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SESQUITERPENOID GLUCOSIDES FROM *LAGGERA PTERODONTA*

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Key Word Index—*Laggera pterodonta*; Compositae; sesquiterpenoid glucoside; eudesmane; pterodontoside A and B.

Abstract—Two new sesquiterpenoid glucosides were isolated from the whole plant of *Laggera pterondonta*, named pterodontoside A and B, characterized as 2α,4β-dihydroxy-11-(β-D-glucopyranosyloxy)-enantio-eudesmane and 1α,11-dihydroxy-4β-(β-D-glucopyranosyloxy) enantio-eudesmane, respectively. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Laggera pterodonta (DC.) Benth is a widely distributed in Yunnan, China. It is used as an antibacterial and anti-inflammatory herbal medicine in Yunnan Province. In previous papers [1–4], we reported the chemical constituents of *Laggera pterodonta* (DC.) Benth, from which eight new eudesmane type sesquiterpenoids (pterodondiol, pterodontriol A and B, pterodontetraol, pterodontic acid, 1β-hydroxy pterodontic acid, 3β-hydroxy pterodontic acid, 2α,3β-dihydroxy pterodontic acid and four known flavonoids) were isolated. As a continuation of this study, we now report the structures of two new sesquiterpenoid glucosides, named pterodontoside A and B from this plant.

RESULTS AND DISCUSSION

The metholic extract of the whole herb of *L. pterodonta* (DC.) Benth were fractionated by a series of solvent partitions to give three fractions. The *n*-BuOH part was chromatographed on silica gel and reversed phase silica gel column to afford two new compounds: pterodontoside A (**1**) and pterodontoside B (**2**) in yields of 0.0006 and 0.01%, respectively.

Pterodontoside A (**1**)

Pterodontoside A (**1**) was a white powder. The negative ion HRFAB-mass spectrum (*m*/*z*): 417.2505 $[M-H]^-$, indicated the molecular formula as $C_{21}H_{38}O_8$. Comparing the ^1H NMR and ^{13}C NMR spectra of **1** with those of pterodontriol A (**3**), a known enantio-eudesmane sesquiterpene, it showed clearly that **1** was a sesquiterpenoid. All of the carbon and proton signals of **1** were assigned by means of the ^1H–^1H correlated spectroscopy ^1H–^1H COSY and ^{13}C–^1H COSY spectra. From the ^{13}C NMR and ^1H NMR spectra of **1**, all of the carbon signals appeared at almost the same positions as those in the spectrum of **3**. In addition, six glucose carbon signals were apparent. Since the C-11 of **1** was shifted downfield to δ 81.5 and the C-12, C-13 were shifted upfield to δ 25.9 and 27.1, respectively (Table 1), it is suggested that the glucose was connected to C-11 of the aglycone. The ^1H NMR spectrum showed that the glucose was in the β-configuration. The structure of **1** was determined as 2α,4β-dihydroxy-11-(β-D-glucopyranosyloxy)-enantio-eudesmane and named pterodontoside A.

Pterodontoside B (**2**)

Pterodontoside B (**2**) was a white powder. The negative ion HRFAB-mass spectrum (*m*/*z*): 417.2479 $[M-H]^-$, indicated the molecular formula $C_{21}H_{38}O_8$. Inspection of the ^1H NMR and ^{13}C NMR spectral signals due to the sugar moieties indicated the presence of a β-D-glucosylmoiety in **2**. Comparison of the ^{13}C NMR spectrum of **2** with that of a known compound, pterodontriol B (**4**) revealed that there was only the signals of C-4 and C-15 differing from each other, which indicated a glycosylation shift at C-4 and C-15 thus suggesting

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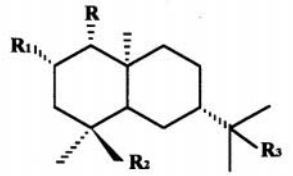

		R	R_1	R_2	R_3
(1) Pterodontoside	A	H	OH	OH	Glu
(2) Pterodontnside	B	OH	H	Glu	OH
(3) Pterodontriol	A	H	OH	OH	OH
(4) Pterodontriol	B	OH	H	OH	OH

that the glucose was linked with C-4 of the aglycone. Therefore, the structure of **2** was determined as 1α,11-dihydroxy-4β-(β-D-glucopyranosyloxy)-enantio-eudesmane and named pterodontoside B.

