Available online at www.sciencedirect.com
ScienceDirect
Chinese Chemical Letters 20 (2009) 833–835
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

A new bidesmoside triterpenoid saponin from *Stauntonia chinensis*

Dong Wang [a], Guo Ping Zhou [a,*], Yi Sheng Yang [a], Ya Lun Su [b], Teng Fei Ji [b,*]

[a] *Jiangxi Provical Institute For Drug And Food Contral, Nanchang 330029, China*
[b] *Key Laboratory of Bioactive Substances and Resources Utilization of Chinese Herbal Medicine, Institute of Materia Medica, Chinese Academy of Medical Sciences & Peking Union Medical College, Beijing 100050, China*

Received 1 December 2008

Abstract

A new bidesmoside triterpenoid saponin, named stauntoside C1 (**1**) has been isolated from *Stauntonia chinensis*. Its structure was established by means of spectral and chemical methods.

Keywords: Bidesmoside triterpenoid saponins; *Stauntonia chinensis*; Stauntoside C1

The stems of *Stauntonia chinensis* DC. (Lardizabalaceae) are used as Chinese herbal medicine for treatment of analgesia and sedation. Wang [1,2] and Yao [3,4] reported many new triterpenoid glycosides from this plant. We now report a new bidesmoside triterpenoid glycoside which named stauntoside C1 (compound **1**) from n-BuOH fraction of H_2O extracted of *S. chinensis* DC. And structure determined as 3-O-β-D-xylopyranosyl-(1 → 4)-O-β-D-xylopyranosyl-(1 → 3)-O-α-L-rhamnopyranosyl (1 → 2)-α-L-arabino-pyranosyl oleanolic acid 28-O-α-L-rhamnopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside on the basis of spectroscopic and chemical evidence.

Compound **1** was an amorphous white powder, mp 238–240, gave positive result to Liebermann–Burchard test. In the (−)- and (+)-ESI-MS of **1**, quasimolecular ion peaks were observed at *m/z* 1467 $[M-H]^-$ and, *m/z* 1491 $[M+Na]^+$, respectively, HR-ESI-MS (*m/z* 1491.6990 $[M+Na]^+$) analysis revealed the molecular formula of **1** to be $C_{69}H_{112}O_{33}Na$ (calcd. 1491.6978). Together with five fragmentary ions at 1021 [M-470+Na], 865 [M-470-132-H], 733 [M-470-132-132-H], 587 [M-470-132-132-146-H] and 455 [M-470-132-132-146-132-H], indicating the sequential losses of seven sugar moieties (four hexoses and three pentoses), the ^1H and ^{13}C NMR spectra of **1** exhibited seven sugar anomeric protons at δ4.72(3-Ara-1), 6.05(3-Rha-1), 5.10(3-xylI-1), 4.74(3-xylII-1), 6.21(28-GlcI-1), 4.85(28-GlcII-1), 5.62(28-Rha-1) and carbons at 103.2, 101.4, 106.4, 104.8, 95.6, 104.3 and 102.4 (Table 1). Acid hydrolysis of **1** with 2N HCl-1,4-dioxane (1:1, v/v) furnished L-arabinose, D-xylose, L-rhamnose, D-glucose in the ratio of 1:2:2:2, which were identified by HPLC analysis of the thiazolidine derivatives [6].

The ^1H NMR of **1** revealed the presence of nine methyl group proton signals at δ_H 0.87(Me-25), 0.88(Me-29), 0.88(Me-30), 1.07(Me-26), 1.14(Me-24), 1.24(Me-27), 1.27(Me-23), due to the oleanic acid skeleton; 1.46(d, 3H, 6.0 Hz), 1.55(d,3H, 6.0 Hz) as methyl proton signals of two rhamnoses; an olefinic proton at δ_H 5.34(s,1H, H-12).

* Corresponding authors.
E-mail address: jitf@imm.ac.cn (G.P. Zhou).

1001-8417/$ – see front matter
doi:10.1016/j.cclet.2009.01.035

Of the 69 carbon signals observed in ^{13}C NMR spectrum of **1**, 30 were assigned to the aglycon and 39 to the oligosaccharide moieties. The signals at δ_C 122.3, 143.9 were assigned to be 12(13)-en of oleanic acid skeleton by comparing with literature [5].

