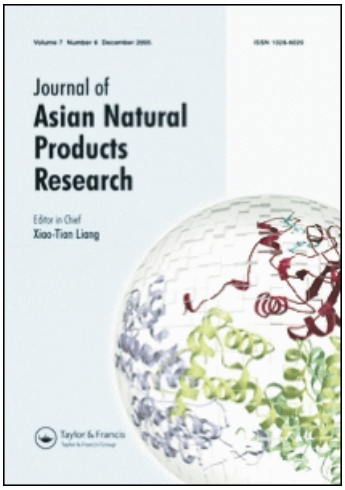

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

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To cite this Article Luo, Y. -M. , Liu, A. -H. , Zhang, D. -M. and Huang, L. -Q.(2005) 'Two new triterpenoid saponins from *Sarcandra glabra*', Journal of Asian Natural Products Research, 7: 6, 829 — 834
To link to this Article: DOI: 10.1080/10286020410001721104
URL: http://dx.doi.org/10.1080/10286020410001721104

Journal of Asian Natural Products Research, Vol. 7, No. 6, December 2005, 829–834

Two new triterpenoid saponins from *Sarcandra glabra*

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(Received 1 January 2004; revised 1 April 2004; in final form 3 April 2004)

Two new triterpenoid saponins, named sarcandroside A and B, have been isolated from *Sarcandra glabra* (Thunb) Nakai. Their structures have been established as 3β,19α,20β-trihydroxyurs-11,13 (18)-diene-28,20β-lactone-3-*O*-β-D-glucopyranosyl (1 → 3)-[α-L-rhamnopyranosyl(1 → 2)]-β-D-xylopyranoside (**1**) and 3-*O*-β-D-glucopyranosyl (1 → 3)-[α-L-rhamnopyranosyl(1 → 2)]-β-D-xylopyranosyl-pomolic acid 28-*O*-β-D-glucopyranosyl ester (**2**) by means of spectral and chemical methods.

Keywords: *Sarcandra glabra*; Chloranthacea; Triterpenoid saponin; Sarcandrosides A and B

1. Introduction

Sarcandra glabra (Thunb) Nakai (Family: Chloranthacea) is distributed in the southern part of China. The whole plant has been used as an antibacterial and antitumour agent in China. Flavonoids, coumarins and sesquiterpenoids have been identified as constituents of the plant [1–6]. In the present paper, we report the isolation and structure elucidation of two new triterpenoid saponins, named sarcandroside A and B, by means of one dimensional and two dimensional NMR spectroscopic techniques, including $^{1}H—^{1}H$ COSY, HSQC and HMBC.

2. Results and discussion

Compound **1** shows a quasi-molecular ion peak $[M + Na]^+$ at *m/z* 931. HR-FABMS assigned the molecular formula of $C_{47}H_{72}O_{17}$. The ^{1}H and ^{13}C NMR spectra of **1** reveal seven methyl groups (δ0.82, 0.87, 1.04, 1.09, 1.20, 1.52, 1.68). The methyl signals at δ1.52 and 1.68 were shifted significantly downfield, indicating that they may be connected with oxygenated carbon atoms. The C-20 (δ85.9) and C-28 (δ175.1) signals confirmed the presence of a δ-lactone ring. The ^{1}H NMR spectrum shows signals of a *cis*-disubstituted olefinic proton [δ7.49 (dd, $J = 2.5, 11$ Hz) and 5.77 (d, $J = 11$ Hz)]. The ^{13}C NMR spectrum exhibits two quaternary

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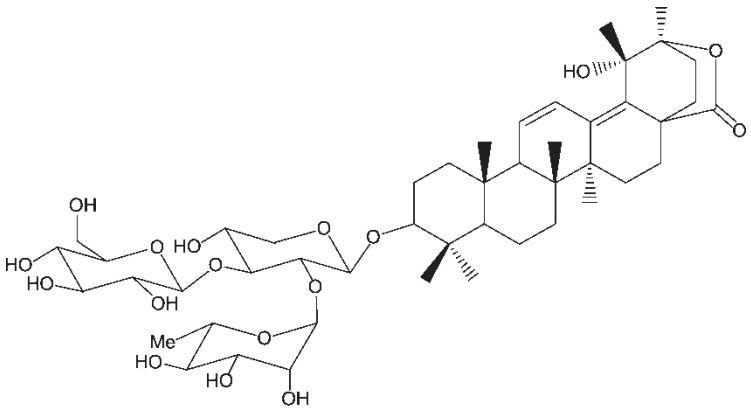
Journal of Asian Natural Products Research
ISSN 1028-6020 print/ISSN 1477-2213 online © 2005 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/10286020410001721104

