatae, isolation, structure elucidation, bio-activities, *ent*-kaurane diterpenoids

Introduction

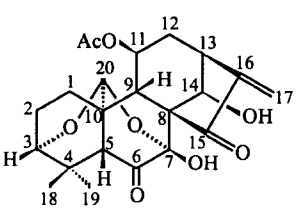
Isodon species, a rich source of *ent*-kaurane diterpenoids, have been extensively investigated phytochemically and biologically.[1-5] Recently, we reported the structures and antitumor activity of 7,20:14,20-diepoxy *ent*-kauranoids from the leaves of *Isodon xerophilus* (C. Y. Wu et H. W. Li) H. Hara (Labiatae).[6] Our continuing fractionation of the EtOAc extract resulted in the isolation of three novel *ent*-kauranoids, xerophilusins D—F (**1—3**), as well as phyllostachysin A (**4**),[7] oleanolic acid,[8] caffeic acid,[9] rosmarinic acid,[9] rutin,[10] quercetin-3-*O*-β-*D*-glucopyranoside,[11] and quercetin.[11] **1** existed as a unique structure having 7, 20: 19, 20-diepoxy units. **2** belongs to a new type of *ent*-kaurane diterpenoids due to a basic skeleton of 3, 20: 7, 20-diepoxy-*ent*-kaur-16-en-15-one. The presence of C—C bond between C-7 and C-20 is characteristic of **3**, which is the third 7, 20-cyclo-*ent*-kauranoid after phyllostachysin A (**4**)[7] and rubescensin D.[12] In this paper, we wish to report the structure elucidation of **1—3** and the cytotoxic effects of **1**, **3**, and **4**.

Results and discussion

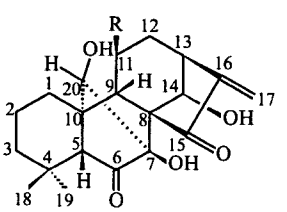
Xerophilusin D (**1**) was obtained as colorless needles, and the positive HRFABMS (obsd 363.1803, calcd 363.1808) indicated the molecular formula of $C_{20}H_{26}O_6$. It contained an *exo*-methylene group conjugated with a carbonyl group on a five-membered ring [UV λ_{max} (MeOH) 238 (log ε 3.99) nm; IR (KBr) ν 1709 and



1



2



3: R = OAc
4: R = OH

* E-mail: hdsun@mail.kib.ac.cn; Tel.: 86-871-5223251; Fax: 86-871-5216343.
Received September 4, 2000; revised November 1, 2000; accepted November 1, 2000.

1650 cm^{-1}; ^1H NMR δ 6.24 and 5.48 (s, each 1H); ^{13}C NMR δ 209.6 (s), 152.8 (s), and 119.5 (t)], and two oxygen-bearing methines [^1H NMR δ 5.11 (s, 1H) and 4.29 (d, J = 2.1 Hz, 1H); ^{13}C NMR δ 73.8 and 72.4 (each d)]. Additionally, signals of one methyl group, six methylenes (including an oxygen-bearing one at δ 68.0), four methines (including an acetal group at δ 98.0), and four quaternary carbons (including a ketalic carbon at δ 99.2) were also shown in the ^{13}C NMR and DEPT spectra. All the above-mentioned signals indicated an *ent*-kaurane diterpenoid with a hexacyclic ring system. The signals of the C-20 methylene usually observed as two AB-type doublets were replaced by a sharp 1H singlet at δ 5.55 in the ^1H NMR spectrum of **1**. Also noticed in its ^1H NMR spectrum were the absence of one methyl signal and the appearance of two AB-type proton signals at δ 3.37 (d, J = 11.7 Hz) and 3.90 (dd, J = 2.7, 11.7 Hz). These evidence, with consideration of the hexacyclic ring system and the structural types of diterpenoids found hitherto,[13] established the basic skeleton of 7β-hydroxy-7α, 20: 19, 20-diepoxy-*ent*-kaur-16-en-15-one, in which two hydroxyl groups were introduced.

