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Spectral Assignments and Reference Data

NMR assignments and single-crystal X-ray diffraction analysis of deoxyloganic acid

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7-Deoxyloganic acid (1), citrusin C (2), 3,4-dihydroxyl benzoic acid (3) and (*E*)-caffeic acid (4) were isolated from the water-soluble fraction of ethanol extracts of *Morina nepalensis* var. *alba* Hand.-Mazz. and their structures were determined on the basis of spectroscopic evidence. The total assignments of ^{1}H and ^{13}C NMR spectra of 1 in solvents CD_3OD, D_2O and $CDCl_3$ were reported, in addition to the single-crystal X-ray diffraction analysis of its tetraacetate 1a. All compounds were obtained from *Morina* genus for the first time. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; *Morina nepalensis* var. *alba* Hand.-Mazz.; *Morina*; 7-deoxyloganic acid; citrusin C; 3,4-dihydroxyl benzoic acid; (*E*)-caffeic acid; X-ray diffraction

INTRODUCTION

Iridoids are of biogenetic and chemotaxonomic importance and have displayed various biological activities.[1] Although it was once considered that iridoids generally have a bicyclic H-5/H-9 *β,β-cis*-fused cyclopentanopyran ring system, two *trans*-fused iridoid glycosides, (5*αH*)-6-epi-dihydrocornin and 10-hydroxyl-(5*αH*)-6-epi-dihydrocornin, were isolated from *Penstemon secundiflorus* in 1992 and 1998, respectively.[2,3] Furthermore, several enantiomeric iridoids have been identified as well.[4–9] These findings suggest that the structures of iridoids have more complex stereochemistry than those first assumed.

7-Deoxyloganic acid and its enantiomeric derivatives are important precursors of some other kinds of iridoids. For example, in biosynthetic experiments, 7-deoxyloganic acid was incorporated into the *trans*-fused iridoid glycosides (5*αH*)-6-epi-dihydrocornin and 10-hydroxyl-(5*αH*)-6-epi-dihydrocornin in *P. secundiflorus*.[3] The hydroxylation of deoxyloganic acid to give loganic acid took place with retention of the 7*α*-hydrogen, followed by ring cleavage to give rise to secologanic acid.[10]

In the course of our ongoing research on bioactive constituents from *Morina nepalensis* var. *alba*,[11–16] one iridoid glucoside (**1**) and several phenolic compounds (**2**–**4**) were isolated from the water-soluble fraction of ethanol extracts of *M. nepalensis* var. *alba* Hand.-Mazz.

Compound **1** was identified preliminarily as 7-deoxyloganic acid by comparing ^{1}H and ^{13}C chemical shifts with those in the literature. However, NOE correlations of **1** from two-dimensional NOESY and one-dimensional SELNOESY spectra in our experiments led to some controversy on the stereochemistry of C-1. In order to confirm further the stereochemistry of compound **1**, single-crystal X-ray diffraction analysis of its tetraacetate (**1a**) was carried out. Herein we report on the single-crystal X-ray diffraction analysis of **1a**, as well as the total assignments of ^{1}H and ^{13}C NMR spectra of **1** in solvents CD_3OD, D_2O and $CDCl_3$ by two-dimensional NMR spectra (^{1}H–^{1}H COSY, HMQC, HMBC, NOESY, *J*-resolved spectra).[17–20]

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RESULTS AND DISCUSSION

The *n*-butanol fraction of ethanol extracts of the whole plant of *M. nepalensis* was subjected repeatedly to silica gel, Sephadex LH-20 and MCI gel CHP-20 column chromatography, which led to the isolation of compounds **1**–**4** (Fig. 1).

Compound **1** was isolated as a white powder with an optical rotation $[\alpha]_D^{22} = -84.34^\circ$ (*c* 0.25, MeOH). The molecular formula of **1** was deduced to be $C_{16}H_{24}O_9$ by a combination of ^{13}C (DEPT) NMR spectra and a negative ion fast atom bombardment mass spectrometry (FABMS) spectrum (*m/z* 360 $[M]^-$). The ^{1}H and ^{13}C NMR spectra in CD_3OD of **1** showed anomeric proton and carbon signals at δ 4.67 (d, $J = 7.9$ Hz) and δ 100.19, respectively, of one glucose moiety. The ^{1}H and ^{13}C chemical shifts of **1** corresponded to those of 7-deoxyloganic acid, a new natural product from *Uncaria tomentosa*,[20] therefore compound **1** was identified as 7-deoxyloganic acid.