Table 1. ^{13}C NMR spectral data for compounds **1–4** (100.6 MHz, pyridine-d_5)

C	1	2	3	4
1	52.7	79.4	52.7	80.1
2	65.3	29.4	65.7	30.1
3	54.3	39.1	54.4	39.0
4	72.7	79.3	72.4	71.7
5	48.1	47.0	49.4	48.2
6	21.8	21.6	21.7	21.8
7	42.5	42.5	43.1	42.8
8	21.6	21.6	21.8	21.9
9	42.7	42.6	42.8	42.4
10	34.3	39.5	34.4	39.6
11	81.5	73.7	73.8	74.0
12	25.9	29.5	29.7	29.8
13	27.1	30.3	30.6	30.4
14	20.5	14.6	20.5	14.4
15	23.9	19.6	24.0	23.1
1′	98.7	98.0		
2′	75.7	75.6		
3′	77.8	77.7		
4′	72.1	71.8		
5′	78.9	78.8		
6′	63.1	62.7		

EXPERIMENTAL

Optical rotations were measured on a Horiba SEAP-300 spectropolarimeter (in MeOH). IR spectra were taken for KBr discs with a Perkin-Elmer IR-577 infrared spectrophotometer. ^1H, ^{13}C and 2D NMR spectra were measured in pyridine-d_5 with Brucker-400 MHz instrument using TMS as int. standard. FAB-MS spectra were recorded with a VG AUTOSPEC-3000 spectrometer.

Plant material *Laggera pterodonta* (DC.) Benth was collected at Mang-shi city, Yunnan province of China in October, 1990 and identified by Professor Z. W. Lin. A voucher specimen (No. 901068CLD) is deposited in the Laboratory of Phytochemistry, Kunming Institute of Botany.

Extraction and purification

Dried whole herb (5.9 kg) of *Laggera pterodonta* (DC.) Benth was extracted 4× with hot MeOH under reflux conditions. The combined extracts were evaporated *in vacuo*. The residue (550 g) was suspended in H_2O, extracted with petrol, EtOAc and *n*-BuOH, respectively. The *n*-BuOH part was concd. to afford a residue (110 g). The residue was repeatedly chromatographed on columns of silica gel H and RP-8, to give **1** (35 mg) and **2** (590 mg).

Pterodontoside A (**1**)

Pterodontoside A (**1**), a white powder, $[\alpha]_D^{16}$ −3.54 (*c* 0.42, MeOH); $C_{21}H_{38}O_8$ (HRFAB-MS *m/z* $[M-H]^-$: found 417.2505, calc. 417.2488). IR ν_{max}^{KBr} cm^{-1}: 3360 (*br.*), 2908, 1632, 1450, 1370, 1150, 1070, 1022, 905: ^1H NMR data (δ): aglycone: 4.20 (1H, *m*, H-2β), 2.63 (1H, *d*, *J* = 10.2 Hz, H-6α), 2.53 (1H, *br*, *d*, *J* = 14.4 Hz, H-7β), 2.31 (1H, *dd*, *J* = 2.1, 10.2 Hz, H-5β), 2.12 (2H, *m*, H-3), 2.00 (1H, *m*, H-8β), 1.86 (2H, *m*, H-1), 1.71 (1H, *m*, H-8α), 1.54 (3H, *s*, H-12), 1.48 (2H, *m*, H-9), 1.46 (3H, *s*, H-13), 1.33 (3H, *s*, H-15), 0.97 (3H, *s*, H-14); Glu: 4.96 (1H, *d*, *J* = 7.64 Hz, H-1), 4.44 (1H, *dd*, *J* = 2.12, 11.40 Hz, H-5), 4.21 (2H, *t*, *J* = 8.96 Hz, H-6), 4.08 (1H, *t*, *J* = 9.04 Hz, H-3), 3.95 (1H, *t*, *J* = 7.72 Hz, H-2), 3.85 (1H, *m*, *J* = 2.88 Hz, H-4); ^{13}C NMR data see Table 1.

Pterodontoside B (**2**)

Pterodontoside B (**2**), white powder, $[\alpha]_D^{16}$: +11.11 (*c* 0.45, MeOH). $C_{21}H_{38}O_8$, (negative ion HRFAB-MS *m/z*: found: 417.2479, calc.: 417.2488); IR ν_{max}^{KBr} cm^{-1}: 3360 (*br.*), 2912, 1640, 1450, 1375, 1071, 1018, 872; ^1H NMR data (δ): aglycone: 3.57 (1H, *m*, H-1β), 2.61 (1H, *dd*, *J* = 3.6, 12.5 Hz, H-6α), 2.39 (1H, *dd*, *J* = 3.6, 12.5 Hz, H-5β), 2.18 (1H, *m*, H-3α), 2.03 (1H, *m*, H-3β), 2.00 (2H, *m*, H-8), 1.98 (2H, *m*, H-9), 1.83 (3H, *m*, H_2-2, 7β), 1.65 (1H, *m*, H-6β), 1.49 (3H, *s*, H-15), 1.43 (6H, *s*, H-12, 13), 1.20 (3H, *s*, H-4); Glu: 5.02 (1H, *d*, *J* = 7.56 Hz, H-1), 4.41 (1H, *dd*, *J* = 2.40, 9.60 Hz, H-5), 4.16 (2H, *t*, *J* = 7.40 Hz, H-6), 4.10 (1H, *t*, *J* = 8.84 Hz, H-3), 3.92 (1H, *t*, *J* = 8.08 Hz, H-2), 3.85 (1H, *m*, *J* = 2.92, H-4); ^{13}C NMR see Table 1.

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