The chemical shifts of C-3 (δ_C 88.6) and C-28 (δ_C 176.5) revealed that **1** was a bisdesmosidic glycoside. The ^{13}C NMR spectroscopic data of the sugar moieties indicated that all the monosacchrides were in pyranose forms as determined from their ^{13}C NMR data. The β-anomeric configuration of the glucose and xylose were determined from $^3J_{H1,H2}$ (7.5–8.5 Hz); the arabinose has α-configuration on the basis of the $^3J_{H1,H2}$ (6.0 Hz) in the $^4C_1$ forms; the anomeric proton of rhamnose was observed as a singlet indicated an α-configuration.

The oligosaccharide sequence and the glycosidic site of **1** were determined by HMQC-TOCSY, HMBC spectrum. The H-1 of arabinose at δ_H 4.72 correlated with C-3 of the aglycone at δ_C 88.6, the H-1 of rhamnose I at t δ_H 6.05 correlated with C-2 of the arabinose at δ_C 75.2, the H-1 of inner xylose at δ_H 5.10 correlated with C-3 of the rhamnose I at δ_C 82.2, the H-1 of the terminal xylose at δ_H 4.74 correlated with C-2 of inner xylose at δ_C 75.5. The trisaccharide part at C-28 was established by HMBC: the H-1 of glucose I at δ_H 6.21 correlated with C-28 (δ_C 176.5) of the aglycone, the H-1 at δ_H 4.85 of the glucose correlated with C-6 (δ_C 69.4) of the glucose I (inner), the H-1 (δ_H 5.62) of rhamnose correlated with C-4 (δ_C 78.3) of the glucose. The sugar linkages of the oligosaccharide chains were shown in Fig. 1.

