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A New Triterpenoid Glycoside from *Decaisnea Fargesii*

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Abstract: A new triterpenoid glycoside, named decaisoside F, has been isolated from *Decaisnea fargesii.* Its structure was determined on basis of chemical method, FAB-MS, homonuclear and heteronuclear correlation experiments, including ^{1}H—^{1}H COSY, ^{1}H—^{13}C COSY, TOSCY, HMBC and NOESY techniques to be 3-O-β-D- xylopyranosyl (1→3)-α-L-rhamnopyranosyl (1→2)-α-L-arabinopyranosyl hederagenin 28-O-β-D-xylopyranosyl (1→4)-β-D-glucopyranosyl (1→6)-β-D-glucopyranoside.

Keywords: *Decaisnea fargesii*; triterpenoid glycoside; decaisoside F; 2D-NMR.

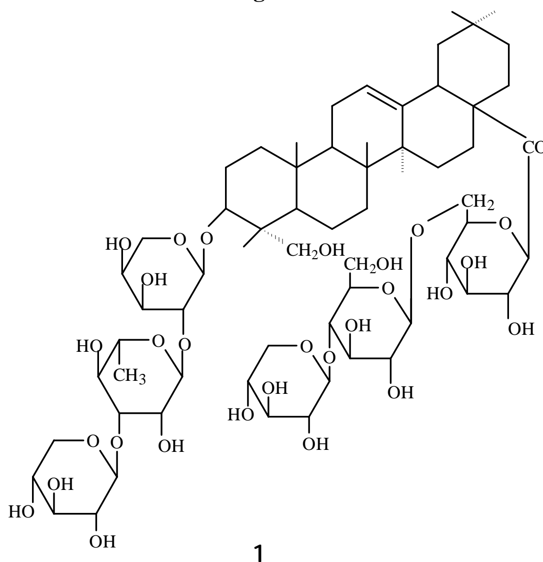
Decaisnea fargesii Franch. is a traditional Chinese medicinal plant widely distributed in China, used as an anti-rheumatic and antitussive drug for a long time in Chinese folk medicine[1]. Its methanol extract showed antitumour acidity *in vivo* against S_{180}, Hepa and Ehrlich cells and its phytochemical studies on saponins has reported[2]. As a continuation of the studies on this plant, we present the spectral and chemical evidence of the structure of a new decaisoside F.

The dried stems (2.23 kg) were percolated with 95% EtOH. After removal of the percolates by evaporators, the residue (380 g) was subjected to macto-porous absorption resin D-101 eluting with aq. MeOH gradiently. The 80% MeOH eluate was concentrated to dryness to give a crude glycoside fraction. This fraction was separated by chromatography (silica gel column and RP-8 column), to afford decaisoside F (860 mg).

Decaisoside F **1**, White powder from MeOH, mp. 227-230 °C (dec.), $[\alpha]_D^{23} -18.9$ (MeOH, c 0.009). It responded positively to the Liebermann Burchard test[3]. Its IR spectra showed ester group aborptions (1730-1740 cm^{-1}) together with hydroxyl absorptions (3400-3420 cm^{-1}), and C=C double bond absorptions (1640-1650 cm^{-1}). Its molecular formula was deduced as $C_{63}H_{102}O_{29}$ by means of ^{13}CNMR, DEPT spectrum and the negative FAB-MS. On acid hydrolysis on TLC[4], **1** yielded rhamnose, arabinose, glucose and xylose. On acid hydrolysis with 0.2 mol/L HCI in 60% EtOH, **1** afforded hederagenin and prosapogenin **2**. Compound **2** was determined to be hederagenin 3-O-β-D-xylopyranosyl (1→3)-α-L-rhamnopyranosyl (1→2)-α-L- arabinopyranoside based on the comparison of ^{1}H, ^{13}CNMR and FAB-MA as well as the result of monosaccharide

analysis. The structure of **2** is identical with saponin PG from *Akebia quinata*[5]. The ^{13}C NMR and CH-COSY spectra of compound **1** showed the presence of six anomeric carbon signals (δ = 95.6, 101.2, 104.5, 104.9, 105.0, 107.5 ppm), and six anomeric proton signals (δ = 6.19, 6.28, 5.03, 4.92, 5.30, 5.29 ppm) by direct correlation peaks. On comparison of the ^{13}C NMR spectrum of compound **1** with that of hederagenin, the glycosylation shifts[6], were observed for C-2, C-3, C-23 and C-28 (δ = 26.3, 80.0, 64.0, 176.5 ppm). The signals of anomeric carbon (δ = 95.6 ppm) and C-28 (δ = 176.5 ppm) all indicated that **1** was a 28-O-glycosidic linkage. The simultaneous presence of a 3-O-glycosidic linkage was easily seen by the attendant downfield shift (δ = 80.0 ppm) for C-3. This information showed that **1** was a 3, 28-di-glycoside of hederagenin[7]. The assignment was supported by data from the HMBC spectrum in which the anomeric proton (δ = 5.03 ppm) showed cross-peak to C-3 (δ = 80.0 ppm), and anomeric proton (δ = 6.19 ppm) showed cross-peak to C-28 (δ = 176.5 ppm).