Compound **1** was assigned to be the C-8-(*S*) isomer of deoxyloganic acid by comparing the ^{13}C chemical shifts with those of deoxyloganic acid isomers with known stereochemistry, and the stereochemical assignment at carbon centers C-1, C-5 and C-9 of **1** was then inferred from ^{1}H–^{1}H NOESY experiments in the literature.[20] Thus we carried out two-dimensional NOESY and one-dimensional selective excitation experiments (SELTOCSY and SELNOESY) in order to confirm further the stereochemistry of **1**. At first, the detailed analysis of two-dimensional NMR spectra (^{1}H–^{1}H COSY, HMQC, HMBC) allowed us to establish the direct, vicinal and long-range H,H and H,C connectivity of **1** (Table 1). The NOE correlations between H-5 (δ 2.86) and H-9 (δ 1.73) from NOESY and one-dimensional SELNOESY spectra (CD_3OD) (Fig. 2) indicated that they were *cis* to each other. Meanwhile, an investigation on the optical rotations of 7-deoxyloganic acid, its 8-epimers, its 1,5,9-epimers and their methyl esters and tetraacetates indicates that these compounds with a 5*S*,9*R* (H-5/H-9 *β,β-cis*) configuration have negative optical rotation values, whereas those with a 5*R*,9*S* (H-5/H-9 *α,α-cis*) configuration have positive optical rotation values.[17–23] Compound **1** should have a 5*S*,9*R* (H-5/H-9 *β,β-cis*) configuration because it has a negative optical rotation value.

On the other hand, NOE correlations (Fig. 2) were observed not only between H-1 (δ 5.20) and H-8 (δ 1.97) (α-face) but between H-1 (δ 5.20) and H-9 (δ 1.73) (β-face) and H-10 (δ 1.08) (β-face), which led to a contradictory result for the stereochemistry of C-1. The results showing the stereochemical determination of solution confirmations of iridoids by means of NOE/ROE data alone led to some controversy owing to the spatial proximity of pertinent protons of the ring system of the iridoid aglycone, so stereochemical determinations should be supported by additional methods such as molecular modeling, single-crystal X-ray diffraction analysis and/or CD spectroscopy.[1]

The absolute stereochemistry of the carbon centers C-1, C-5, C-8 and C-9 were finally confirmed to be 1*S*, 5*S*, 8*S* and 9*R* by a single-crystal X-ray diffraction analysis of the tetraacetate (**1a**) (Fig. 3). The X-ray diffraction analysis shows that one unit cell of **1a** contains two asymmetric molecules, but the stereochemistry of four chiral carbon centers of the monoterpene moiety of two molecules is the same. The two molecules in the unit cell do not fully overlap with each other due to the rotation around the glycosidic bond. The five-membered ring A has an envelope conformation and the six-membered ring B has a twist-boat conformation. Ring A and B are *syn* with dihedrals 145.3 (5)° and 116.9 (5)°, respectively, for each molecule. There are no intermolecules or intramolecule hydrogen bonds. To our best knowledge, this is the first report on the crystallography of the tetraacetate of 7-deoxyloganic acid (**1a**).

The complete ^{1}H and ^{13}C chemical shifts of **1** have been reported only in CD_3OD but its epimers and derivatives have been reported in $CDCl_3$ and D_2O as well, which stimulated us to assign the ^{1}H and ^{13}C NMR spectra of **1** in $CDCl_3$ and D_2O by two-dimensional NMR spectra (Table 2).

