

A New Triterpene from the Orchid *Pholidota yunnanensis*

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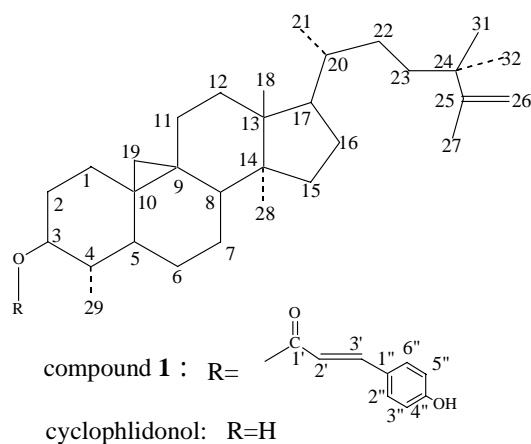
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Abstract: A new triterpene, 25-methylenecyclopholidonolyl *p*-hydroxy-*trans*-cinnamate, was isolated from a orchid *Pholidota yunnanensis*. The structure elucidation and ^1H , ^{13}C -NMR assignments were achieved by spectral and chemical method.

Keywords: Orchidaceae, *Pholidota yunnanensis*, 25-methylenecyclopholidonolyl *p*-hydroxy- *trans*-cinnamate.

Pholidota yunnanensis Rolfe (Orchidaceae), called “ShiXianTao” in China is a perennial herb distributed in Guangxi, Sichuan and Yunnan provinces. Systematic chemical investigations of a series of Chinese medicinal orchids in our department led to the isolation of several phenanthrenes, bibenzyl derivatives, anthraquinone and steroids¹⁻⁴, in this paper, we report the isolation of a new triterpene from *Pholidota yunnanensis*. The structure of the new compound **1** was established as 25-methylenecyclopholidonolyl *p*-hydroxy-*trans*-cinnamate (**Figure 1**) by the spectral and chemical evidences.

Figure 1 The structure of compound **1** and related compounds



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Table 1 ^{13}C -NMR spectra data of compound **1** and related compounds (CDCl_3 , δppm)

Positio	Compound 1	Cvclophlidonol	Compound 1a
1	31.1	30.8	30.8
2	35.1	34.8	34.8
3	78.7	76.6	76.6
4	41.7	44.6	44.6
5	43.5	43.4	43.3
6	24.7	24.7	24.7
7	28.1	28.1	28.1
8	46.9	46.8	46.9
9	23.7	23.6	23.6
10	29.4	29.7	29.5
11	25.1	25.1	25.2
12	35.4	35.4	35.4
13	45.3	45.3	45.3
14	48.9	48.9	48.9
15	32.8	32.8	32.8
16	27.3	27.2	27.2
17	52.1	52.1	52.1
18	17.8	17.7	17.7
19	27.0	27.0	27.0
20	36.6	36.6	36.6
21	18.5	18.5	18.5
22	30.8	30.8	30.8
23	37.4	37.4	37.4
24	38.7	38.7	38.7
25	152.4	152.3	152.4
26	109.3	109.3	109.3
27	19.4	19.4	19.4
28	19.1	19.2	19.1
29	14.5	14.4	14.4
30			
31	27.2	27.2	27.2
32	27.5	27.5	27.5
1'	167.2		
2'	116.4		
3'	144.0		
1''	127.5		
2'',6''	129.9		
3'',5''	115.8		
4''	157.4		

The 95% EtOH extract of *P. yunnanensis* was partitioned with petroleum ether and acetone, successively. The petroleum ether fraction was further fractionated on silica gel column chromatography to afford the compound **1**. Compound **1** was isolated as colourless needles, mp 197~198°C, $[\alpha]_D^{20} +46.2$ (*c* 0.20, CHCl_3), [APCI-MS $[\text{M}+\text{H}]^+$ at m/z 587] (calcd. for $\text{C}_{40}\text{H}_{58}\text{O}_3$ 586.89), EI-MS m/z 422 $[\text{M}-\text{C}_9\text{H}_8\text{O}_3]^+$ corresponding to the fragment of loss of *p*-hydroxycinnamic acid. The presence of *p*-hydroxycinnamate

moiety was supported by its UV [λ_{\max} (MeOH): 200, 226(sh) and 312 nm], IR(KBr, cm^{-1}) [ν 3414(OH), 1710(conjugated C=O), 980(*trans*-CH=CH-) and 830(1,4 disubstituted benzene) cm^{-1}] and $^1\text{H-NMR}$ (CDCl_3 , δ ppm) [7.62 and 6.31(d, each 1H, $J=15.7\text{Hz}$; *trans*-olefinic protons), 7.43 and 6.84(d, each 2H, $J=8.5\text{Hz}$; four aromatic protons of the *p*-disubstituted benzene moiety) and 5.25(s, 1H, disappeared on deuterium exchange; phenolic OH)].

The $^1\text{H-NMR}$ spectrum of **1** also displayed signals for a methine proton (δ 4.65, m, 1H) linked to the carbon atom bearing the above ester function, two methylene protons (δ 0.43 and 0.17, d, each 1H, $J=4.0\text{Hz}$) of a cyclopropane similar to those presented in cycloartenol and related compounds⁵⁻⁷, two terminal olefinic methylene protons (δ 4.66 and 4.72, d, each 1H, $J=1.0\text{Hz}$) and seven C-methyls [δ 1.69, 1.02($2\times\text{CH}_3$), 0.96, 0.90, 0.88, 0.87].

The $^{13}\text{C-NMR}$ data of compound **1** indicated that the two fragments are connected in a manner as expressed in **Figure 1**. The degree of protonation of each carbon atom was determined by DEPT experiments, and the carbon chemical shifts were assigned by comparison with the δ_{c} values of structurally related compounds⁵⁻⁷. The HMBC spectrum showed that the signal at $\delta_{\text{c}}78.7$ (C-3) was correlated with the signal at $\delta_{\text{H}}0.88$ (H-29), $\delta_{\text{c}}152.4$ (C-25) was correlated with the signals at $\delta_{\text{H}}1.69$ (H-27) and 1.02 (H-31, H-32). The structure of **1** was further confirmed by alkaline hydrolysis to compound **1a**. The EI-MS of **1a**, is at m/z 440 $[\text{M}]^+$, mp 169~171°C. The physical constants and spectral data of **1a** were coincident with those of cyclopholidonol⁵. In conclusion, the structure of compound **1** was determined to be 25-methylenecyclopholidonol *p*-hydroxy-*trans*-cinnamate. $^{13}\text{C-NMR}$ spectral data of compound **1** and related compounds are listed in **Table 1**.

Acknowledgments

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