Figure 1.



In the negative FAB-MS of **1**, besides the quasimolecular ion peak, fragment ion peaks at m/z 1337 $[M-H]^-$, 1205 $[M-Xyl-H]^-$, 881 $[M-2Glc-Xyl-H]^-$,749 $[M-2Glc-2Xyl-H]^-$ were observed. The HMBC spectrum gives the correlation peaks of the terminal xylose H-1 (δ = 5.03 ppm) to the inner glucose C-4 (δ = 80.7 ppm) and the inner glucose H-1 (δ = 4.92 ppm) to inner-28-O-glucose C-6 (δ = 69.5 ppm); the terminal xylose H-1 (δ = 5.29 ppm) to the rhamnose C-3 (δ = 82.8 ppm) and the rhamnose H-1 (δ = 6.28 ppm) to arabinose C-2 (δ = 74.4 ppm). The other proton and carbon resonance in the middle of rings were identified by the correlation with anomeric, methylene and methyl protons using COSY, TOCSY, CH-COSY and NOESY spectra (see **Table 1** and **2**). Thus, the structure of **1** was established to be 3-O-β-D-xylopyranosyl (1→3)-α-L-rhamnopyranosyl (1→2)-α-L-arabinopyranosyl hederagenin 28-O-β-D-xylopyranosyl (1→4)-β-D-glucopyranosyl (1→6)-β-D-glucopyranoside.

Table 1 ^{13}CNMR data for the triterpene moiety of decaisoside F in pyridine-d_5 (δ ppm)

C		H	C		H
1	39.0	1.03α, 1.50β	16	23.8	1.87α, 1.98β
2	26.3	1.98α, 2.17β	17	47.0	
3	80.0	4.22α	18	41.6	3.13
4	43.5		19	46.2	1.15α, 1.64β
5	48.1	1.72α	20	30.7	
6	18.1	1.65a, 1.65b	21	33.9	1.06α, 1.23β
7	32.5	1.69α, 1.82β	22	32.7	1.21α, 1.55β
8	38.9		23	64.0	3.86α, 4.24β
9	47.6	1.72α	24	14.1	1.10
10	36.8		25	16.1	0.94
11	23.3	1.87a, 1.87b	26	17.5	1.07
12	122.9	5.37	27	26.0	1.15
13	144.1		28	176.5	
14	42.1		29	33.0	0.82
15	28.8	1.06α, 2.24β	30	23.6	0.83

Table 2. ^{1}HNMR and ^{13}CNMR data for the saccharides of decaisoside F in pyridine-d_5 (δ ppm)

Residue		C	H	
α-ara p	1	104.5	5.03	(d, J=5.5Hz)
	2	74.7	4.52	
	3	75.5	4.00	
	4	69.5	4.06	
	5	66.0	3.68α, 4.18β	
α-rha p	1	101.2	6.28	(s)
	2	71.9	4.86	
	3	82.8	4.72	
	4	72.9	4.42	
	5	69.5	4.66	
	6	18.3	1.55	
β-xyl p	1	107.5	5.29	(d, J=7.5Hz)
	2	74.9	3.94	
	3	78.2	4.07	
	4	70.9	4.19	
	5	67.2	3.68α, 4.16β	
β-glc p	1	95.6	6.19	(d, J=8.5Hz)
	2	73.8	4.08	
	3	76.2	4.15	
	4	70.7	4.32	
	5	77.7	4.05	
	6	69.5	4.08α, 4.26β	
β-glc p	1	104.9	4.92	(d, J=7.5Hz)
	2	74.9	3.98	
	3	76.1	4.15	
	4	80.7	4.20	
	5	76.4	3.76	
	6	61.6	4.35α, 4.45β	
β-xyl p	1	105.0	5.30	(d, J=8.0Hz)
	2	74.8	3.94	
	3	78.0	4.08	
	4	70.8	4.12	
	5	67.2	3.61α, 4.17β	

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