Compound **2** was isolated as a white powder. Its molecular formula was proposed as $C_{16}H_{22}O_7$ based on its ^{13}C (DEPT) NMR spectra and negative-ion FABMS showing a quasimolecular ion at *m/z* 325 $[M-1]^-$. The ^{1}H and ^{13}C NMR spectra showed an anomeric proton at δ 4.84 (d, $J = 7.4$ Hz) and an anomeric carbon at δ 103.08 of one glucose unit. The signals at δ 6.81 (d, $J = 1.8$ Hz), 7.07 (d,

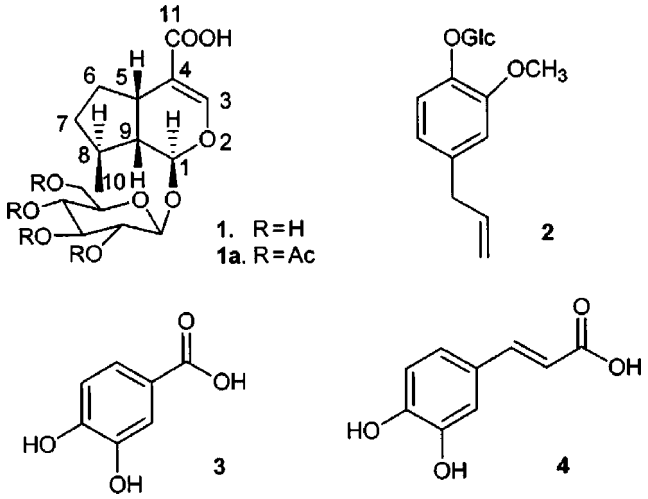

Figure 1. Structures of compounds **1**–**4**.

J = 8.2 Hz) and 6.71 (dd, J = 8.2, 1.8 Hz) were characteristic of H-2, H-5 and H-6 of a 1,3,4-trisubstituted benzyl group. Compound **2** was identified as citrusin C by comparing ^{1}H and ^{13}C chemical shifts with those in the literature.[24,25] The ^{1}H and ^{13}C spectra of **2** were assigned unambiguously by two-dimensional NMR spectra (^{1}H–^{1}H COSY, HMQC and HMBC), which led to the revision of chemical shifts of C-1, C-2, C-5 and C-8[24] and H-7, H-9, H-4′ and H-5′.[25]

Compounds **3** and **4** were determined to be 3,4-dihydroxyl benzoic acid (**3**) and (*E*)-caffeic acid (**4**), respectively, based on their ^{1}H and ^{13}C chemical shifts.

EXPERIMENTAL

General[11–16]

Standard pulse sequences in Bruker XWINNMR software were used for SELNOESY and SELTOCSY experiments with Z-PFGs. A Gaussian-shaped pulse with 1024 data points was used. A 64.5 dB pulse level and 60 ms pulse length for 180° were utilized for the shaped pulse. A mixing time of 500 ms was used for one-dimensional SELNOESY and a spin lock of 100 ms was used for one-dimensional SELTOCSY.

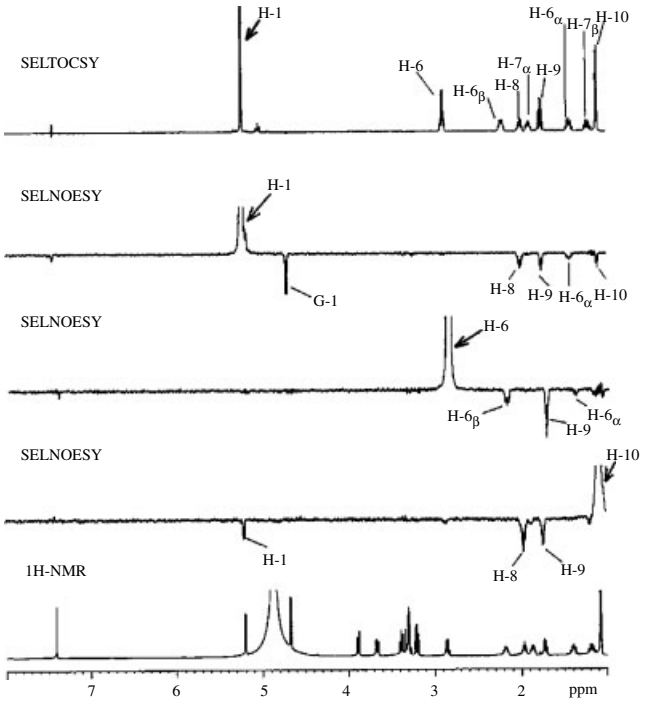

Figure 2. One-dimensional SELTOCSY and SELNOESY spectra **1**.

