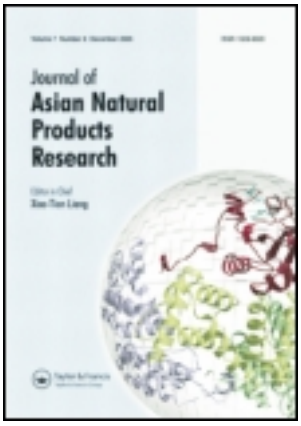

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A new nortriterpenoid saponin from the roots of *Symplocos caudata* Wall

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A new nortriterpenoid saponin, 3β,17β-dihydroxy-28-nor-12-oleanen-16-one 3-*O*-β-D-galactopyranosyl (1 → 2)-{α-L-arabinopyranosyl (1 → 3)-[α-L-arabinofuranosyl (1 → 4)-β-D-glucuronopyranoside]} (**1**), along with two pairs of known isomers, was isolated from the roots of *Symplocos caudata* Wall. Their structures were elucidated by spectroscopic and chemical methods.

Keywords: *Symplocos caudata* Wall; nortriterpenoid; saponin

1. Introduction

Symplocos caudata Wall is distributed in Jiangxi and Zhejiang provinces of China. The roots of this plant are used as a remedy for icterus and arthritis in Chinese folk medicine [1]. In previous paper, we have reported the structural elucidation of three new phenolic compounds isolated from this plant [2]. Continued research has resulted in the isolation of a new compound, 3β,17β-dihydroxy-28-nor-12-oleanen-16-one 3-*O*-β-D-galactopyranosyl (1 → 2)-{α-L-arabinopyranosyl (1 → 3)-[α-L-arabinofuranosyl (1 → 4)-β-D-glucuronopyranoside]} (**1**), along with two pairs of known isomers, 2α,3β,19α,23-tetrahydroxy-12-oleanen-28-oic acid 28-β-D-glucopyranosyl ester (**2**) [3] and 2α,3β,19α,23-tetrahydroxy-12-ursen-28-oic acid 28-β-D-glucopyranosyl ester (**3**) [4], 2α,3β,19α,23,24-pentahydroxy-12-oleanen-28-oic acid 28-β-D-glucopyranosyl ester (**4**) [5], and 2α,3β,19α,23,24-pentahydroxy-12-ursen-28-oic acid 28-β-D-glucopyranosyl ester (**5**) [5] (Figure 1). Their structures were elucidated by spectroscopic and chemical methods.

2. Results and discussion

Compound **1** was obtained as white amorphous powder, $[\alpha]_D^{25}$ −33.3. The absorption bands of its IR spectrum suggested the presence of hydroxyl groups (3371 cm^{-1}) and carbonyl (1707 cm^{-1}) functional groups. The positive ESI-MS of **1** exhibited a quasimolecular ion peak at *m/z* 1067 $[M + Na]^+$. The molecular formula $C_{51}H_{80}O_{22}$ was indicated by the positive HR-FAB-MS at *m/z* 1089.4887 $[M + 2Na - H]^+$. Compound **1** was confirmed to be a triterpenoid saponin by the positive results of Liebermann–Burchard and Molish reaction.

The ^1H NMR spectrum of **1** (Table 1) showed seven methyl singlets at δ_H 0.74 (3H, s), 0.85 (3H, s), 0.94 (3H, s), 1.02 (3H, s), 1.17 (3H, s), 1.17 (3H, s), and 1.29 (3H, s) in the higher field region, four anomeric proton signals at δ_H 4.77 (1H, d,

