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Two Triterpenoid Saponins from *Lonicera Japonica*

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Abstract: A new triterpenoid saponin, together with a known saponin, was isolated from the flowers of *Lonicera Japonica* Thunb. Using chemical and spectroscopic methods, mainly 2D NMR technique, their structures were deduced to be 3-β–D-glucopyranosyl-(1 → 4)-β–D-glucopyranosyl-(1→3)-α-L-rhamnospyranosyl-(1→2)-α-L-arabinopyranosyl hederagenin 28-O-β–D-glucopyranosyl-(1 → 6)-β–D-glucopyranoside and 3-α-L-rhamnospyranosyl-(1 → 2)-α-L-arabinopyranosyl hederagenin 28-O-α-L-rhamnospyranosyl- (1 → 2)-[β–D-xylcopyranosyl--(1→6)]-β–D-glucopyranoside, respectively.

Keywords: Triterpnoid saponin, *Lonicera Japonica*, 2D NMR.

The flowers of *Lonicera Japonica* Thunb are a Chinese traditional medicine and have the functions such as anti-bacteria, anti-virus and hepato-protective. A new triterpenoid saponin **2**, together with a known saponin **1**, was obtained from its flowers. This paper mainly discussed the structure elucidation of these two saponins.

Acid hydrolysis of saponin 1 and 2 yielded the same aglycon. By comparing 1H and 13C NMR data, the aglycon was determined to be hederagenin1. This result was also confirmed by 2D NMR spectra. Using HMQC and DQF-COSY, 13C and some of 1H NMR signals of the aglycon were assigned (Table 1).

Saponin 1, white amorphous powder, FDMS showed quasi-molecular ion peak at m/z 1213 [M+Na]+. In combination with 1H and 13C NMR spectra, its molecular formula was deduced to be C58H94O25. Acid hydrolysis of 1 on TLC gave glucose, xylose, arabinose, rhamnose by comparison with authentic samples.

HMQC spectra showed five anomeric proton signals at δ5.10 (1H,d,J=5.97Hz)、δ6.22 (1H, brs), δ6.13 (1H,d,J=7.8Hz), δ6.51 (1H,brs）, δ4.88 (1H,d,J=7.53Hz) attached to five anomeric carbon signals at δ104.5, δ101.8, δ94.9, δ101.7, δ105.6, respectively. It suggested that **1** contains five sugar moieties. As we know, HMQC-TOCSY is very useful to assign the ^{1}H and ^{13}C NMR signals of sugar moieties especially when NMR signals are overlapped; From HMQC-TOCSY, ^{1}H and ^{13}C NMR information of each sugar could be obtained and distinguished from each other[2-3]. For example, from cross-peak between anomeric proton δ4.88 (1H,d,J=7.53Hz) and anomeric carbon δ105.6, we find four carbons at δ78.1, δ74.9, δ71.2, δ67.1 correlated to

this anomeric proton. meanwhile, five protons δ4.27 (1H,m), δ4.25 (1H,m), δ4.08 (1H,m), δ3.91 (1H,t,J=8.8Hz) and δ3.58 (1H,brd,J=10.12 Hz) correlated to that anomeric carbon. Compared with ^{13}C data of reference [4], it was deduced to be a β–D-xylcopyranose. Combined DQF-COSY and HMQC, those signals of carbons were assigned to C-3, C-2, C-4, C-5 and signals of protons were assigned to be H-4, H-5_a, H-3, H-2, H-5_b of the β–D-xylcopyranose respectively. The complete assignments of the other four sugar moieties were similar (**Table 2**). These assignments were also confirmed by HMBC.

The linkages of oligosaccharide chain and linkage sites to the aglycon were decided by HMBC which observed cross-peaks between the following carbons and protons in saponin **1**: C-3 (δ81.4) of aglycon and H-1 (δ5.10) of ara., C-2 (δ76.1) of ara. and H-1 (δ6.22) of rha., C-28 (δ176.8) of aglycon and H-1 (δ6.13) of glc.,C-6 (δ69.3) of glc. and H-1 (δ4.88) of xyl., and C-2 (δ75.9) of glc. and and H-1 (δ6.51) of rha. So the structure of saponin **1** was deduced to be 3-α-L-rhamnospyranosyl-(1→2)-α-L-arabinopyranosyl hederagenin
28-O-α-L-rhamnospyranosyl-(1→2)-[β–D-xylcopyranosyl-(1→6)]-β–D-glucopyranoside (**Figure 1**). It has been isolated by H. X. Lou[5].

Saponin **2**, white amorphous powder, FDMS showed quasi-molecular ion peak at m/z: 1421 [M+Na]+. In combination with 1H and 13C NMR spectra, its molecular formula was deduced to be C65H106O32. Acid hydrolysis of 2 on TLC gave glucose, arabinose, rhamnose by comparison with authentic samples.