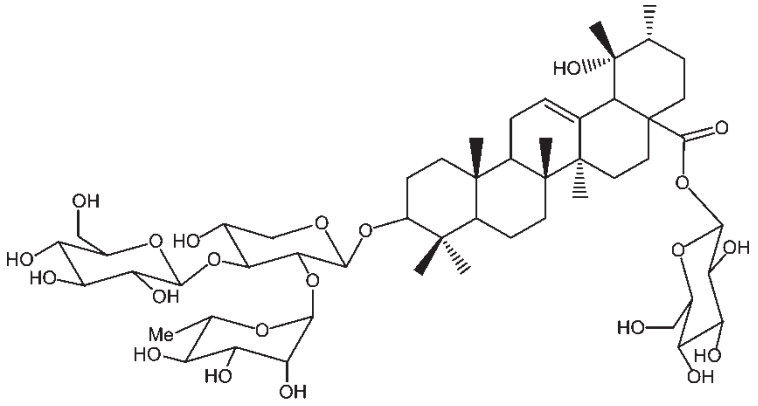
olefinic carbons [δ140.7 (C-13) and 135.0 (C-18)] in an HSQC experiment, which are ascribed to a tetrasubstituted double bond. The observed HMBC cross peaks between H-12 and C-13 suggest the presence of a conjugated double bond system. The characteristic cross peaks appear between the quaternary carbon C-4 and H-23, H-24 and H-3; between the quaternary carbon C-10 and H-25, H-11 and H-9; between the quaternary carbon C-18 and H-12 and H-16; between the quaternary carbon C-13 and H-12 and also between C-19 and H-30; between C-20 and H-29. These data suggest that the aglycone of **1** is 3β,19α,20β-trihydroxyurs-11,13(18)-diene-28,20β-lactone, which has been reported previously [7]. The ^{1}H and ^{13}C NMR spectra of compound **1** show that this saponin contains three sugars, with signals of anomeric carbons at δ104.8, 104.7 and 101.9, corresponding to the anomeric protons at δ4.86, 5.16 and 6.17 respectively (table 2). On acid hydrolysis, **1** yielded a mixture of xylose, glucose and rhamnose. HMBC cross peaks appear between H-1 (δ4.8) of xylose and Cy3 (δ88.2) of the aglycone, between H-1 (δ6.17) of rhamnose and C-2 (δ74.86) of xylose, between H-1 (δ5.16) of glucose and C-3 (δ82.2) of xylose. These data indicate the presence of a rhamnopyranosyl(1 → 2)-[glucopyranosyl(1 → 3)]-xylopyranosyl moiety at C-3. The anomeric configuration of the sugars was determined from examination of the respective coupling constants. Thus the structure of saponin **1** was determined as 3β,19α,20β-trihydroxyurs-11,13(18)-diene-28,20β-lactone-3-*O*-β-D-glucopyranosyl(1 → 3)-[α-L-rhamnopyranosyl(1 → 2)]-β-D-xylopyranoside.



1

Compound **2** shows a quasi-molecular ion peak $[M + Na]^{+}$ at *m*/*z* 1097. HR-FABMS assigned the molecular formula of $C_{53}H_{86}O_{22}$. Compound **2** displays four anomeric proton signals at δ4.85, 5.10, 6.11 and 6.30 in the ^{1}H NMR spectrum, and four anomeric carbon signals at δ95.8, 101.9, 104.5, 104.6 in the ^{13}C NMR spectrum. On acid hydrolysis, **2** yielded a mixture of xylose, glucose and rhamnose. In the aglycone region, the ^{1}H NMR spectrum of **2** shows signals due to seven methyl groups (δ0.88, 1.05, 1.11, 1.16, 1.18, 1.37, 1.69), assigned as six tertiary methyls and one secondary methyl [a doublet signal at δ1.05 (d, $J = 7$ Hz, CH_3-20)] and an olefinic proton (δ5.53). The ^{13}C NMR spectrum reveals seven methyls, nine methylenes, five methines and eight quaternary carbons. The olefinic carbon signals at δ128.4 and at 140.7 are attributed to C-12 and C-13, respectively. These spectral data indicate that **2** has an urs-12-en-skeleton. In fact, the ^{13}C NMR spectral data of **2** are very similar to those of pomolic acid [8]. In the sugar region, the sugar linkages were

determined on the basis of the HMBC spectrum, showing correlations between C-28 (δ176.9) of the aglycone and H-1 (δ6.29) of a glucose and between C-3 (δ88.2) of the aglycone and H-1(δ4.85) of xylose. The sugar chain at C-3 was identical as that in compound **1**. These data indicate the presence of a rhamnopyranosyl (1 → 2)-[glucopyranosyl(1 → 3)]-xylopyranosyl moiety at C-3 and a glucopyranosyl moiety at C−28 in the structure of **2**. The anomeric configuration of the sugars was determined from examination of the respective coupling constants. Based on the above data, **2** was established as 3-*O*-β-D-glucopyranosyl(1 → 3)-[α-L-rhamnopyranosyl(1 → 2)]-β-D-xylopyranosyl-pomolic acid 28-*O*-β-D-glucopyranosyl ester.



