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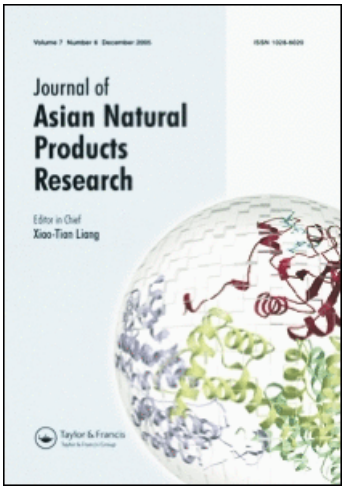

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New lignan glycosides from *Cupressus duclouxian* (Cupessaceae)

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From the branches and leaves of *Cupressus duclouxiana* two new lignan glycosides named cupressoside A (1) and cupressoside B (2), together with matairesinoside (3), dihydrodehydrodiconiferyl alcohol (4), dihydrodehydrodiconiferyl alcohol-9-*O*-α-L-rhamnopyranoside (5), dihydrodehydrodiconiferyl alcohol-4-*O*-α-L-rhamnopyranoside (6), (−)-isolariciresinol (7) and (−)-isolariciresinol-9-*O*-β-D-xylopyranoside (8), were isolated. The structures of these compounds were determined on the basis of their HR-FAB-MS, IR, UV, ^{1}H and ^{13}C NMR (DEPT), and 2D NMR (HMQC, HMBC, COSY, NOESY) spectral data.

Keywords: *Cupressus duclouxiana*; Cupessaceae; Lignan glycosides; Cupressoside A; Cupressoside B

1. Introduction

Cupressus duclouxiana (Cupessaceae) is a common ornamental tree distributed in Yunnan and Sichuan Province of Southwest China [1], on which no chemical studies have thus far been reported. As part of an investigation on Gymnosperm, the chemical constituents of *C. duclouxiana* collected at Kunming Institute of Botany were investigated. Eight lignans were isolated, i.e. cupressoside A (1) and cupressoside B (2), together with matairesinoside (3), dihydrodehydrodiconiferyl alcohol (4), dihydrodehydrodiconiferyl alcohol-9-*O*-α-L-rhamnopyranoside (5), dihydrodehydrodiconiferyl alcohol-4-*O*-α-L-rhamnopyranoside (6), (−)-isolariciresinol (7) and (−)-isolariciresinol-9-*O*-β-D-xylopyranoside (8), among which compounds 1 and 2 are new compounds. In this paper we describe the isolation and structural elucidation of compounds1–8.

2. Results and discussion

Cupressoside A (1) was isolated as white amorphous powder; high-resolution FAB^{-}-MS of 1 indicated a molecular formula of $C_{25}H_{32}O_{10}$ with 10 degrees of unsaturation. IR absorption

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bands at 3431 and 1614 cm^{-1} were characteristics of OH and aromatic groups, respectively. The ^{13}C NMR spectrum (DEPT) showed six quaternary C-atoms, 13 CH, four CH_2 and two Me. The ^{1}H NMR spectrum showed six aromatic-proton signals at δ 6.99 (d, $J = 2.0$ Hz), 6.83 (d, $J = 8.1$ Hz), 6.87 (dd, $J = 2.0, 8.1$ Hz), 6.74 (d, $J = 2.1$ Hz), 6.86 (d, $J = 8.3$ Hz) and 6.69 (dd, $J = 2.1, 8.3$ Hz), which were assigned to two 1,2,4-substituted benzene rings.