Plant material

Refer to Refs. 11–16

Table 1. Two-dimensional NMR data of iridoid glucoside **1** (CD_3OD)

	HMQC					
	δ_H	δ_C	COSY (H)	HMBC (C)	NOESY (H)	One-dimensional SELNOESY (H)
1	5.20	97.95	9	3, 5, 8, 9, Glc-1	6α (weak), 8, 9, 10, Glc-1	8, 9, 6α (weak), 10, Glc-1
3	7.41	152.68		1, 4, 5, COOH		
5	2.86	35.31	6α, 6β, 9	1, 3, 4, 6, 8, 9, COOH	6β, 6α (weak), 9	6β, 6α (weak), 9
6α	1.39	33.35	5, 6β, 7α, 7β	4, 5, 8, 9	1, 6β, 7α	
6β	2.18		5, 6α, 7α, 7β	4, 5, 8, 9	5, 6α, 7β	
7α	1.87	34.18	6α, 6β, 7β, 8	5, 9	6α, 7β	
7β	1.18		6α, 6β, 7α, 8	5, 9, 10	6β, 7α	
8	1.97	36.55	7α, 7β, 9, 10	1, 7, 9, 10	1, 10	
9	1.73	49.34	1, 5, 8	1, 5, 7, 8, 10,	1, 5, 10	
10	1.08	20.85	8	7, 8, 9	1, 8, 9	1, 8, 9
Glucosyl						
Glc-1	4.67	100.19	Glc-2	1, Glc-2, -3	1, Glc-2, -3, -5	
Glc-2	3.20	74.77	Glc-1, -3	Glc-1, -3	Glc-1, -3	
Glc-3	3.37	78.05	Glc-2, -4	Glc-2, -4	Glc-1, -2, -5	
Glc-4	3.30	71.61	Glc-3, -5			
Glc-5	3.29	78.34	Glc-4, -6b		Glc-1, -3, -6a	
Glc-6a	3.88	62.77	Glc-6b	Glc-4, -5	Glc-5, -6b	
Glc-6b	3.66		Glc-5, -6a	Glc-4, -5	Glc-5, -6a	

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Table 2. The ^{1}H and ^{13}C NMR data of iridoid glucoside **1** and its tetraacetate (**1a**) (^{13}C 125 MHz, ^{1}H 500MHz; δ in CD_3OD, D_2O and $CDCl_3$; J in Hz)

	Compound **1**						Compound **1a** (in CD_3OD)	
	CD_3OD		D_2O		$CDCl_3$			
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1	5.20 d $J = 5.8$	97.95	5.31 d $J = 4.5$	99.70	5.04 d $J = 4.9$	96.45	5.18 d $J = 4.0$	97.10
3	7.41d $J = 1.6$	152.68	7.45 brs	154.25	7.33 d $J = 0.9$	151.27	7.33 d $J = 1.0$	151.34
4		113.05		114.92		111.99		114.43
5	2.86 dddd $J = 1.6, 7.0, 8.0, 8.7$	35.31	2.88 dq $J = 7.2$	35.28	2.81 dq $J = 7.5$	32.87	2.84	34.02[a]
6α	1.39 dddd $J = 7.3, 8.0, 10.0, 13.1$	33.35	1.39	33.84	1.34	31.66	1.47	32.27
6β	2.18 dddd $J = 3.8, 7.0, 8.2, 13.1$		2.15		2.11		2.15	
7α	1.87 dddd $J = 3.8, 7.3, 6.6, 12.7$	34.18	1.85	35.03	1.78	33.25	1.83	34.02[a]
7β	1.18 dddd $J = 8.2, 8.9, 10.0, 12.7$		1.21		1.11		1.20	
8	1.97 ddd $J = 6.6, 6.7, 6.8, 8.9$	36.55	1.89	37.49	1.82	35.07	1.85	36.80
9	1.73 ddd $J = 5.8, 6.8, 8.7$	49.34	1.82	50.39	1.68	48.01	1.73	49.90
10	1.08 d $J = 6.7$	20.85	1.06 d $J = 6.3$	21.89	0.98 d $J = 6.5$	19.99	1.05 d $J = 6.3$	19.92
COOH		171.11		174.01		169.95		171.24
CH_3COO							2.08, 2.00, 1.95, 1.94	20.45, 20.55, 20.62 (2C)
CH_3COO								172.28, 171.57, 170.94, 170.48
Glucosyl								
Glc-1	4.67 d $J = 7.9$	100.19	4.79 d $J = 7.8$	101.40	4.60 d $J = 7.9$	98.68	5.04 d $J = 9.5$	97.58
Glc-2	3.20 dd $J = 7.9, 9.1$	74.77	3.29 t $J = 9.1$	75.30	3.22 dd $J = 7.9, 9.3$	73.06	4.89 dd $J = 9.5, 8.0$	72.30
Glc-3	3.37 t $J = 9.1$	78.05	3.51 t $J = 9.4$	78.31	3.39	75.91	5.27 t $J = 9.5$	73.99
Glc-4	3.30	71.61	3.42 t $J = 9.1$	72.16	3.41	69.84	5.01 dd $J = 5.0, 8.0$	69.69
Glc-5	3.29	78.34	3.47 ddd $J = 9.6, 1.9, 5.6$	78.89	3.26	76.12	3.94	73.12
Glc-6a	3.88 dd $J = 2.0, 11.9$	62.77	3.92 dd $J = 1.9, 12.2$	63.29	3.79 dd $J = 3.0, 12.1$	61.65	4.28 dd $J = 5.0, 12.5$	62.86
Glc-6b	3.66 dd $J = 5.4, 11.9$		3.73 dd $J = 5.6, 12.2$		3.72 dd $J = 4.4, 12.1$		4.17 dd $J = 2.5, 12.5$	