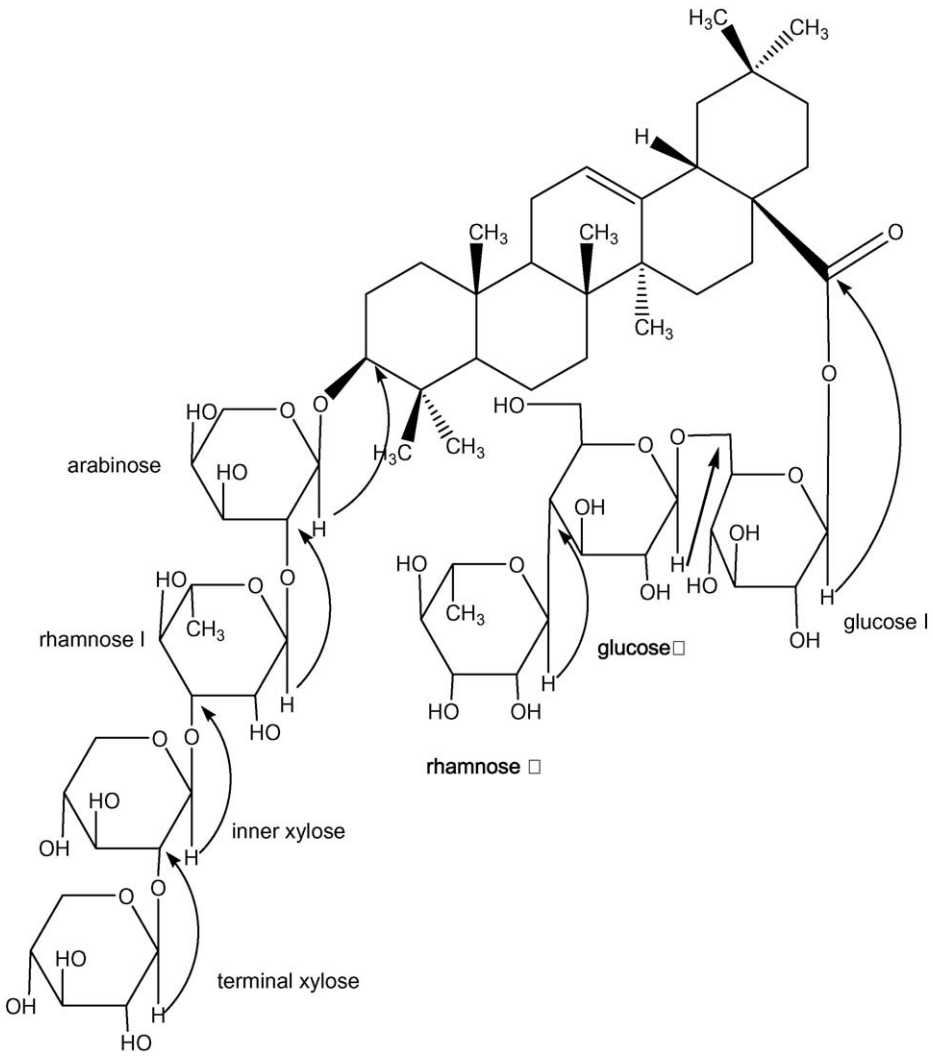

Fig. 1. Key HMBC correlations of compound **1**.

Table 1
^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data of **1** in pyridine-d_5, δ ppm.

Position	**1**-3-sugar chain		Position	**1**-28-sugar chain	
	^{13}C(DEPT)	^{1}H		^{13}C(DEPt)	^{1}H
3-Ara-1	103.2(CH)	4.72,1H,d,7.0 Hz	28-Glc I-1	95.6(CH)	6.21,1H,d,8.5 Hz
2	75.2(CH)	4.50,s	2	73.8(CH)	4.08,m
3	73.5(CH)	4.22,m	3	78.1(CH)	4.15,m
4	69.4(CH)	4.22,m	4	70.1(CH)	4.28,m
5	66.9(CH_2)	4.27/3.70,d,12.0 Hz	5	78.1(CH)	4.11,m
3-Rha-1	101.4(CH)	6.05,1H,s	6	69.4(CH_2)	4.64/4.30,m
2	71.4(CH)	4.71	28-GlcII-1	104.3(CH)	4.85,1H,d,8.0 Hz
3	82.2(CH)	4.45,m	2	73.8(CH)	3.925,m
4	73.8(CH)	4.20,s	3	76.7(CH)	4.11,m
5	69.4(CH)	4.73,m	4	78.3(CH)	4.28,m
6	18.2(CH_3)	1.46,3H,d,6.0 Hz	5	76.7(CH)	3.64,11.5 Hz
3-xyl I-1	106.4(CH)	5.10,1H,d,7.5 Hz	6	60.9(CH_2)	4.18/4.06,m
2	75.5(CH)	4.10,m	28-Rha-1	102.4(CH)	5.62,1H,s
3	74.9(CH)	3.88,m	2	72.1(CH)	4.69,s
4	73.5(CH)	4.07,m	3	72.4(CH)	4.54,s
5	64.4(CH_2)	3.44,11.5 Hz/4.30	4	72.2(CH)	4.28,m
3-xylII-1	104.8(CH)	4.74,1H,d,6.0 Hz	5	70.1(CH)	4.72, d,1H,8.0 Hz
2	75.2(CH)	3.95,m	6	18.2(CH_3)	1.55,d,3H,6.0 Hz
3	75.5(CH)	4.15,m			
4	70.2(CH)	4.27,m			
5	66.9(CH_2)	4.29,m/3.68,11.5 Hz/4.25			

References

[1] H.B. Wang, R. Mayer, G. Rücker, Phytochemistry 34 (5) (1993) 1389.
[2] H.B. Wang, R. Mayer, G. Rücker, Phytochemistry 34 (6) (1993) 1469.
[3] G. Hao, W. Zhao, X.S. Yao, et al. Magn. Reson. Chem. 46 (7) (2008) 630.
[4] H. Gao, X. Zhang, N.L. Wang, et al. J. Asian Nat. Prod. Res. 9 (2) (2007) 175.
[5] F.J. Guo, Y.C. Li, et al. Helv. Chim. Acta 89 (3) (2006) 468.
[6] R. Oshima, Y. Yamauchi, J. Kumanotani, Carbohydr. Res. 107 (1982) 169.