HMQC spectra showed that six anomeric proton signals at δ4.99 (1H,d,J=7.20Hz), δ6.25 (1H,brs.), δ5.42 (1H,d,J=7.92Hz), δ5.14 (1H,d,J=7.68Hz), δ6.22 (1H,d,J=7.68Hz), δ5.02 (1H,d,J=7.92Hz) attached to six anometic carbon signals at δ105.0, δ101.4, δ106.7, δ104.8, δ95.7, δ105.3, respectively. It suggested that **2** contain six sugar moities. Combining DQF-COSY and HMQC, we assigned the ^{1}H and ^{13}C NMR signals on the basis of the NMR information of all carbons and protons of each sugar moiety from HMQC-TOCSY spectra (**Table 2**). These assignments were confirmed by TOCSY, HMBC and ROESY.

The linkages of oligosaccharide chain and linkage sites to the aglycon were decided by HMBC and ROESY. ROESY spectra of **2** showed cross peaks between H-3 (δ4.23) of aglycon and H-1 (δ4.99) of ara., H-1 (δ6.25) of rha. and H-2 (δ4.51) of ara., H-1 (δ5.42) of ^{1}glc. and H-3 (δ4.77) of rha., H-1 (δ5.14) of ^{2}glc. and H-4 (δ4.31) of ^{1}glc., H-1 (δ5.02) of ^{2}glc. and H-6 (δ4.32) of ^{1}glc. Meanwhile, the HMBC spectra revealed cross peaks between C-3 (δ81.2) of aglycon and H-1 (δ4.99) of ara., C-2 (δ76.1) of ara. and H-1 (δ6.25) of rha., C-3 (δ83.5)of rha. and H-1 (δ5.42) of ^{1}glc., C-4 (δ81.2) of ^{1}glc. and H-1 (δ5.14) of ^{2}glc., C-28 (δ176.6) of aglycon and H-1 (δ6.22) of ^{1}glc., C-6 (δ69.5) of ^{1}glc. and H-1 (δ5.02) of ^{2}glc. So the structure of saponin **2** was deduced to be 3-β–D-glucoyranosyl-(1 → 4)-β–D-glucoranosyl-(1 → 3)-α-L-rhamnospyranosyl-(1 → 2)α-L-arabinopyranosyl hederagenin 28-O-β–D-glucopyranosyl-(1 → 6)-β–D-glucopyranoside (**Figure.2**).It is a new natural product.

Table 1. ^{1}H(500MHz) and ^{13}C(125MHz) NMR data of aglycon of **1** and **2** (δ in pyrdine-d_5)

	1		**2**			**1**		**2**	
	^{13}C	^{1}H	^{13}C	^{1}H		^{13}C	^{1}H	^{13}C	^{1}H
1	39.3		39.1		16	24.1		23.9	
2	26.4		26.4		17	47.4		47.1	
3	81.4	4.19(m)	81.2[a]	4.23(m)	18	42.2	3.11(br.d,J=10.64Hz)	41.8	3.16(dd,J=14.16 Hz,4.08Hz)
4	43.7		43.7		19	46.6		46.3	
5	47.9		47.7		20	30.9		30.8	
6	18.5		18.2		21	34.2		34.1	
7	32.5		32.6		22	33.1		32.8	
8	40.2		40.0		23	64.2	4.06(m); 3.64(m)	64.1	4.23(m); 3.86(m)
9	48.4		48.3		24	14.2	0.98(s)	14.2	1.10(s)
10	37.1		37.0		25	16.5	0.99(s)	16.3	0.96(s)
11	23.6		23.5		26	17.7	1.08(s)	17.6	1.12(s)
12	123.0	5.40(br s.)	123.0	5.38(br s.)	27	26.2	1.17(s)	26.2	1.17(s)
13	144.3		144.2		28	176.8		176.6	
14	42.5		42.2		29	33.4	0.84(s)	33.2	0.85(s)
15	28.8		28.4		30	24.1	0.89(s)	23.8	0.85(s)