In the $^{1}H-^{1}H$ COSY spectrum of 1 the proton signal at δ 3.66 (t, $J = 6.5$ Hz) was coupled with two protons at δ 1.85 (m), which was further coupled with benzyl methylene protons at δ 2.60 (t, $J = 7.1$ Hz), suggesting the presence of an *n*-propanol moiety. The anomeric proton at δ 4.63 (brs) and the ^{13}C NMR spectrum (DEPT) signals at δ 101.7, 72.4, 72.6, 74.1, 69.8 and 18.0 suggested the presence of an α-L-rhamnopyranosyl group. Therefore, according to the above data, compound 1 was established to be a lignan glycoside. HMBC data allowed to correlate the proton signal at δ 3.86 (OMe) with the C-signal at δ 149.2 (C(3)), suggesting OMe at C(3).This was father confirmed by the NOESY spectrum. The proton signal at δ 2.6 (H-C(7′)) was correlated with the C-signals at δ 117.7 (C(2′)), 136.1 (C(1′)) and 122.4 (C(6′)), in accord with *n*-propanol substitution at C(1′). The anomeric proton signal at δ 4.63 was correlated with the C-signal at δ 67.7 (C(9′)), suggesting that the rhamnopyranosyl group was located at C(9′). In the ^{1}H NMR spectrum the coupling constants and chemical shifts of H–C(7) and H–C(8) at δ 4.83 (d, $J = 10.4$ Hz) and 4.00 (ddd, $J = 2.5, 4.8, 10.4$ Hz) showed that H–C(7) and H–C(8) were in a *trans*-arrangement. Acid hydrolysis of 1 gave the aglycone 1a, its ^{1}H NMR and ^{13}C NMR spectral data were identical to those of (7*S*,8*S*)-3-methoxy-3′,7-epoxy-8,4′-oxyneolignan-4,9,9′-triol [2].The optical rotation of 1a ($[\alpha]_D^{24.7} + 0.39$) suggested that it has the same stereochemistry as the aglycone ($[\alpha]_D^{25} + 0.34$) obtained by Fang *et al.* [2]. This provided evidence that 1 has the same 7*S*,8*S* configuration. Finally the structure of compound 1 was determined to be (7*S*,8*S*)-3-methoxy-3′,7-epoxy-8,4′-oxyneoligna-4,9,9′-triol-9′-*O*-α-L-rhamnopyranoside (figure 1).

Cupressoside B (2) was obtained as white amorphous powder. The FAB^{+}-MS exhibited the $[M + 1]^{+}$ at 463.The molecular formula was established as $C_{24}H_{30}O_9$ by positive mode TOF-MS. IR absorption bands at 3416, 1614 and 1511 cm^{-1} were characteristics of OH and aromatic groups, respectively.

The ^{1}H NMR spectrum of compound 2 showed three aromatic proton signals at δ 6.71 (d, $J = 8.1$ Hz), 6.99 (dd, $J = 1.6, 8.1$ Hz) and 7.05 (d, $J = 1.6$ Hz), which were assigned to three protons in a 1,2,4-substituted benzene ring. Another four aromatic proton signals at δ

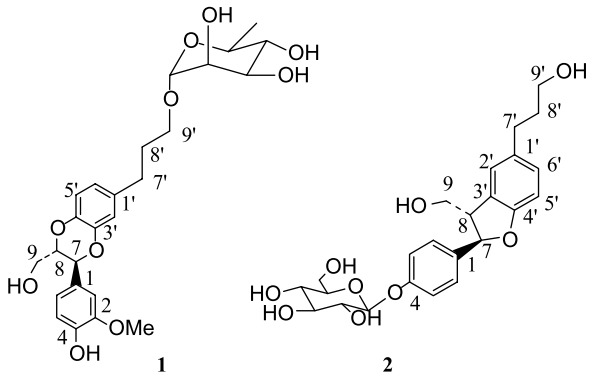

Figure 1. Structures of isolated compounds 1 and 2.

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7.28 (2H, d, $J = 8.6$ Hz) and 7.06 (2H, d, $J = 8.6$ Hz) formed AA′BB′ systems arising from the protons of a 1,4-disubstituted benzene ring.