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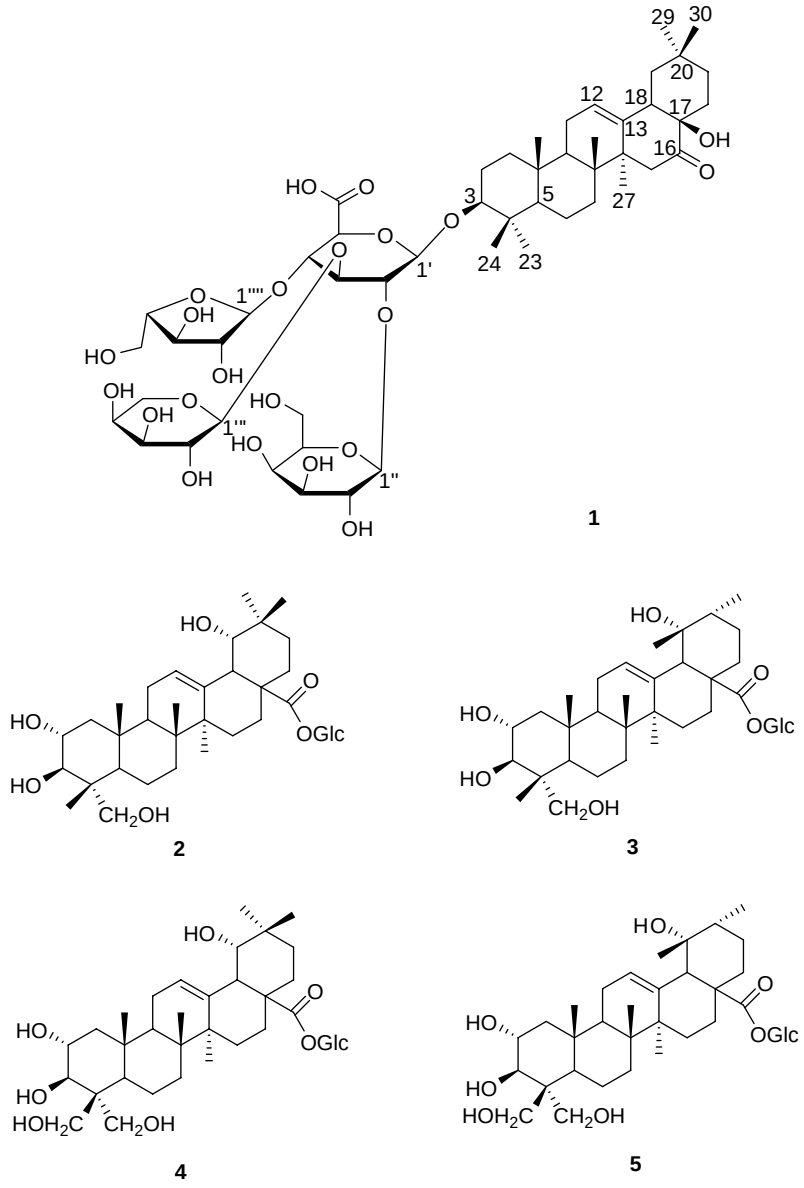

Figure 1. Structures of compounds **1**–**5**.

$J = 7.0$ Hz, H-1′), 5.49 (1H, d, $J = 7.5$ Hz, H-1″), 5.57 (1H, d, $J = 7.0$ Hz, H-1‴), and 6.12 (1H, br s, H-1⁗), and a single proton signal of an olefinic bond at δ_H 5.45 (1H, m, H-12). The ^{13}C NMR spectrum of **1** (Table 1) showed 51 carbon signals, and the DEPT experiment differentiated them to be $7 \times CH_3$, $12 \times CH_2$, $23 \times CH$, and $9 \times C$. On the basis of the chemical shift values, the nine quaternary carbons were assigned to be two carbonyls at δ_C 216.0 and 176.7, a sp^2 carbon at δ_C 142.9, and six sp^3 carbons (an oxygen bearing at δ_C 76.7). In the ^{13}C NMR spectrum, the signals at δ_C 124.2 and 142.9 belonging to C-12 and C-13 suggested a Δ^{12} oleanene

Table 1. ^{1}H and ^{13}C NMR spectral data of compound **1** (pyridine-d_5).

No.	δ_H (J, Hz)	δ_C	No.	δ_H (J, Hz)	δ_C
1	0.61 m, 1.22 m	38.7	GlcA-1′	4.77 d (7.0)	105.6
2	1.69 m, 2.02 m	26.7	2′	4.50 m	80.8
3	3.07	89.9	3′	4.44 m	79.6
4		39.8	4′	4.60 m	75.3
5	0.59 m	55.9	5′	4.37 m	78.6
6	1.37	18.7	6′		176.7
7	1.15 m, 1.29 m	33.5	Gal-1″	5.49 d (7.5)	104.3
8		40.4	2″	4.40 m	73.9
9	1.45 m	47.2	3″	4.14 m	75.1
10		37.1	4″	4.52 m	70.0
11	1.87 m	24.2	5″	3.95 m	77.1
12	5.45 m	124.2	6″	4.31 m	61.8
13		142.9	Ara-1‴	5.57 d (7.0)	104.1
14		48.5	2‴	4.38 m	73.1
15	1.88 d (13.5), 3.64 d (13.5)	43.7	3‴	4.02 m	74.6
16		216.0	4‴	4.09 m	70.0
17		76.7	5‴	3.53 m, 4.14 m	67.2
18	3.09 m	53.0	Ara-1⁗	6.12 br s	108.2
19	1.45 m	48.7	2⁗	4.71 m	81.7
20		31.3	3⁗	4.43 m	79.2
21	1.29 m, 1.84 m	37.5	4⁗	4.95 m	87.4
22	1.76 m, 2.47 d (12.5)	31.8	5⁗	3.92 m	62.8
23	1.17 s	28.3			
24	1.02 s	17.1			
25	0.74 s	15.7			
26	1.17 s	18.0			
27	1.29 s	27.5			
28	–	–			
29	0.85 s	33.1			
30	0.94 s	24.0			

