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Chemical Components of *Helicia nilagirica* Beed. I. Structure of Three New Flavonol Glycosides

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Abstract: Three new flavonol glycosides were isolated from the leaves of *Helicia nilagirica* Beed.. The structures were elucidated as kaempferol-3-O-β-D-xylopyranosyl-(1→6)-β-D-glycopyranosyl-(1→2)-α-L-rhamnopyranoside, quercetin-3-O-β-D-xylopyranosyl-(1→6)-β-D-glycopyranosyl-(1→2)-[-β-D-xylopyranosyl-(1→4)]-α-L-rhamnopyranoside, and quercetin-3-O-β-D-xylopyranosyl-(1→6)-β-D-glycopyranosyl-(1→2)-α-L-rhamnopyranoside, named as Helicianeoside A、B and C, respectively.

Keywords: *Helicia nilagirica* Beed., Proteaceae, flavonol glycosides.

Helicia nilagirica Beed. belongs to the plant of Proteaceae family. The seeds of the plant is for treatment of insomnia and neurasthenia in Jingpo nationality in Yunnan Province[1]. Helicid and helicidol were isolated from the seeds of the plant[2,3], and the helicid was recorded in the Yunnan Pharmacopoea at the 1987 edition. The chemical constituents of the leaves of this plant has not been reported yet in the literature. This paper is concerning the study of the chemical component of the leaves. Twenty-five compounds have been isolated from the water soluble part of the leaves, among them three flavonol glycosides were isolated as new compounds ,named helicianeoside A、B and C, respectively. The structure elucidation of the three flavonol glycosides is as follows. Helicianeoside A (**1**), a blue-yellow powder, mp. 208°C[α]$_D^{18.5}$ -1.02 (c 0.95, MeOH),had a molecular formula $C_{32}H_{38}O_{19}$ based on the elemental analysis and positive FAB-MS. The acid hydrolysis of **1** gave aglycone moiety, identified by direct comparison by TLC, ^{1}H and^{13}C-NMR spectra with literature values as kaempferol[4,5], and D-xylose, D-glucose and L-rhamnose sugars moiety. In the ^{1}H and ^{13}C-NMR data showed three anomeric protons [δ 6.36 (s, 1H, rha H-1″), 5.26 (d, 1H, J=10Hz, Glc H-1‴)and 4.98 (d, 1H, J=7.2Hz, xyl H-1⁗)],and three carbons signals [δ 102.458, 107.2 and 105.679] to anomeric carbons of the sugars moiety. The HMBC experiment showed that the trisaccharide moiety were linked to the C-3 hydroxy groups of the aglycone, moreover, long-range correlation were observed between the H-1″ of the rhamnopyranosyl moiety and the C-3 of the aglycone, between the H-1‴of the glucopyranosyl moiety and the C-2″ of rhamnopyranosyl moiety and between the

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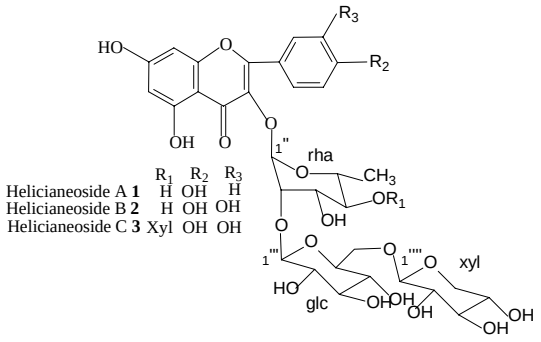
H-1‴of the xylopyranosyl moiety and the C-6‴of the glucopyranosyl moiety. From the above evidence, the structure of **1** was concluded to be kaempferol-3-O-β-D-xylopyranosyl-(1→6)-β-D-glycopyranosyl-(1→2)- α-L-rhamnopyranoside.

Figure1 The structures of compounds **1-3**



Helicianeoside B (**2**), a yellow oil, $[\alpha]_D^{18.5}$ -0.80 (c 0.80, MeOH), had a molecular formula $C_{32}H_{38}O_{20}$ base on the elemental analysis and the positive FAB-MS. The acid hydrolysis of **2** gave aglycone moiety, identified by direct comparison by TLC and ^{1}H and ^{13}C-NMR spectra with literature values as quercetin[6,7], and D-xylose, D-glucose and L-rhamnose sugars moiety, respectively. The ^{1}H and ^{13}C-NMR data of sugar moiety were also in good agreement with those of **1**. So, the structure of **2** was determined to be quercetin-3-O-β-D-xylopyranosyl-(1→6)-β-D-glycopyranosyl-(1→2)-α-L-rhamnopyranoside.