In the ^{13}C NMR (DEPT) spectrum, the presence of a dihydrobenzofuran skeleton and a glucose were suggested. One anomeric proton signal at δ 4.88 (d, $J = 7.6$ Hz) and the ^{13}C NMR (DEPT) signals at δ 102.3, 74.9, 78.0, 71.4, 78.1 and 62.5 suggested the presence of a β-D-glucopyranosyl group. This was also confirmed by a fragment *m/z* 300 ($[M + H\text{-}163]^+$) in the FAB$^+$-MS. Three methylene proton signals at δ 1.79 (m), 2.61 (t, $J = 7.7$ Hz) and 3.55 (t, $J = 6.6$ Hz) were coupled reciprocally, indicating the presence of a *n*-propanol side-chain. 2D-NMR data including HMBC and NOESY of compound 2 established the connectivity of partial structures and substituents. HMBC spectrum allowed to correlate the signal at δ 2.61 (H–C(7′)) with the C-signals at δ 125.9 (C(2′)), 135.7 (C(1′)) and 129.7 (C(6′)), suggesting *n*-propanol side-chain substitution at C(1′).The anomeric proton signal at δ 4.88 was correlated with the C-signal at δ 158.7 (C(4)), which suggested that the β-D-glucopyranosyl group was located at C(4). Comparison of the ^{1}H NMR and ^{13}C NMR data of 2 with (7*R*,8*S*)-dihydrodehydrodiconiferyl alcohol 4-*O*-β-D-glucopyranoside [3] showed that the absence of the two methoxy signals at δ 3.83 (MeO–C(3)) and 3.86 (MeO–C(3′)), and the presence of further two aromatic proton signals at δ 6.70 and 7.06 in the ^{1}H NMR of 2 were the main difference. Since the coupling constant between H–C(7) and H–C(8) was 5.6 Hz, the relative configuration at C-7 and C-8 was decided to be *trans*. The absolute configuration was assigned on the basis of circular dichroism (CD) spectrum. A negative Cotton effect at 238 nm and a positive one at 221 nm allowed the assignment of 7*R*,8*S* configuration for compound 2. Therefore, the structure of 2 was established as (7*R*,8*S*)-3,3′-didemethoxy-dihydrodehydrodiconiferyl alcohol-4-*O*-β-D-glucopyranoside (figure 1).

Comparison of the chemical properties with reported data allowed us to identify compounds 3–8 as matairesinoside (3) [4], dihydrodehydrodiconiferyl alcohol(4) [2], dihydrodehydrodiconiferyl alcohol-9-*O*-α-L-rhamnopyranoside (5) [7], dihydrodehydrodiconiferyl alcohol-4-*O*-α-L-rhamnopyranoside (6) [7], (−)-isolariciresinol (7) and (−)-isolariciresinol-9-*O*-β-D-xylopyranoside (8) [6], respectively.

3. Experimental

3.1 General experimental procedures

Optical rotations were recorded on a Horiba SEPA-300 polarimeter (Horiba, Tokyo, Japan). UV spectra were recorded on a UV 210A spectrometer. IR spectra were recorded on a Bio-Rad FTS135 spectrophotometer, KBr pellets. 1D- and 2D-NMR spectra were measured with a Bruker AM-400 and Buker AM-500 spectrometer, respectively, using TMS as internal standard. MS data were measured with a VG-Auto-Spec-3000 mass spectrometer. CD spectra were determined with a J-20C automatic spectropolarimeter. Silica gel (200–300 mesh) for column chromatography (CC) and GF_{254} for TLC were obtained from the Qingdao Marine Chemical Factory, Qingdao, Peoople's Republic of China.

3.2 Plant material

The branches and leaves of *Cupressus duclouxiana* were collected in Kunming Institute of Botany, Kunming, Yunnan Province of P.R. China in May 2002. It was identified by Professor

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Ning-hua Tan, and a voucher specimen is deposited in the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

3.3 Extraction and isolation

Dried branches and leaves of *Cupressus duclouxiana* (21.0 kg) were extracted three times with 95% EtOH under reflux (3 × 50 l) for 4, 2 and 1 h, respectively. After evaporation of the combined extracts, the residue was suspended in H_2O and then extracted with petroleum ether (60–90°C), EtOAc and *n*-BuOH. The *n*-BuOH extract (600.0 g) was decoloured on Dian HP 20 with a gradient H_2O/EtOH 1:0 → 0:1. The 70% EtOH eluate (170.0 g) was subjected to column chromatography (silica gel, $CHCl_3$/MeOH 95:5 → 25:75; RP-18, MeOH/H_2O 3:7 → 7:3), and resubmitted to column chromatography (silica gel, $CHCl_3$/MeOH 95:5 → 20:80) to afford compounds 1 (10 mg), 2 (9 mg), 3 (14 mg), 4 (19 mg), 5 (65 mg), 6 (8 mg), 7 (21 mg) and 8 (13 mg).

