A New Nortriterpenoid Glycoside from *Sinofranchetia chinensis*

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Abstract: A new 30-nortriterpenoid glycopside, 3-O-α-L-arabinopyranosyl-30-norhederagenin 28-O-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl (1→6)-β-D-glucopyranoside **1**, named sinofoside A was isolated from *Sinofranchetia chinensis*. Its structrue was elucidadated by spectra FAB-MS, 2D-NMR including ^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY, TOSCY, HMBC and NOESY techniques.

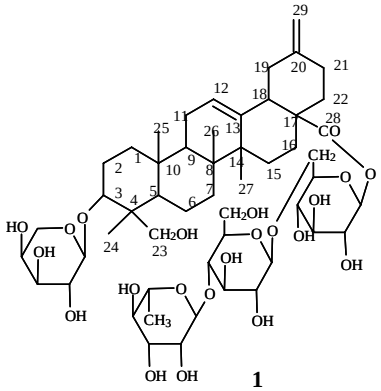
Keywords: *Sinofranchetia chinensis*, nortriterpenoid glycopside, sinofoside A, 2D-NMR.

Sinofranchetia chinensis is a traditional Chinese medicinal plant widely distributed in China, which has been used as an antirheumatic, antiphlogistic, analgesic and diuretic drug[1]. We isolated a new 30-nortriterpenoid saponin **1**. This paper deals with the structural elucidation of **1**.

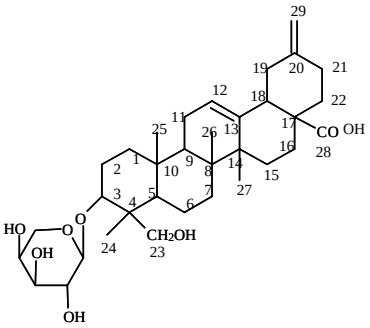
Sinofoside A (**1**). White powder from MeOH, mp. 225-230°C (dec.). It responded positively to the Libermann Burchard test[2]. Its IR absorptions($\nu_{cm^{-1}}$): 1730-1740 ester group, 3400-3420 hydroxyl, and 1640-1650 C=C. Its molecular formula was deduced as $C_{52}H_{82}O_{22}$ by means of ^{13}C NMR, DEPT spectrum and the negative FAB-MS. The ^{1}H NMR spectrum exhibited the presence of four single methyl groups (δ 0.89, 0.92, 1.06, 1.08), a characteristic oxomethylene group at δ 4.65 (1H, s) and δ 4.70 (1H, s). The ^{13}C NMR spectrum showed the presence of two olefinic bonds. One of them was located between C-12 (δ 123.2) and C-13 (δ 143.4) and the other signals appeared at δ 148.3 and δ 107.3 indicating the presence of an oxomethylene group which involving C-20 and C-29[3]. Furthermore, the carbon signal of a hydroxymethylene group at C-23 was exhibited at δ 64.4. The aglycone moiety of **1** was presumed to be 30-norhederagenin preciously reported from the callus tissues of *Paeonia japonica*[4]. The ^{13}C NMR spectra indicated the presence of four anomeric carbon signals (δ 95.6, 102.0, 104.8, 106.6 ppm).

The signals at about 95.6 ppm and 81.7 ppm suggested that **1** have a 28-O-glycosidic linkage. Thus, the saponin was bisdesmosides[5].

Figure 1



1



2

Acid hydrolysis on TLC, **1** gave arabinose, rhamnose and glucose. In alkaline hydrolysis, **1** afforded 30-norhederagenin and prosapogenin **2**. The compound **2** was determinede to be 30-norhederagenin-α-L-arabinopyranoside based on the comparison with spectra ^{1}H, ^{13}C NMR and FABMS of compounds as well as the result of monosaccharide analysis. The structure of **2** was identical with quinatoside A from callus tissues of *Akebai quinata*[6]. The sugar sequence and interglycosidec linkage positions were established as follows. In the negative FABMS of **1**, besides the quasimolecular ion peak *m/z* 1056 $[M-H]^-$, fragment ion peaks at *m/z* 586 $[M\text{-}Rha\text{-}2Glc\text{-}H]^-$, 454 $[M\text{-}Rha\text{-}2Glc\text{-}Ara\text{-}H]^-$ were observed. The ^{13}C NMR spectrum suggested that it was 28-O-triglycoside of 30-norheceragenin in terms of glycosylation shifts. The HMBC spectrum gives the correlation peak of the terminal rhamnose H-2 to the inner glucose C-4 at 78.7 ppm and the inner glucose H-2 to inner-28-O-glucose C-6 at 69.6 ppm. The other proton and corbon 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**). Thus, the structure of **1** was established to be 3-O-α-L-arabinopyranosyl 30-norhederagenin 28-O-α-L-rhamnopyranosyl (1→4)-β-D-glucopyranosyl (1→6)-β-D-glucopyranoside.

Tabal 1 ^{1}H NMR and ^{13}C NMR data for sinofoside A in pyridine-d_5 (δ ppm)

C	δ_C	δ_H		C	δ_C	δ_H
1	38.8	0.99α, 1.52β		27	26.0	1.08
2	28.2	0.98α, 2.21β		28	175.7	
3	81.7	4.25		29	107.3	4.65α, 4.70β
4	43.4		α-Ara p	1	106.6	5.03 (d, J=5.5Hz)
5	48.1	1.67		2	73.0	4.52
6	18.1	1.66a, 1.66b		3	74.8	4.00
7	32.7	1.54α, 1.80β		4	69.5	4.06
8	39.9			5	66.8	3.68α, 4.18β
9	47.4	1.63 α	β-Glc p	1	95.6	6.19 (d, J=8.5Hz)
10	36.6			2	73.9	4.08
11	23.4	1.86a, 1.86b		3	78.3	4.15
12	123.2	5.40		4	70.8	4.32
13	143.4			5	77.1	4.05
14	43.0			6	69.2	4.08α, 4.26β
15	30.0	1.08α, 2.20β	β -Glc p	1	104.8	4.92 (d, J=7.5Hz)
16	23.7	1.85α, 1.96β		2	75.2	3.98
17	47.2			3	76.4	4.15
18	47.4	3.09		4	78.7	4.20
19	46.0	2.09α, 2.47β		5	77.6	3.76
20	148.3			6	61.3	4.35α, 4.45β
21	37.6	1.61α, 1.76β	α-Rha p	1	102.8	6.28 (s)
22	30.0	1.86α, 2.06β		2	72.5	4.86
23	64.4	3.76α, 4.13β		3	72.7	4.72
24	13.5	0.89		4	73.7	4.42
25	16.1	0.92		5	70.7	4.66
26	17.5	1.06		6	18.4	1.55

Acknowledgment

This work as supported by "Light of West China" project, sponsored by Chinese Academy of Sciences, Gansu Nature Sciences Foundation and the Science Foundation of Northwest Normal University P. R. China. We thank Dr. Q-X Zhu (National Laboratory of Applied Organic Chemistry Lanzhou University) for the NMR spectral measurements and Dr Royji Kasai (Institute of Pharmaceutical Sciences, Hiroshima University School of Medicine, Japan) for performing negative FAB-MS analysis. Thanks Prof. G-L Zhang (Biology Department Lanzhou University) for the providing plants of *S. Chinensis*.

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Received May 30, 2000