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Two New Isobutyltartrate Monoesters from *Coeloglossum viride* (L.) Hartm. var. *bracteatum* (Willd.) Richter

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Abstract: Two new isobutyltartrate monoesters, coelovirin A (**1**) and B (**2**), were isolated from the rhizomes of *Coeloglossum viride* (L.) Hartm. var. *bracteatum* (Willd.) Richter (Orchidaceae). Their structures were elucidated as (2*R*, 3*S*)-2-isobutyltartrate–1-(4-β-D-glucopyranosyloxybenzyl) ester **1** and (2*R*, 3*S*)-2-isobutyltartrate–4-(4-β-D-glucopyranosyloxybenzyl) ester **2** on the basis of physical constants and spectroscopic methods including 2D NMR techniques.

Keywords: *Coeloglossum viride* (L.) Hartm. var. *bracteatum* (Willd.) Richter, Orchidaceae, isobutyltartrate monoester, coelovirin A and B.

Coeloglossum viride (L.) Hartm. var. *bracteatum* (Willd.) Richter is a plant of the Orchidaceae family, distributed in the Xinjiang, Inner Mongolia, Gansu and Qinghai provinces of China[1]. Its dried rhizomes have been used as a tonic in chinese folk medicine[2]. No chemical constituent is reported from this plant. The present paper deals with the isolation and structural elucidation of two new isobutyltartrate monoesters, named coelovirin A **1** and B **2**.

The ethanolic extract of the air-dried and ground rhizomes of *Coeloglossum viride* (L.) Hartm. var. *bracteatum* (Willd.) Richter was subjected to column chromatography on normal and reversed phase silica gel successively, and further purified by reversed phase HPLC to yield compounds **1** and **2**.

Compound **1**, white amorphous powder, $[\alpha]_D^{25}$ -27.8 (*c* 0.12, MeOH), UVλ_{max} (MeOH) nm (log ε): 229 (3.10), 270 (2.93), 277 (2.85). Its IR spectrum showed a strong broad absorption band for hydroxyl groups (3425 cm^{-1}), characteristic bands for carbonyl group (1732 cm^{-1}), aromatic ring (1614, 1514, 829 cm^{-1}) and gem-dimethyl groups (1386, 1369 cm^{-1}). The negative FABMS spectrum of **1** exhibited a quasi-molecular ion peak at *m/z* 473 $[M-H]^-$. The molecular formula of **1** was determined as $C_{21}H_{30}O_{12}$ by negative HRFABMS at *m/z* 473.1667 $[M-H]^-$ (calcd. for $C_{21}H_{29}O_{12}$ 473.1659). The ^1H NMR spectrum showed the presence of an isobutyl group at δ 0.72 and 0.87 (d, each 3H, *J* = 6.5 Hz, $_3$-7 and H_3-8), 1.59 (m, 1H, H-6), 1.65 (dd, 1H,

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J = 14.0, 6.0 Hz, H_A-5) and 1.83 (dd, 1H, *J* = 14.0, 6.5 Hz, H_B-5) and a para-substituted benzyloxyl moiety at δ 7.03 and 7.28 (br d, each 2H, *J* = 8.5 Hz, H-3′,5′ and H-2′,6′), 5.03 and 5.08 (d, each 1H, *J* = 12.0 Hz, H_A-7′ and H_B-7′). In addition, the ^{1}H NMR data (**Table 1**) indicated that there is a sugar unit with a β configuration at the anomeric carbon and an isolated proton singlet geminal to an oxygen at δ 4.24. The ^{1}H-^{1}H COSY spectrum confirmed the above conclusions. The ^{13}C NMR and DEPT spectra revealed the presence of five quaternary carbons in compound **1,** including a pair of carbonyl carbons at δ 174.9 (C-1) and δ 174.5 (C-4), two aromatic carbons at δ 130.8 (C-1′) and δ 159.3 (C-4′) and an oxygenated aliphatic carbon at δ 80.8 (C-2). The protonated carbon signals (**Table 1**) were assigned by HMQC experiment. The chemical shifts and coupling patterns of proton and carbon signals for the sugar moiety were in good agreement with those found in gastrodin[3], indicating that the sugar unit is a β-D-glucopyranosyl group. In the HMBC spectrum two- and three-bond correlations from H-3 to C-1, C-2, C-4 and C-5, and correlations from both H_A-5 and H_B-5 to C-1, C-2, C-3, C-6, C-7 and C-8 (**Figure 1**) established the structural residue of 2-isobutyltartrate in compound **1**. Furthermore, the correlations from two geminal protons H_A-7′ and H_B-7′ to C-1, C-1′,C-2′ and C-6′ established the para-substituted benzyloxyl moiety which is esterified at C-1 of the 2-isobutyltartrate residue, while the correlations from the anomeric proton of the glucose moiety to C-4′ unambiguously indicated that the glucoside position is at C-4′ of para-substituted benzyloxyl moiety in the structure of **1**. By comparison of the optical specific rotation of **1** with those of related compounds in literatures[4, 5], the absolute configurations at C-2 and C-3 were assigned to be (2*R*, 3*S*). Thus, the structure of **1** was determined as (2*R*, 3*S*)-2-isobutyltartrate–1-(4-β-D-glucopyranosyloxybenzyl) ester, named coelovirin A.