[a] Signals are overlapped with each other.

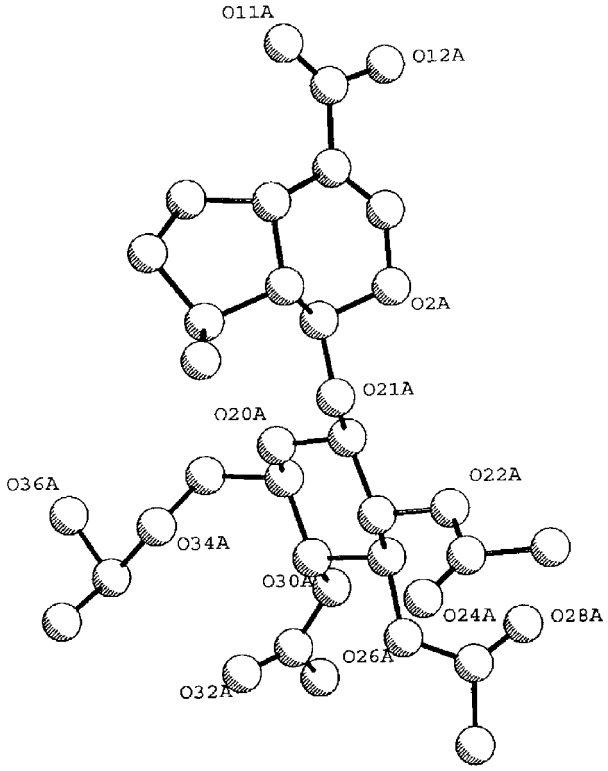

Figure 3. Stereostructure of compound **1a** from single-crystal X-ray analysis.

Isolation and extraction[11–16]

Sample Fr I (1 g) was subjected to Sephadex LH-20 to give **3** (20 mg) and **4** (35 mg) by eluting with aqueous methanol. Sample Fr III (22 g) was loaded to the silica gel column and eluted with acetate–acetone–water (6 : 2 : 0.6, v/v/v) to give five fractions Fr III-1–Fr III-5. Fraction Fr III-2 were subjected repeatedly to silica gel column chromatography by eluting with chloroform–methanol–water and then to MCI gel CHP-20 column chromatography by eluting with aqueous methanol to give **1** (320 mg) and **2** (14 mg).

*7-Deoxyloganic acid (**1**)*

White powder, m.p. 88–90 °C, $[\alpha]_D^{22} = -84.34°$ (c 0.25, MeOH). Negative-ion FABMS: *m/z* 360 $[M]^-$, 345 $[M-15]^-$, 197 $[M-H-162]^-$, 168, 135, 92, 60. IR (cm^{-1}): ν_{max}^{KBr} 3426 (br), 2945, 2877, 1687, 1631, 1074, 1018. UV λ_{max}^{MeOH} nm (log ε): 233 (3.96). ^1H and ^{13}C NMR data: see Table 2.