Figure 1. HMBC of saponin **1**

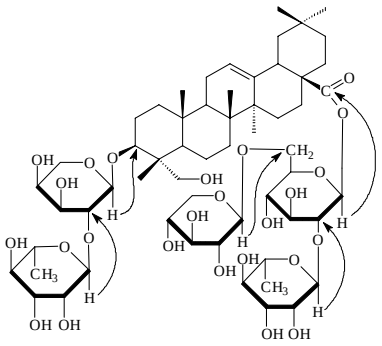

Figure 2. HMBC(⟶) and ROESY(⟷) of saponin **2**

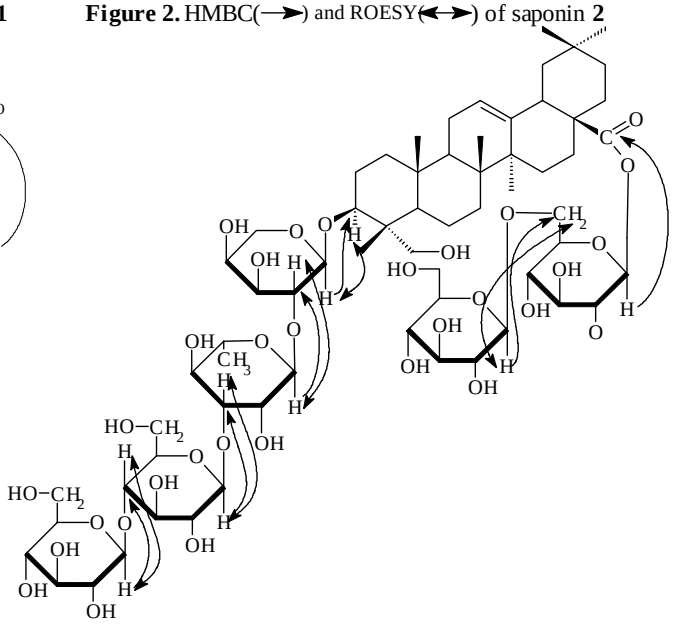

Table 2. ^{1}H(500MHz) and ^{13}C(125MHz) NMR data of sugar moietis of **1** and **2** (δ in pyrdine-d_5)

		1				**2**	
		^{13}C	^{1}H			^{13}C	^{1}H
3-O-ara				3-O-ara			
	1	104.5	5.10(d,J=5.97Hz)		1	105.0	4.99(d,J=7.20Hz)
	2	76.1	4.50(m)		2	75.4	4.51(t,J=7.44Hz)
	3	74.7	4.08(m)		3	75.0	3.94(m)
	4	69.4	4.16(m)		4	69.7	4.08(m)
	5	65.7	4.23(m);3.68(dd,J=15.22, 8.35Hz)		5	66.3	4.20(m); 3.62(brd,J=13.68Hz)
rha	1	101.8	6.22(brs.)	rha	1	101.4	6.25(brs.)
	2	72.4	4.59(m)		2	71.8	4.90(brs.)
	3	72.7[f]	4.68(brs.)		3	83.5	4.77(dd,J=8.40Hz, 3.60Hz)
	4	73.9	4.23(m)		4	73.0	4.46(m)
	5	69.9	4.62(m)		5	69.7	4.65(m)
	6	18.7	1.64(d,J=5.79Hz)		6	18.5	1.52(d,J=6.00Hz)
28-O-glc	1	94.9	6.13(d,J=7.80Hz)	^{1}glc	1	106.7	5.42(d,J=7.92Hz)
	2	75.9	4.30(m)		2	75.5	4.08(m)
	3	79.6	4.22(m)		3	76.8[c]	4.25(m)
	4	71.2[f]	4.10(m)		4	81.2[a]	4.31(m)
	5	77.7	4.01(m)		5	76.8[c]	3.90(m)
	6	69.1	4.58(m); 4.23(m)		6	61.9	4.46(m); 4.36(m)
rha	1	101.7	6.51(brs.)	^{2}glc	1	104.8	5.14(d,J=7.68Hz)
	2	72.3	4.50(m)		2	74.8	4.02(m)
	3	72.7[f]	4.74(brs.)		3	78.5[b]	4.12(m)
	4	74.2	4.30(m)		4	71.6[d]	4.14(m)
	5	70.1	4.46(m)		5	78.3	3.96(m)
	6	19.0	1.76(d,J=5.79Hz)		6	62.5	4.50(m); 4.24(m)
xyl				28-O-^{1}glc			
	1	105.6	4.88(d,J=7.53Hz)		1	95.7	6.22(d,J=7.68Hz)
	2	74.9	3.91(t,J=8.80Hz)		2	74.0	4.09(m)
	3	78.1	4.08(m)		3	78.5[b]	4.22(m)
	4	71.2[e]	4.27(m)		4	71.0	4.26(m)
	5	67.1	4.25(m); 3.58(brd.,J=10.12Hz)		5	78.0	4.19(m)
					6	69.5	4.68(brd.,J=9.36Hz); 4.32(m)
				^{2}glc	1	105.3	5.02(d,J=7.92Hz)
					2	75.2	3.97(m)
					3	78.8	4.16(m)
					4	71.6[d]	4.18(m)
					5	78.5[b]	3.84(m)
					6	62.7	4.44(m); 4.32(m)

[a-f] signals may be interchangeable in the same column.

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