

A Novel Diterpenoid, 11-O- β -D-glucopyranosylneo-triptophenolide, from *Tripterygium wilfordii* Hook. f

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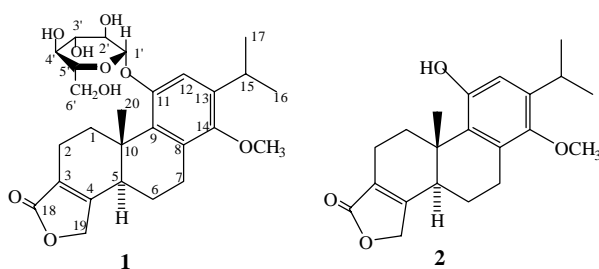
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Abstract: A new diterpenoid was isolated from the ethanolic extract of the dried root bark of *Tripterygium wilfordii* Hook.f. It is the first example of abietane diterpenoid glycoside isolated from *Tripterygium wilfordii* Hook.f. Its structure was identified to be 11-O- β -D-glucopyranosyl-neotriptophenolide based on spectral methods.

Keywords: *Tripterygium wilfordii* Hook.f (family Celastraceae), abietane diterpenoid, neotriptophenolide, 11-O- β -D-glucopyranosyl-neotriptophenolide.

Tripterygium wilfordii Hook. f has been used as Chinese folk medicine for its anti-inflammatory property. Up to now, *Tripterygium wilfordii* Hook. f and its preparation used for treatment of rheumatoid arthritis and some skin diseases, have attracted more and more

Figure 1 The structure of **1** and **2**



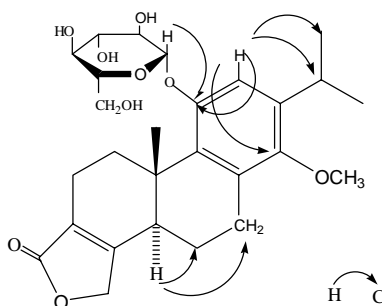
attention in the medical field¹. Pharmacological experiments revealed that they have intensive anti-inflammatory, immunosuppressive, anti-malefertility and anti-tumor properties. In our previous papers^{2,3,4,5}, we reported four new diterpenoids, three new triterpenoids and ten known triterpenoids isolated from this plant. The present paper describes the isolation and structural elucidation of another new diterpenoid glycoside.

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The ethanolic extract of the dried root bark of *Tripterygium wilfordii* Hook. f was fractionated by column chromatography on silica gel and reverse phase silica gel RP-18 successively. Further purification of the compound was achieved by rechromatography on silica gel.

Compound **1** was isolated as yellow oil, $[\alpha]_D^{20} +22$ (c=1.05, CHCl₃). According to its EIMS (m/z 504 [M⁺]), ¹H-NMR and ¹³C-NMR spectral data, its molecular formula was deduced to be C₂₇H₃₆O₉, which was further confirmed by its ESIMS (m/z 527.5 [M+Na]⁺). Its IR spectral data revealed the presence of α,β -unsaturated five-membered lactone (1735,1670 cm⁻¹) and aromatic ring (1466 cm⁻¹), which was further confirmed by ¹³C-NMR (δ =110.7,130.6,131.7,139.6,150.3,152.5) and ¹H-NMR data (δ =7.26, s, 1H), it can be concluded that the aromatic ring was a five-substituted ring. The ¹³C-NMR and DEPT spectra exhibited signals of four methyl, six methylene, eight methine and nine quaternary carbons. Its ¹H-NMR spectrum showed the presence of an isopropyl group at δ 3.22 (m, 1H, J=7 Hz) and δ 1.15(d, 6H, J=7Hz), a methoxy group at δ 3.65(s, 3H) and the presence of a methylene group at δ 4.78, 4.66 (ABq, 2H, J=17.4 Hz). Moreover, the main structural fragments, -CH₂-CH₂- and -CH-CH₂-CH₂-, were obtained from the study of its ¹H-¹H COSY spectrum. All of the above spectral data suggested that this compound was an abietane diterpenoid with an aromatic C-ring which was the typical compound isolated from *Tripterygium wilfordii* Hook. f. In addition, comparison of the ¹³C NMR spectra between compound **1** and the known compound **2** — neotriptophenolide⁶ isolated from the same plant previously, showed that

Figure 2 The HMBC correlations of **1**



the signals of **1** were in agreement with those of **2** except for extra signals of glucose unit. In ¹³C-NMR spectra, the signal of anomeric carbon atom(C-1') is at δ 100.4 ppm, and other carbon signals in the glucose unit are at δ 61.7, 69.8, 73.6, 75.7, 77.0 ppm respectively, and the signals of protons in the glucose unit are at 3.46 (1H), 3.66 (3H), 3.76 (1H), and 5.01 (1H) respectively. The peaks at m/z 504 [M]⁺ and 342 [M-162 (C₆H₁₀O₅)]⁺ in EIMS spectrum confirmed the conclusion.

To determine the position of the glucose unit, its HMBC spectrum was studied. In the HMBC spectrum, the correlation of H-1' with C-11 (δ =152 ppm) pointed that the glucose unit is linked with hydroxyl group at C-11. In the ¹H-NMR spectrum, the signal of H-1' was observed to be doublet, and the coupling constant value (J =7.9 Hz) of the signal of H-1' revealed the linkage of glucose unit with the hydroxyl group of C-11

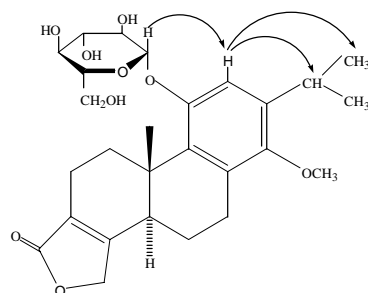
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is β -linkage. In addition, in the NOESY spectrum, the cross peak between H-12 with H-15, H-16, and H-17 proved the positions of all the substituted groups at the aromatic ring. The assignments of all the protons and carbons in compound **1** were made by means of $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, $^1\text{H-}^1\text{H COSY}$, HMBC and HMQC. Thus, the above evidence led to establish the structure of compound **1** as 11-O- β -D-glucopyranosyl-neo-triptophenolide. To our best knowledge, this compound is the first example of abietane diterpenoid glycoside isolated from *Tripterygium wilfordii* Hook. f. Moreover, natural abietane diterpenoids which are linked to a glucose unit. The diterpenoids with such a structure are seldom reported.

Table 1 $^1\text{H NMR}$ (400M Hz), $^{13}\text{C NMR}$ (100M Hz) and DEPT data of **1**
(CDCl₃, TMS, δ ppm)

No	δ_{H}	δ_{C}	DEPT
1	1.26(m), 3.65 (m)	31.39	CH ₂
2	2.33(m), 2.32 (m)	18.65	CH ₂
3	/	125.08	C
4	/	164.33	C
5	2.69(br, d)	44.23	CH
6	1.43(m), 1.26 (m)	19.34	CH ₂
7	3.03(m), 3.02 (m)	25.50	CH ₂
8	/	131.74	C
9	/	130.66	C
10	/	37.40	C
11	/	152.48	C
12	6.80 (s)	110.73	CH
13	/	139.57	C
14	/	150.30	C
15	3.22 (m)	26.28	CH
16	1.15 (d, J=7.1Hz)	23.88	CH ₃
17	1.14 (d, J=7.1Hz)	23.60	CH ₃
18	/	175.37	C
19	4.78, 4.66 (ABq, J=17.4Hz)	71.06	CH ₂
20	1.10 (s)	17.69	CH ₃

Figure 3 The NOE of **1**



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