3.3.1 Acid hydrolysis. Compound 1 (5 mg) was dissolved in MeOH (1.0 ml) and 2 N HCl (1.0 ml), and hydrolysed by refluxing in a boiling water bath for 2 h. The hydrolysate was allowed to cool, diluted twofold with H_2O and neutralized by 0.5 N NaOH. The aglycone was extracted with $CHCl_3$ and purified on a silica gel column with solvent ($CHCl_3$/MeOH, 95:5) to give the aglycone 1a (1 mg). The aqua layer was evaporated to give a residue. A rhamnose was identified in the residue by paper chromatography (BuOH/AcOH/H_2O 5:1:5, upper layer) comparison with an authentic sample.

Table 1. ^{1}H NMR and ^{13}C NMR data (CD_3OD) of 1.

	δ (H)	*δ (C)*	*^{1}H–^{1}H COSY*	*HMBC (H → C)*
C(1)		129.7		
H–C(2)	6.99 (d, $J = 1.9$)	112.2	H-6	C-7, C-4, C-1
C(3)		149.2		
C(4)		148.3		
H–C(5)	6.83 (d, $J = 8.1$)	116.3	H-6	C-1, C-3
H–C(6)	6.87 (dd, $J = 1.9, 8.1$)	121.7	H-2, H-5	C-7, C-2, C-4
H–C(7)	4.83 (d, $J = 10$)	77.7	H-8	C-2, C-6, C-1
H–C(8)	4.00 (ddd, $J = 2.5, 4.8, 10.4$)	79.8	H-7, H-9	
CH_2(9)	3.37 (dd, $J = 13.9$)	62.2	H-8	
C(1′)		136.1		
H–C(2′)	6.74 (d, $J = 2.1$)	117.7	H-6′	C-7′, C-6′, C-3′, C-1′
C(3′)		145.1		
C(4′)		143.0		
H–C(5′)	6.86 (d, $J = 8.3$)	117.7	H-6′	C-1′, C-3′, C-4′
H–C(6′)	6.69 (dd, $J = 2.1, 8.3$)	122.4	H-5′, H-2′	C-7′, C-2′, C-4′
CH_2(7′)	2.60 (m)	32.4	H-8′	C-8′, C-9′, C-1′, C-2′
CH_2(8′)	1.85 (m)	32.6	H-7′, H-9′	C-7′, C-9′, C-1′
CH_2(9′)	3.36 (m), 3.66 (m)	67.7	H-8′	
H–C(1″)	4.63 (brs)	101.7	H-2″	C-9′, C-5″, C-3″
H–C(2″)	3.79 (m)	72.4	H-1″, H-3″	
H–C(3″)	3.66 (m)	72.6	H-2″, H-4″	
H–C(4″)	3.36 (m)	74.1	H-3″, H-5″	
H–C(5″)	3.55 (m)	69.8	H-4″, H-6″	
Me(6″)	1.23 (d, $J = 6.2$)	18.0	H-5″	
MeO–C(3)	3.86 (s)	56.6		C-3

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Table 2. ^{1}H NMR and ^{13}C NMR data (CD_3OD) of 2.