Compound **2**, white amorphous powder, $[\alpha]_D^{25}$ –23.6 (*c* 0.14, MeOH), UVλ_{max} (MeOH) nm (logε): 222 (3.01), 270 (2.87), 276 (2.79); IR (KBr) cm^{-1}: 3425, 1734, 1614, 1514, 1387, 1369, 1234, 1076, 831. The positive ESIMS spectrum of **2** exhibited a quasi-molecular ion peak at *m/z*: 497 $[M+Na]^+$. The molecular formula of **2** was established as $C_{21}H_{30}O_{12}$ by HRESIMS at *m/z*: 497.1641 (calcd. for $C_{21}H_{30}O_{12}Na$ 497.1637). The ^{1}H, ^{13}C NMR and DEPT spectral data (**Table 1**) were similar to those of **1**, except for the carbonyl signals of C-1 and C-4 which were shifted from δ 174.9 and 174.5 in **1** to δ 176.7 and 172.8 in **2**, respectively. These observations indicated that the

Figure 1 Key HMBC Correlations of **1**

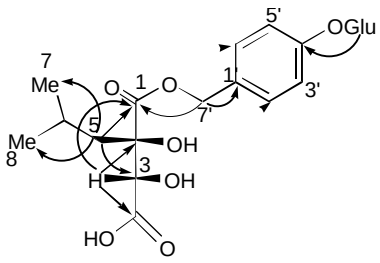

Figure 2 Key HMBC Correlations of **2**

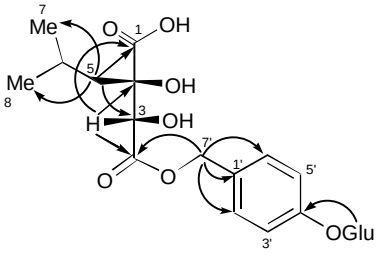

Table 1 NMR Data for compound **1** and **2**

No.	**1**		**2**	
	δ_H [a]	δ_C [b]	δ_H [a]	δ_c [b]
1		174.9 s		176.7 s
2		80.8 s		80.8 s
3	4.24 s	77.3 d	4.34 s	77.5 d
4		174.5 s		172.8 s
5	1.65 dd (14.0, 6.0) 1.83 dd (14.0, 6.5)	45.2 t	1.66 dd (13.5, 5.0) 1.82 dd (13.5, 5.5)	45.0 t
6	1.59 m	25.2 d	1.70 m	25.3 d
7	0.72 d (6.5)	24.0 q	0.83 d (6.5)	24.1 q
8	0.87 d (6.5)	24.6 q	0.90 d (6.5)	24.6 q
Benzyl moiety				
1′		130.8 s		130.8 s
2′.6′	7.28 d (8.5)	131.3 d	7.27 d (9.0)	131.0 d
3′.5′	7.03 d (8.5)	117.7 d	7.02 d (9.0)	117.6 d
4′		159.3 s		159.1 s
7′	5.03 d (12.0) 5.08 d (12.0)	68.0 t	4.98 d (12.0) 5.10 d (12.0)	67.8 t
Glucosyl moiety				
1	4.85 d (7.5)	102.3 d	4.84 d (7.5)	102.2 d
2	3.39 m	74.9 d	3.40 m	74.9 d
3	3.38 m	78.0 d	3.38 m	77.5 d
4	3.36 m	71.4 d	3.37 m	71.4 d
5	3.34 m	78.2 d	3.35 m	78.2 d
6	3.64 dd (12.0, 5.5) 3.83 dd (12.0, 2.0)	62.5 t	3.64 dd (12.0, 5.5) 3.83 dd (12.0, 2.0)	62.5 t

[a]Measured at 500 MHz in CD_3OD. Coupling constants (J) in Hz are given in parentheses. The assignments were based on ^1H-^1H COSY, HMQC and HMBC. [b]Measured at 125 MHz in CD_3OD. The assignments were based on DEPT, HMQC and HMBC.

4-β-D-glucopyranosyloxybenzyloxyl moiety is esterified at C-4 of the 2-isobutyltartrate residue in the molecule of **2**, this was further confirmed by correlations from two geminal protons at δ 4.98 and 5.10 (H_A-7′ and H_B-7′) to C-4, C-1′, C-2′ and C-6′ in the HMBC spectrum of **2** (**Figure 2**). Accordingly, the structure of **2** was determined as (2*R*, 3*S*)-2-isobutyltartrate–4-(4-β-D-glucopyranosyloxybenzyl) ester, named coelovirin B.

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