Two hydroxyl groups were determined at C-6 and C-14 on the basis of ^1H-^1H COSY spectrum, and further tested by the HMQC experiment. The signal at δ 4.29 (d, J = 2.1 Hz, 1H) had a correlation with a doublet at δ 1.43 (d, J = 2.1 Hz, 1H, H-5β). The broad singlet at δ 5.11 coupled with a doublet at δ 3.16 (d, J = 9.7 Hz, 1H, H-13α), which coupled with a multiplet at δ 2.31 (m, 1H, H-12α) and showed no cross peak with H-12β owing to the ca. 90° dihedral angle. Two ether linkages formed from C-20 to C-7 and C-19 were confirmed by the following HMBC correlations: H-20 with C-19 and C-7; H-19b with C-20 (Fig. 1). The

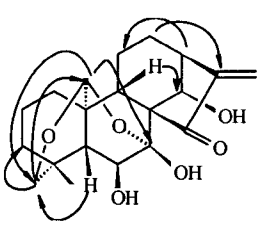


Fig. 1 Selected HMBC correlations of **1**.

β-orientation of two hydroxyl groups were deduced from the cross peaks in the NOESY spectrum: H-14α with H-11α and H-20; H-6α with H-19a and Me-18 (Fig. 2). Thus, the structure of xerophilusin D (**1**) was established to be 6β, 7β, 14β-trihydroxy-7α, 20: 19, 20-diepoxy-*ent*-kaur-16-en-15-one.

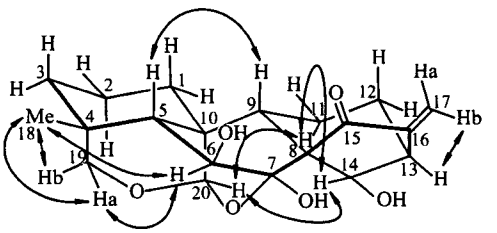


Fig. 2 Key NOESY correlations of **1**.

Xerophilusin E (**2**), a minor constituent in the leaves of this plant, was obtained as prisms, and produced $[M+H]^+$ quasi-molecular ion peak in EIMS at m/z 419. In conjunction with the analysis of the ^{13}C NMR and DEPT spectra, its molecular formula was deduced to be $C_{22}H_{26}O_8$. Its UV, IR, and NMR spectra also revealed a partial structure of α, β-unsaturated ketone. Furthermore, the NMR spectra of **2** gave the signals of an acetoxyl group [δ 1.95 (s, 3H), δ 170.4 (s), and 21.1 (q)], two methyls, three methylenes, an acetal group [δ 5.78 (brs, 1H) and δ 97.0 (d)], six methines including three oxygenated ones, and five quaternary carbons including a carbonyl group at δ 203.5 and a ketalic carbon at δ 98.8. These data combined with the degree of unsaturation suggested an *ent*-kauranoid with two epoxy units, a carbonyl group, a secondary hydroxyl group, and a secondary acetoxyl group.

^1H-^1H COSY and HMQC spectra permitted an unambiguous assignment of all protons and related carbons, displaying the carbonyl group at C-6 (δ 203.5) and three oxygenated methine at C-3 (δ 77.2), C-11 (δ 65.2), and C-14 (δ 73.0), respectively. In the HMBC spectrum of **2**, the following long range couplings: H-3 with C-20; H-20 with C-3 and C-7; H-11 with OAc (δ 170.4) disclosed the 3α, 20: 7α, 20-diepoxy moiety and the acetoxy group at C-11 (Fig. 3). Obviously, C-14 was substituted by the hydroxyl group. Each substituent in **2** had β-orientation based on X-ray crystallographic analysis, by which the conformations of ring A [C(1), C(2), C(3), C(4), C(5), C(10)], B [C(5), C(6), C(7), C(8), C(9), C(10)], and C [C(9), C(11), C(12), C(13), C(14), C(8)] were all concluded to be boat forms (Fig. 4). Conse-

quently, xerophilusin E (**2**) was identified as 7β,14β-dihydroxy-11β-acetoxy-3α, 20: 7α, 20-diepoxy-*ent*-kaur-16-en-6,15-dione.[14]

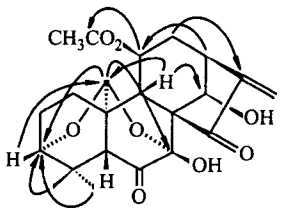


Fig. 3 Selected HMBC correlations of **2**.