2

3. Experimental

3.1 General experimental procedures

Melting points were determined on an X-4 micromelting apparatus and are uncorrected; FAB-MS was recorded in positive ion mode on a VG ZAB-HS mass spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a INOVA-500 spectrometer (^{1}H, 500 MHz, ^{13}C, 125 MHz). IR spectra were obtained on a Nicolet IMPACT 400 spectrometer. HPLC was performed using an ODS column (Waters Nova-Pak C18, 3.9 × 150 mm). Column chromatography (CC) was carried out on silica gel and Sephadex LH-20 (Pharmacia Biotech). TLC was conducted on silica gel 60 F_{254} (Merck). Spots were detected after spraying with 10% H_2SO_4.

3.2 Plant material

Sarcandra glabra were collected at Chongyi County, Jiangxi Province, China in July of 1999 and identified by Professor L.Q. Huang, Institute of Chinese Materia Medica, China Academy of Traditional Chinese Medicine. A voucher specimen (99-07-16) of the plant has been deposited at the Herbarium of Jiangxi University of Traditional Chinese Medicine.

Table 1. ^{13}C NMR spectral data[a] of **1** and **2** in pyridine-d_5.

Carbon	***1***	***2***	***S***[b]
1	38.4	39.1	38.7
2	26.4	26.1	28.0
3	88.2	88.2	78.2
4	39.6	39.5	39.3
5	55.3	56.1	55.8
6	18.4	18.7	18.9
7	32.9	33.5	33.6
8	42.1	40.5	40.3
9	54.5	47.7	47.7
10	36.6	37.0	37.3
11	127.2	24.0	24.0
12	128.4	128.4	128.1
13	140.7	139.2	139.9
14	42.2	42.1	42.1
15	25.8	29.2	29.2
16	26.3	26.6	26.6
17	43.8	48.6	48.2
18	135.0	54.4	54.5
19	74.1	72.6	72.7
20	85.9	42.1	42.3
21	28.5	26.7	27.0
22	32.9	37.7	37.4
23	27.7	28.1	28.7
24	16.5	17.0	16.7
25	16.4	15.7	15.5
26	18.6	17.4	17.1
27	18.7	24.6	24.6
28	175.1	176.9	180.6
29	23.7	27.0	26.8
30	19.5	16.6	16.4
C-3			
Xyl 1	104.8	104.6	
2	74.9	74.7	
3	82.2	81.6	
4	72.4	72.4	
5	64.9	64.7	
Glc 1	104.7	104.6	
2	73.9	73.9	
3	78.6	78.5	
4	68.2	68.0	
5	78.2	78.9	
6	62.6	62.5	
Rha 1	101.9	101.9	
2	71.5	71.4	
3	72.5	72.5	
4	74.8	74.9	
5	70.0	70.0	
6	18.3	18.6	
C-28			
Glc 1		95.8	
2		74.1	
3		79.2	
4		71.2	
5		78.2	
6		62.3	

[a] Assignments based upon HSQC and HMBC experiments.
[b] Values taken from Ref. [8].

Table 2. ^{1}H NMR spectral data[a] of compounds **1** and **2** in pyridine-d_5.

Proton	***1***	***2***
Aglycone 3	3.28 (dd, $J = 5$, 11.5 Hz)	3.27 (dd, $J = 4.5$, 11.5 Hz)
11	7.49 (dd, $J = 2.5$, 11 Hz)	2.00 (m)
12	5.77 (d, $J = 11$ Hz)	5.53 (br s)
18		2.92 (m)
20		1.29 (m)
23	1.20 (s)	1.18 (s)
24	1.09 (s)	1.11 (s)
25	0.81 (s)	0.88 (s)
26	0.87 (s)	1.16 (s)
27	1.04 (s)	1.37 (s)
29	1.68 (s)	1.69 (s)
30	1.52 (s)	1.05 (d)
C-3		
Xyl 1	4.86 (d,$J = 6$ Hz)	4.85 (d, $J = 6$ Hz)
2	4.66 (m)	4.64 (m)
3	4.33 (m)	4.30 (m)
4	4.58 (m)	4.57 (m)
5	3.75 (dd, $J = 11.5$, 1.5 Hz) 4.24 (dd, $J = 11.5$, 4.5 Hz)	3.72 (dd, $J = 9.5$, 1.5 Hz) 4.21 (dd, $J = 9.5$, 1.5 Hz)
Glc 1	5.16 (d, $J = 8$ Hz)	5.10 (d, $J = 6.5$ Hz)
2	4.27 (m)	4.26 (m)
3	3.93 (m)	3.91 (m)
4	4.53 (m)	4.53 (m)
5	4.15 (m)	4.27 (m)
6	4.26 (dd, $J = 9.5$, 2 Hz), 4.49 (dd, $J = 9.5$, 2 Hz)	4.24 (dd, $J = 9.5$, 1.5 Hz) 4.32 (dd, $J = 9.5$, 1.5 Hz)
Rha 1	6.17 (br.s)	6.11 (br.s)
2	4.17 (m)	4.16 (m)
3	4.73 (m)	4.71 (m)
4	3.95 (m)	3.93 (m)
5	4.51 (m)	4.52 (m)
6	1.63 (d, $J = 6.5$ Hz)	1.61 (d, $J = 6$ Hz)
C-28		
Glc 1		6.29 (d,$J = 8$ Hz)
2		4.20 (m)
3		4.05 (m)
4		4.28 (m)
5		4.15 (m)
6		4.36 (dd, $J = 9.2$ Hz) 4.47 (dd, $J = 9.2$ Hz)