*Citrusin C (**2**)*

White powder. Negative-ion FABMS: *m/z* 325 $[M-H]^-$, 163 $[M-H-162]^-$, 148 $[M-H-162-15]^-$, 115, 99, 83, 69. IR (cm^{-1}): ν_{max}^{KBr} 3445 (br), 2927, 1710, 1637, 1595, 1512, 1264, 1224, 1132, 1076, 1029, 912, 804. ^1H NMR (500 MHz, δ in CD_3OD, *J* in Hz): δ 6.81 (d, $J = 1.8$ Hz, H-2), 7.07 (d, $J = 8.2$ Hz, H-5), 6.71 (dd, $J = 1.8$, 8.2 Hz, H-6), 3.32 (d, $J = 6.6$ Hz, H-7), 5.84 (ddt, $J = 10.0$, 17.0, 6.6 Hz, H-8), 5.04 (dd, $J = 2.2$, 17.0 Hz, H-9a), 5.01 (dd, $J = 2.2$, 10.0 Hz, H-9b), 3.83 (s, Me), 4.84 (d, $J = 7.4$ Hz, H-1′), 3.46 (m, H-2′), 3.48 (m, H-3′), 3.37 (m, H-4′), 3.39 (m, H-5′), 3.86 (dd, $J = 1.9$, 12.4 Hz, H-6′a) 3.68 (dd, $J = 4.7$, 12.7 Hz, H-6′b). ^{13}C NMR (125 MHz, δ in CD_3OD): δ 136.46 (C-1), 114.17 (C-2), 150.78 (C-3), 146.34 (C-4), 118.30 (C-5), 122.10 (C-6), 40.74 (C-7), 138.98 (C-8), 115.86 (C-9), 56.70 (Me), 103.08 (C-1′), 74.93 (C-2′), 77.82 (C-3′), 71.35 (C-4′), 78.15 (C-5′), 62.51 (C-6′).

*3,4-Dihydroxyl benzoic acid (**3**)*

Yellow powder. ^1H NMR (500 MHz, δ in CD_3OD, *J* in Hz): δ 7.74 (d, $J = 1.9$ Hz, H-2), 6.79 (d, $J = 8.1$ Hz, H-5), 7.42 (dd, $J = 8.1$, 1.9 Hz, H-6); ^{13}C NMR (125 MHz, δ in CD_3OD): δ 123.22 (C-1), 115.74 (C-2), 145.98 (C-3), 151.43 (C-4), 117.70 (C-5), 123.88 (C-6), 170.45 (COOH).

*(E)-Caffeic acid (**4**)*

Yellow powder. ^1H NMR: δ 7.03 (d, $J = 1.5$ Hz, H-2), 6.77 (d, J = 8.1 Hz, H-5), 6.92 (dd, $J = 8.1$, 1.5 Hz, H-6), δ7.52 (d, $J = 16.4$ Hz, H-7), δ6.22 (d, $J = 16.4$ Hz, H-8); ^{13}C NMR: δ 127.84 (C-1), 115.82 (C-2), 146.71 (C-3), 149.33 (C-4), 116.40 (C-5), 122.81 (C-6), 146.84 (C-7), 115.09 (C-8), 171.41 (COOH).

Acetylation of 7-deoxyloganic acid (1)

A 50 mg amount of **1** in Ac_2O–pyridine (1 : 1, v/v) was left at room temperature overnight and then diluted with 2 ml of water and extracted with EtOAc (3 × 10 ml). The EtOAc extracts was dried over Na_2SO_4 and then evaporated to dryness. Compound **1a** (transparent column crystal) was crystallized from the $CHCl_3$ solution of EtOAc extracts and recrystallized in $CHCl_3$ solution.