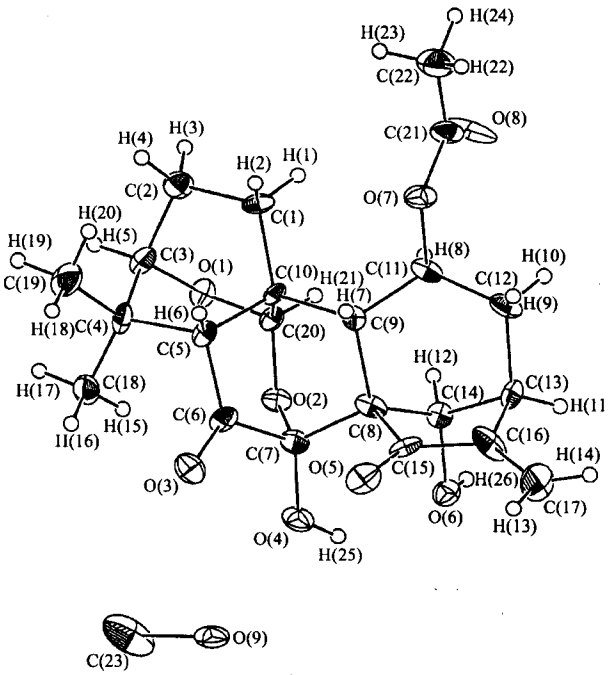


Fig. 4 Molecular structure of **2**.

Xerophilusin F (**3**), colorless crystals, had a molecular formula of $C_{22}H_{28}O_7$ (positive HRFABMS obsd 405.1981, calcd 405.1913). A singlet at δ 1.97 (s, 3H) in the ^1H NMR spectrum and two signals at δ 170.1 (s) and 21.3 (q) in the ^{13}C NMR spectrum exhibited the presence of an acetoxyl group. Comparison of other NMR data of **3** with those of phyllostachysin A (**4**)[7] indicated that the hydroxyl group at C-11 in **4** was replaced by the acetoxyl group in **3** and presumable 11-acetylated phyllostachysin A was proved by its HMBC spectrum. NOESY experiment of **3** showed that it had the same stereochemistry as **4**. The β-orientation of the acetoxyl group was decided by the NOESY correlations: H-11α with H-14α, H-12α and H-1α. The configuration at C-20 in **3** was assigned as *R* from the NOE effects of H-20 with Me-19 and H-2α. In conclusion, xerophilusin F (**3**) was characterized as 7β,14β,20(*R*)-trihydroxy-11β-acetoxy-7, 20-cyclo-*ent*-kaur-16-en-6, 15-dione.[14]

Compounds **1**, **3**, and **4** were studied for their cytotoxicity against four kinds of human tumor cells: K562, HL-60, HCT, and MKN-28. The 50% inhibitory concentration (IC_{50}) values of these compounds are listed in Table 1, in which mitoxantrone is included as a positive reference substance. The IC_{50} values of **1** against K562, HL-60, HCT, and MKN-28 cells were all less than 16 μg/mL, indicating its broad spectra inhibiting human tumor cells and prominent activity. **3** was more cytotoxic against K562, HL-60, and MKN-28 cells (IC_{50} values < 3 μg/mL) than HCT cells (IC_{50} = 80.80 μg/mL). **4** was inactive to HCT and MKN-28 cells (IC_{50} > 1000 μg/mL), but it had the selectivity on K562 (IC_{50} = 8.00 μg/mL) and HL-60 (IC_{50} = 2.82 μg/mL) cells.

Table 1 Cytotoxic activity of compounds **1**, **3** and **4**

Compound	M. W.	IC_{50} (μg/mL)			
		K562	HL-60	HCT	MKN-28
1	362	0.83	0.47	15.38	0.46
3	404	2.96	0.44	80.80	2.19
4	362	8.00	2.82		
Mitoxantrone	444.5	0.29	0.29	0.02	1.54

Experimental

General procedures

All melting points were measured on an XRC-1 micro melting point apparatus and uncorrected. Optical rotations were taken on a SEPA-300 polarimeter. IR spectra were measured on a Bio-Rad FTS-135 spectrometer with KBr pellets. UV spectra were obtained on a UV 210A spectrometer. MS were recorded on a VG Auto Spec-3000 spectrometer. 1D- and 2D-NMR spectra were run on a Bruker AM-400 and DRX-500 instrument with TMS as internal standard, respectively.