	δ (H)	*δ (C)*	*^{1}H–^{1}H COSY*	*HMBC (H → C)*
C(1)		128.6		
H–C (2, 6)	7.28 (d, $J = 8.6$)	127.9	H-3, H-5	C-3, C-4, C-5, C-7
H–C(3, 5)	7.06 (d, $J = 8.6$)	117.8	H-2, H-6	C-4
C(4)		158.7		
H–C(7)	5.49 (d, $J = 5.6$)	87.9	H-8	C-8, C-9, C-2, C-6
H–C(8)	3.39 (m)	55.2	H-7, H-9	C-1, C-3′, C-4′
CH_2(9)	3.83 (m)	65.3	H-8	C-7, C-8
C(1′)		135.7		
H–C(2′)	7.05 (d, $J = 1.6$)	125.9	H-6	C-3′, C-4′, C-6′
C-(3′)		137.7		
C-(4′)		159.4		
H–C(5′)	6.71 (d, $J = 8.1$)	109.8	H-6′	C-1′, C-4′
H–C(6′)	6.99 (dd, $J = 1.6$, 8.1)	129.7	H-2′, H-5′	C-2′, C-4′, C-7′
CH_2(7′)	2..61 (t, $J = 7.1$)	32.5	H-8′	C-1′, C-2′, C-6′, C-8′, C-9′
CH_2(8′)	1.79 (m)	35.9	H-7′, H-9′	C-1′, C-7′, C-9′
CH_2(9′)	3.55 (t, $J = 6.5$)	62.3	H-8′	C-7′, C-8′
H–C(1″)	4.88 (d, $J = 7.6$)	102.3	H-2″	C-4, C-3″
H–C(2″)	3.44 (t, $J = 3.7$)	74.9	H-1″	
H–C(3″)	3.39 (m)	78.0	H-2″, H-4″	
H–C(4″)	3.36 (m)	71.4	H-3″, H-5″	
H–C(5″)	3.42 (m)	78.1	H-4″, H-6″	
CH_2(6″)	3.85 (m)	62.5	H-5″	

3.3.2 Cupressoside A (1). White amorphous powder. $[\alpha]_D^{23.1}$ −22.8 (c 0.373, MeOH). IR: 3431, 2926, 1614, 1507, 1276, 1128, 1093, 1046. UV: 205, 226, 282. ^{1}H NMR and ^{13}C NMR: see table 1. FAB$^-$-MS: 491 ($[M - H]^-$). HR-FAB$^-$-MS: 491.1921 $[C_{25}H_{32}O_{10}\text{-}H]^-$ (calcd for $C_{25}H_{31}O_{10}$, 491.1927).

1a: $[\alpha]_D^{24.7}$ + 0.39 (c 0.502, MeOH). ^{1}H NMR (CD_3OD, 400 Hz): δ 1.79 (2H, m), 2.58 (2H, t, $J = 7.3$ Hz), 3.54 (2H, t, $J = 6.5$ Hz), 3.46 (1H, dd, $J = 4.6$, 12.3 Hz), 3.66 (1H, d, $J = 12.3$ Hz), 3.86 (3H, s), 4.00 (1H, $J = 2.0$, 3.6, 10.1 Hz), 4.86 (1H, d, $J = 9.3$ Hz), 6.69 (1H, d, $J = 8.2$, 1.9 Hz), 6.74 (1H, d, $J = 1.9$ Hz), 6.83 (1H, d, $J = 8.2$ Hz), 6.85 (1H, dd, $J = 8.2$ Hz), 6.89 (1H, dd, $J = 8.2$, 1.8 Hz), 6.99 (1H, d, $J = 1.8$ Hz).

3.3.3 Cupressoside B (2). White amorphous powder. $[\alpha]_D^{23.1}$ −7.35 (c 0.408, MeOH). IR: 3416, 2929, 2365, 1614, 1511, 1489, 1235, 1074. UV: 202, 223, 228. ^{1}H NMR and ^{13}C NMR: see table 2. CD (c 0.11 mg/ml, MeOH) Δε (nm): − 1.5 (238), + 1.2 (221). FAB$^+$-MS: 463 ($[M + 1]^+$). TOF$^+$-MS: 485.1789 $[C_{24}H_{30}O_9 + Na]^+$ (calcd for $C_{24}H_{30}O_9 + Na$, 485.1787).

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