X-ray diffraction analysis of compound 1a

A crystal of dimensions 0.01 × 0.10 × 1.00 mm was used for X-ray measurements on a MAC DIP-2030K diffractometer with a graphite monochromator, maximum 2θ value of 50.0°. The total number of independent reflections measured was 4372, 4282 of which were considered to be observed ($|F|^2 \geq 8\sigma|F|^2$). Crystal data: asymmetric unit cell chemical formula: $(C_{24}H_{32}O_{13})_2$, single molecular weight M = 528.5, monoclinic system, space group $P2_1$, $a = 16.5740(14)$, $b = 7.4610(3)$, $c = 22.6580(18)$ Å, $\beta = 72.818(4)°$, $V = 2676.8(3)$ Å^3, $Z = 4$, $d = 1.311$ g cm^{-3}, Mo Kα radiation, linear absorption coefficient $\mu = 0.08$ mm^{-1}. The structure was solved by the direct method SHELX-86 (G.M. Sheldrick, University of Göttingen, Germany, 1985) and expanded using difference Fourier techniques, refined by the program and method NOMCSDP[26] and full-matrix least-squares calculations. The final indices were $R_f = 0.076$ and $R_w = 0.067$ ($w = 1/\sigma|F|^2$).

REFERENCES

1. Tasdemir D, Scapozza L, Zerbe O, Linden A, Calis I, Sticher O. *J. Nat. Prod.* 1999; **62**: 811.
2. Fuderaro TA, Stermitz FR. *Tetrahedron Lett.* 1992; **33**: 2953.
3. Krull RE, Stermitz FR, Franzyk H, Jensen SR. *Phytochemistry* 1998; **49**: 1605.
4. Murai F, Tagawa M, Inouye H, Ishida T, Inoue M. *Chem. Pharm. Bull.* 1987; **35**: 2533.
5. Xie S, Uesato S, Inouye H, Fujita T, Murai F, Tagawa M, Shigu T. *Phytochemistry* 1988; **27**: 469.
6. Fuderaro TA, Stermitz FR. *Phytochemistry* 1992; **31**: 4191.
7. Tasdemir D, Wright AD, Sticher O, Calis I, Linden A. *J. Nat. Prod.* 1995; **58**: 1543.
8. Tasdemir D, Wright AD, Sticher O, Calis I. *J. Nat. Prod.* 1996; **59**: 131.
9. Tasdemir D, Sticher O, Calis I, Linden A. *J. Nat. Prod.* 1997; **60**: 874.
10. Damtoft S, Franzyk H, Jensen SR. *Phytochemistry* 1995; **38**: 615.
11. Teng RW, Zhen QA, Wang DZ, Yang CR. *Acta Botan. Sin.* 2003; **45**: 122.
12. Teng RW, Xie HY, Liu XK, Wang DZ, Yang CR. *J. Asian Nat. Prod. Res.* 2003; **5**: 75.
13. Teng RW, Xie HY, Li HZ, Wang DZ, Yang CR. *Chin. J. Org. Chem.* 2002; **8**: 560.
14. Teng RW, Xie HY, Wang DZ, Yang CR. *Magn. Reson. Chem.* 2002; **40**: 603.
15. Teng RW, Xie HY, Li HZ, Liu XK, Wang DZ, Yang CR. *Magn. Reson. Chem.* 2002; **40**: 415.
16. Teng RW, Zhou ZH, Wang DZ, Yang CR. *Chin. J. Magn. Reson.* 2002; **19**: 167.
17. Rao CB, Vijayakumar EKS, Vijayalakshmi KV. *Planta Med.* 1981; **41**: 80.

Spectral Assignments and Reference Data

18. Tagawa M, Murai F. *Planta Med.* 1983; **47**: 109.
19. Murai F, Tagawa M, Damtoft S, Jensen SR, Nielsen BJ. *Chem. Pharm. Bull.* 1984; **32**: 2809.
20. Muhammad I, Dunba DC, Khan RA, Ganzera M, Khan IA. *Phytochemistry* 2001; **57**: 781.
21. Takeda Y, Ooiso Y, Masuda T, Honda G, Otsuka H, Sezik Ekrem, Erdem Y. *Phytochemistry* 1998; **49**: 787.
22. Nakamura M, Kido K, Kinjo J, Nohara T. *Phytochemistry* 2000; **53**: 253.
23. Su BN, Zhai JJ, Jia ZJ. *J. Asian Nat. Prod. Res.* 1998; **1**: 103.
24. Fujita T, Nakayama M. *Phytochemistry* 1992; **31**: 3265.
25. Schwab W, Scheller G, Schreier P. *Phytochemistry* 1990; **29**: 607.
26. Lu Y, Wu BM. *Chin. Chem. Lett.* 1992; **3**: 637.