Plant material

The leaves of *I. xerophilus* were collected in

Yuanyang prefecture of Yunnan Province in November, 1998, and air-dried. The identity of plant material was verified by Prof. Zhong-Wen Lin, and a voucher specimen (KIB 98-11-25 Lin) is deposited in the Herbarium of the Department of Taxonomy, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and isolation

The dried and powdered leaves (8.3 kg) were extracted with 70% Me_2CO and filtered. The filtrate was concentrated and extracted with EtOAc and *n*-BuOH successively. A part (440 g) of the EtOAc extract (660 g) was applied to column chromatography over Si gel column eluting with a $CHCl_3$—Me_2CO (1:0—0:1) gradient system to yield fractions I—VII. Fraction IV was chromatographed over Si gel (petroleum ether:Me_2CO = 7:3) to produce five fractions. The second fraction was subjected to column chromatography over Si gel ($CHCl_3$:MeOH = 30:1), followed by RP-18 column (MeOH:H_2O = 9:1) to yield **1** (160 mg) and **4** (350 mg). Fraction V was further purified by repeated column chromatography over Si gel (petroleum ether:isopropyl alcohol = 9:1), MCI gel CHP 20P (MeOH:H_2O = 9:1), and RP-18 (MeOH:H_2O = 8:2) to afford **2** (4 mg) and **3** (482 mg).

A part (100 g) of *n*-BuOH extract (350 g) was subjected to column chromatography over DM-130 eluting with H_2O, 60% MeOH and 70% Me_2CO successively. The elute from 60% MeOH was purified by a combination of rechromatography over Si gel and RP-18 to give six known compounds: oleanolic acid (1.7 g), caffeic acid (50 mg), rosmarinic acid (3.6 g), rutin (107 mg), quercetin-3-*O*-β-*D*-glucopyranoside (52 mg), and quercetin (20 mg).

Xerophilusin D (**1**) colorless needles (Me_2CO), m.p. 209—210 ℃, $[\alpha]_D^{23}$ − 120.8 (*c* 0.39, C_5H_5N), UV (MeOH) λ_{max}: 238 (log ε 3.99) nm; ^{1}H NMR (C_5D_5N, 400 MHz) δ: 6.24 (s, 1H, H-17a), 5.55 (s, 1H, H-20), 5.48 (s, 1H, H-17b), 5.11 (br s, 1H, H-14α), 4.29 (d, *J* = 2.1 Hz, 1H, H-6α), 3.90 (dd, *J* = 2.7, 11.7 Hz, 1H, H-19a), 3.37 (d, *J* = 11.7 Hz, 1H, H-19b), 3.16 (d, *J* = 9.7 Hz, 1H, H-13α), 2.31 (m, 1H, H-12α), 2.19 (m, 1H, H-2β), 1.77 (dd, *J* = 6.4, 12.9 Hz, 1H, H-9β), 1.62 (dd, *J* = 5.2, 14.6 Hz, 1H, H-1α), 1.56 (overlap, 1H, H-11α), 1.53 (dd, *J* = 4.8, 13.2 Hz, 1H, H-3α), 1.43 (d, *J* = 2.1 Hz, 1H, H-5β), 1.42 (overlap, 1H, H-12β), 1.41 (overlap, 1H, H-2α), 1.33 (m, 1H, H-11β), 1.26 (m, 1H, H-3β), 1.01 (td, *J* = 6.2, 13.5 Hz, 1H, H-1β), 0.85 (s, 3H, Me-18); ^{13}C NMR (C_5D_5N, 100 MHz) δ: 209.6 (s, C-15), 152.8 (s, C-16), 119.5 (t, C-17), 99.2 (s, C-7), 98.0 (d, C-20), 73.8 (d, C-14), 72.4 (d, C-6), 68.0 (t, C-19), 62.2 (s, C-8), 54.5 (d, C-5), 48.4 (d, C-9), 43.7 (d, C-13), 39.9 (t, C-3), 36.3 (s, C-10), 33.4 (s, C-4), 30.3 (t, C-12), 30.1 (t, C-1), 22.7 (q, C-18), 21.2 (t, C-2), 17.5 (t, C-11); IR (KBr) ν: 3387, 3181, 2934, 2872, 1709, 1650, 1445, 1345, 1218, 1191, 1110, 1086 cm^{-1}; EIMS (70 eV) *m/z* (%): 362 (M^+, 25), 344 ([M − H_2O]$^+$, 100), 326 ([M − 2 × H_2O]$^+$, 7), 316 (9), 298 (12), 285 (10), 269 (11); HRFABMS calcd for $C_{20}H_{27}O_6$ 363.1808, found 363.1803.