[a] Assignments based upon ^{1}H—^{1}H COSY, HSQC and HMBC experiments.

3.3 Extraction and isolation

The dried and powdered plant (6.5 kg) was extracted (3 ×) with methanol (3 × 15 l) for 2 h under reflux, and the combined extracts were concentrated *in vacuo*. The resulting extract (480 g) was then suspended in water and successively extracted with light petroleum, chloroform and butanol saturated with water to give the respective extracts after solvent removal. The butanol-solution portion (80 g) was subjected to column chromatography on silica gel (10 × 100 cm) with $CHCl_3$–MeOH–H_2O (7:3:0.5) to give five fractions (Fractions I–V). Fraction V was further subjected to a silica-gel column eluted with $CHCl_3$–MeOH–H_2O (6:4:1) to give six fractions (Va–Vf). Subfraction Vb was subjected to preparative HPLC [H_2O–CH_3CN (72:28), 5 ml min^{-1}, monitored at 210 nm] to afford **1** (38 mg) and **2** (16 mg).

Sarcandroside A (**1**) was obtained as an amorphous solid, mp 279–281°C. HR-FABMS (positive ion mode) *m/z* 931.4650 $[M + Na]^+$ (calcd for $C_{47}H_{72}O_{17}Na$ 931.4686); FAB-MS *m/z* 931 $[M + Na]^+$, 947 $[M + K]^+$, 785 $[(M + Na) - rha]^+$; UV(MeOH) λ_{max} (nm):260. IR (KBr) (ν cm^{-1}): 3413, 2937, 1720, 1635, 1456, 1388, 1250, 1130, 1074, 984, 945, 816, 787. ^1H and ^{13}C NMR (pyridine-d_5): Tables 1 and 2, respectively.

Sarcandroside B (**2**) was obtained as an amorphous solid, mp: 267–269°C. HR-FABMS (positive mode) *m/z* 1097.5521 $[M + Na]^+$ (calcd for $C_{53}H_{86}O_{22}Na$ 1097.5509); FAB-MS *m/z* 1097 $[M + Na]^+$, 935 $[(M + Na) - glc]^+$, 639 $[(M + Na) - glc–rha–xyl–H_2O]^+$, 495 $[(M + Na) - 2glc–rha–xyl]^+$. IR (KBr) ($\nu cm^{-1}$) : 3408, 2931, 1732, 1645, 1456, 1385, 1136, 1074, 814, 781. ^1H and ^{13}C NMR (pyridine-d_5): Tables 1 and 2, respectively.

Acknowledgements

The authors are grateful to the Natural Science Foundation of Jiangxi Province and the Education Bureau of Jiangxi Province for financial supports.

References

[1] Y. Takeda, H. Yamashita, T. Matsumoto. *Phytochemistry*, **33**, 713 (1993).
[2] W.Y. Sui, G.D. Brown. *Phytochemistry*, **43**, 819 (1996).
[3] H. Okamora, N. Nakashima, T. Iwagawa. *Chem. Lett.*, 1541 (1994).
[4] A.Q. Wang, S.C. Fong, X. Hou. *Acta Pharmacol. Sin.*, **23**, 64 (1988).
[5] A.Q. Wang, P. Xie, Y.H. Yi. *Acta Pharmacol. Sin.*, **14**, 37 (1983).
[6] D.Q. Wang, X.C. Li. *Chin. Trad. Herb. Drugs*, **27**, 337 (1996).
[7] M. Ochi, K. Ochiai, K. Nagao. *Bull. Chem. Soc. Jpn.*, **48**, 937 (1975).
[8] B.S. Mahato, P.A. Kundu. *Phytochemistry*, **37**, 1517 (1994).