Table 1 ^{1}H-NMR data for compounds**1**~**3** (400 MHz, DMSO-d_6, δppm, J_{Hz})

	1(C_5D_5N)	**2**	**3**
Aglycone			
H-2′	8.054,d(8.8)	7.362,d(2)	7.317,d(2)
H-3′	7.299,d(8.8)	—	—
H-5′	7.299,d(8.8)	6.883,d(8.4)	6.880,d(8.4)
H-6′	8.054,d(8.8)	7.286,dd(8.4,2)	7.276,dd(8.4,2)
H-6	6.749,s	6.197,d(1.6)	6.198,d(2)
H-8	6.749,s	6.388,d(1.6)	6.384,d(2)
Sugars			
Rha H-1″	6.36,s	5.46,s	5.50,s
-CH_3″	1.48,d(6)	0.90,d(6.4)	0.90,d(6.4)
Glc H-1‴	5.26,d(10)	4.20,d(7.2)	4.40,d(7.2)
Xyl H-1⁗	4.98,d(7.2)	4.06,d(8.0)	4.10,d(8.0)
Xyl H-1⁗′	—	—	4.35,d(8.0)

Helicianeoside C (**3**), obtained as a yellow oil, $[\alpha]_D^{18.5}$ -0.24 (c 0.40, MeOH). In the ^{13}C-NMR data of **3**, the signals due to the aglycone moiety were analogous to that of **2**, meanwhile, a molecular formula $C_{37}H_{46}O_{24}$ was higher by $C_5H_8O_4$ than that of **2**. On acid hydrolysis, **3** afforded D-glucose, D-xylose and L-rhamnose. The ^{1}H-NMR spectra of **3** showed four anomeric protons [δ 5.50 (s, 1H, rha H-1″), 4.40 (d, 1H, J=7.2Hz, glc H-1‴), 4.10 (d, 1H, J=8.0Hz, xyl H-1⁗) and 4.35 (d, 1H, J= 8.0Hz, xyl H-1⁗′)]. The

HMBC experiment of **3** showed the same result as that of **2** except long-range correlation between H-1‴″of xylopyranosyl moiety and the C-4″of the rhamnopyranosyl moiety linked to the C-3 hydroxy group of the aglycone. Consequently, the structure of **3** was determined to be quercetin-3-O-β-D-xylopyranosyl-(1→6)β-D-glycopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→4)]-α-L-rhamnopyranoside. They are reported for first time in flavonol glycosides.

Table 2 ^{13}C-NMR data for compounds**1**~**3** (400 MHz, DMSO-d_6, δppm, J_{Hz})

	1(C_5D_5N)	**2**	**3**
Aglycone			
2	157.20	156.65	156.65
3	138.88	134.67	134.11
4	178.83	178.00	177.80
5	162.92	161.55	161.51
6	98.58	98.96	98.97
7	166.53	164.53	164.51
8	92.55	93.88	93.89
9	157.53	157.01	156.65
10	105.19	104.19	104.31
1′	121.61	120.80	121.29
2′	131.31	115.72	115.83
3′	116.29	145.43	145.47
4′	161.64	148.84	148.85
5′	116.29	115.78	115.65
6′	131.31	121.17	120.70
Rhamnose			
1″	102.48	101.08	100.46
2″	82.25	81.52	80.09
3″	72.26	70.44	70.05
4″	73.67	71.98	78.54
5″	71.48	70.58	70.48
6″	18.08	17.64	17.61
Glucose			
1‴	107.20	106.33	105.63
2‴	75.38*	73.96	74.07
3‴	76.82	76.31	76.06
4‴	70.98*	68.75	68.86
5‴	78.23	75.29	74.47
6‴	69.20	67.59	67.76
Xylose			
1⁗-1⁗′	105.69-—	104.19-—	104.28-104.71
2⁗-2⁗′	74.57*-—	73.51-—	73.94-73.55
3⁗-3⁗′	77.67-—	76.64-—	76.66-76.66
4⁗-4⁗′	70.97*-—	69.69-—	69.69-69.69
5⁗-5⁗′	66.83-—	65.76-—	65.79-65.88

*The value assignments may be interchanged

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