Xerophilusin E (**2**) colorless prisms (MeOH), m.p. 223—225 ℃, $[\alpha]_D^{20}$ − 32.0 (*c* 0.06, MeOH); UV (MeOH) λ_{max}: 229.2 (log ε 3.82) nm; ^{1}H NMR (C_5D_5N, 400 MHz) δ: 5.93 (s, 1H, H-17a), 5.78 (br s, 1H, H-20), 5.49 (s, 1H, H-17b), 5.10 (m, 1H, H-11α), 4.85 (br s, 1H, H-14α), 3.50 (t, *J* = 2.2 Hz, 1H, H-3β), 3.06 (d, *J* = 9.2 Hz, 1H, H-13α), 3.05 (overlap, 1H, H-12α), 2.12 (s, 1H, H-5β), 1.95 (s, 3H, OAc), 1.92 (overlap, 1H, H-1α), 1.91 (d, *J* = 9.0 Hz, 1H, H-9β), 1.70 (m, 1H, H-2α), 1.68 (m, 1H, H-1β), 1.32 (m, 1H, H-2β), 1.30 (dd, *J* = 9.0, 13.7 Hz, 1H, H-12β), 1.09 (s, 3H, Me-18), 1.08 (s, 3H, Me-19); ^{13}C NMR (C_5D_5N, 100 MHz) δ: 210.3 (s, C-15), 203.5 (s, C-6), 170.4 (s, OAc), 151.5 (s, C-16), 118.8 (t, C-17), 98.8 (s, C-7), 97.0 (d, C-20), 77.2 (d, C-3), 73.0 (d, C-14), 65.2 (d, C-11), 59.0 (s, C-8), 57.8 (d, C-5), 49.1 (d, C-9), 43.1 (d, C-13), 38.0 (s, C-4), 37.6 (s, C-10), 37.2 (t, C-12), 30.4 (q, C-18), 25.9 (q, C-19), 23.0 (t, C-1), 21.1 (t, C-2), 21.1 (q, OAc); IR (KBr) ν: 3437, 2956, 1738 (br), 1644, 1456, 1371, 1240, 1190 cm^{-1}; EIMS (70 eV) *m/z* (%): 419 ([M + H]$^+$, 4), 390 ([M − CO]$^+$, 42), 374 (50), 358 ([M − AcOH]$^+$, 13), 346 (48), 330 (16), 314 (51), 296 (61), 268 (30).

Xerophilusin F (**3**) colorless prisms ($CHCl_3$), m.p. 193—195℃, $[\alpha]_D^{23}$ + 12.2 (*c* 0.31, C_5H_5N);

UV (MeOH) λ_{max}: 227.5 (log ε 3.95) nm; ^{1}H NMR (Me_2CO-d_6, 400 MHz) δ: 5.92 (s, 1H, H-17a), 5.67 (m, 1H, H-11α), 5.46 (s, 1H, H-17b), 5.23 (br s, 1H, H-14α), 4.10 (d, J = 4.2 Hz, 1H, H-20), 2.95 (d, J = 9.0 Hz, 1H, H-13α), 2.88 (ddd, J = 9.0, 9.0, 13.5 Hz, 1H, H-12α), 2.05 (s, 1H, H-5β), 1.97 (s, 3H, OAc), 1.94 (d, J = 11.4 Hz, 1H, H-9β), 1.90 (d, J = 13.8 Hz, 1H, H-1α), 1.52 (dd, J = 4.3, 13.8 Hz, 1H, H-1β), 1.45 (m, 2H, H-2α, β), 1.37 (m, 1H, H-3α), 1.32 (dd, J = 9.0, 13.5 Hz, 1H, H-12β), 1.20 (s, 3H, Me-18), 1.18 (overlap, 1H, H-3β), 0.82 (s, 3H, Me-19); ^{13}C NMR (Me_2CO-d_6, 100 MHz) δ: 210.0 (s, C-6), 203.0 (s, C-15), 170.1 (s, OAc), 151.6 (s, C-16), 118.1 (t, C-17), 89.2 (s, C-7), 80.9 (d, C-20), 72.9 (d, C-14), 68.7 (d, C-11), 61.2 (d, C-5), 59.7 (d, C-9), 59.2 (s, C-8), 47.2 (s, C-10), 43.1 (d, C-13), 41.3 (t, C-3), 38.8 (t, C-12), 34.9 (q, C-18), 33.9 (s, C-4), 24.1 (t, C-1), 23.8 (q, C-19), 21.3 (q, OAc), 19.4 (t, C-2); IR (KBr) ν: 3445, 2970, 2940, 1748, 1725, 1645, 1449, 1389, 1299, 1236, 1104, 1046, 1030 cm^{-1}; EIMS (70 eV) m/z (%): 404 (M^+, 51), 375 (15), 344 ([M - AcOH]$^+$, 65), 325 (19), 314 (92), 297 (53), 286 (17), 268 (41), 260 (16), 242 (27); HRFABMS calcd for $C_{22}H_{29}O_7$ 405.1913, found 405.1981.

X-ray crystallographic analysis of xerophilusin E (**2**)[15]

A colorless prismatic crystal of **2** having approximate dimensions 0.40 × 0.30 × 0.30 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-K_α radiation (λ = 0.071070 nm).

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions: a = 0.7080 (4) nm, b = 1.881 (4) nm, c = 0.8399 (5) nm, β = 92.67 (5)°, V = 1.1174 nm^3. For Z = 2 and FW = 418.44, the calculated density is 1.24 g/cm^3. The space group was determined to be $P2_1$(#4).

The structure was solved by direct methods (SIR92) and expanded using Fourier techniques (DIRDIF94). The final cycle of fullmatrix least-squares refinement was based on 1070 observed reflections (I > 3.00σ(I)) and 290 variable parameters and converged (largest parameter shift was 0.05 times its esd) with unweighted and weighted agreement factors of R = 0.089, R_w = 0.118. The maximum and minimum peaks on the final difference Fourier map corresponded to 380 and -350 e$^-$/nm^3, respectively. All calculations were performed using the texsan crystallographic software package of Molecular Structure Corporation.

Cytotoxicity against four kinds of human tumor cells

The cytotoxicity assays were performed in a method of MTT, the experimental details of which have been reported previously.[6]

Acknowledgements

We wish to thank Prof. Ma-Lin Li (Kunming Medical College, Kunming, China) for cytotoxicity assays. Thanks are also extended to Analytical Center of Zhengzhou University (China) for the X-ray crystallographic analysis.

References

1 Fujita, E.; Nagao, Y.; Kaneko, K.; Nakazawa, S.; Kuroda, H. *Chem. Pharm. Bull.* **1976**, *24*, 2118.
2 Fuji, K.; Node, M.; Sai, M.; Fujita, E.; Takeda, S.; Unemi, N. *Chem. Pharm. Bull.* **1989**, *37*, 1472.
3 Zhao, Q. S.; Tian, J.; Yue, J. M.; Lin, Z. W.; Sun, H. D. *J. Nat. Prod.* **1997**, *60*, 1075.
4 Wang, Y. H.; Chen, Y. Z.; Lin, Z. W.; Sun, H. D.; Fan, J. S. *Phytochemistry* **1998**, *48*, 1267.
5 Zhao, Q. S.; Lin, Z. W.; Jiang, B.; Wang, J.; Sun, H. D. *Phytochemistry* **1999**, *50*, 123.
6 Hou, A. J.; Li, M. L.; Jiang, B.; Lin, Z. W.; Ji, S. Y.; Zhou, Y. P.; Sun, H. D. *J. Nat. Prod.* **2000**, *63*, 599.
7 Fujita, T.; Sun, H. D.; Takeda, Y.; Minami, Y.; Marunaka, T.; Lin, Z. W.; Xu, Y. L. *J. Chem. Soc., Chem. Commun.* **1985**, 1738.
8 Maillard, M.; Adewunmi, C. O.; Hostettmann, K. *Phytochemistry* **1992**, *31*, 1321.
9 Kelley, C. J.; Harruff, R. C.; Carmack, M. *J. Org. Chem.* **1976**, *41*, 449.
10 Wenkert, E.; Gottlieb, H. E. *Phytochemistry* **1977**, *16*, 1811.
11 Markham, K. R.; Ternai, B.; Stanley, R.; Geiger, H.; Mabry, T. J. *Tetrahedron* **1978**, *34*, 1389.

12 Sun, H. D.; Zhou, Q. Z.; Fujita, T.; Takeda, Y.; Minami, Y.; Marunaka, T.; Lin, Z. W.; Shen, X. Y. *Phytochemistry* **1992**, *31*, 1418.

13 Nomoto, K.; Rüedi, P.; Eugster, C. H. *Helv. Chim. Acta* **1976**, *59*, 772.

14 Hou, A. J.; Yang, H.; Jiang, B.; Zhao, Q. S.; Liu, Y. Z.; Lin, Z. W.; Sun, H. D. *Chin. Chem. Lett.* **2000**, *11*, 795.

15 Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-(0) 1223-336033 or E-mail: deposit@ccdc.cam.ac.uk).

(E200009187 LI, L. T.)