skeleton [6] with four saccharide moieties in the structure of **1** coupling with ^{1}H NMR spectral data. In addition, four saccharide moieties were concluded to be glucuronopyranosyl at δ_C 105.6, 80.8, 79.6, 75.3, 78.6, and 176.7, galactopyranosyl at δ_C 104.3, 73.9, 75.1, 70.0, 77.1, and 61.8, arabinopyranosyl at δ_C 104.1, 73.1, 74.6, 70.0, and 67.2, and arabinofuranosyl at δ_C 108.2, 81.7, 79.2, 87.4, and 62.8 by 2D NMR spectra ($^{1}H-^{1}H$ COSY, TOCSY, HSQC, HMBC, and NOESY). Furthermore, the stereochemistries of four saccharide moieties were confirmed to be β-D-glucuronopyranosyl, β-D-galactopyranosyl, α-L-arabinopyranosyl, and α-L-arabinofuranosyl by anomeric proton coupling constants at δ_H 4.77 (1H, d, $J = 7.0$ Hz, H-1′, GlcA), 5.49 (1H, d, $J = 7.5$ Hz, H-1″, Gal), 5.57 (1H, d, $J = 7.0$ Hz,H-1‴, Ara), and 6.12 (1H, br s, H-1⁗, Ara). According to the above conclusion, except for 22 carbons of saccharide moieties, the residual 29 carbons suggested that compound **1** was a nortriterpenoid compound. The assignments of the proton and the carbon resonances of the nortriterpenoid moiety, which were secured by $^{1}H-^{1}H$ COSY, HSQC, and HMBC experiments, allowed identification of this moiety as noroleanene with 29 carbons. Furthermore, the NMR spectral data due to this moiety except for saccharide moieties were in accord with those reported for the aglycone as camellioside A [7].

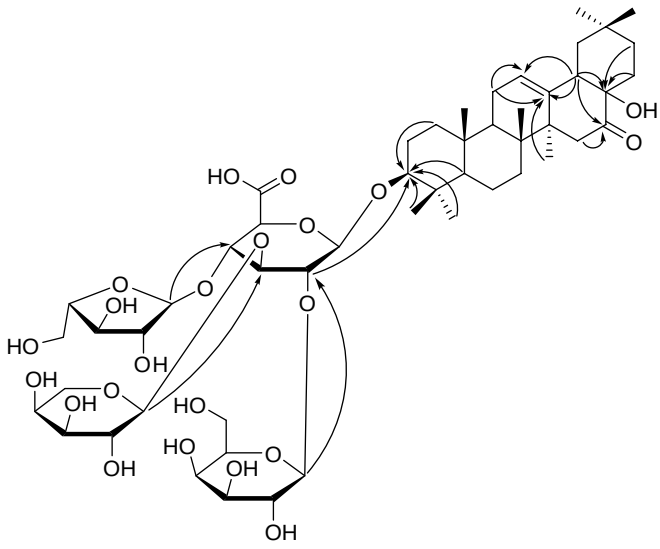

Figure 2. Selected HMBC correlations of compound **1**.

This aglycone moiety was further confirmed by the detailed HMBC analysis (Figure 2). In HMBC spectrum, the correlations of C-17/H-22a, H-22b, H-21a, H-21b, and H-18 suggested that an OH was linked to C-17. And the carbonyl was on C-16 by correlations between C-16 and H-18, H-15a, H-15b. Furthermore, the olefinic bond was located at C-12 and C-13 according to the correlations of C-13/H-11, H-18, H-27, and C-12/H-11, H-18. In addition, the other correlations of C-3 with H-1b, H-5, H-23, and H-24 suggested that C-3 was oxygen methine. On the basis of the foregoing data, **1** was concluded to be 3β,17β-dihydroxy-28-nor-12-oleanen-16-one with four saccharide moieties.

The HMBC correlations between H-1′ (δ_H 4.77, GlcA) and C-3 (δ_C 89.9) of the aglycone, H-1″ (δ_H 5.49, Gal) and C-2′ (δ_C 80.8, GlcA), H-1‴ (δ_H 5.57, Ara) and C-3′ (δ_C 79.6, GlcA), and H-1⁗ (δ_H 6.12, Ara) and C-4′ (δ_C 75.3, GlcA) confirmed that β-D-glucuronopyranosyl, β-D-galactopyranosyl, α-L-arabinopyranosyl, and α-L-arabinofuranosyl were on C-3 of the aglycone, C-2′, C-3′, and C-4′ of glucuronopyranosyl, respectively (Figure 2). So, compound **1** was confirmed as 3β,17β-dihydroxy-28-nor-12-oleanen-16-one 3-*O*-β-D-galactopyranosyl (1 → 2)-{α-L-arabinopyranosyl (1 → 3)-[α-L-arabinofuranosyl (1 → 4)-β-D-glucuronopyranoside]}.

3. Experimental

3.1 General experimental procedures

The optical rotations were measured on a Jasco P-2000 polarimeter. IR spectra were recorded on an IMPACT 400 (KBr) spectrometer. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz), ^{1}H–^{1}H COSY, TOCSY, HSQC, HMBC, and NOESY spectra were run on an INOVA-500 spectrometer with TMS as internal standard, and values are given in ppm (δ). HR-FAB-MS were performed on VG-Autospec-300 mass spectrometer. ESI-MS were recorded on an Agilent 1100 series LC/MSD TOF from Agilent Technologies. Silica gel (200–300 mesh, Qingdao Marine Chemical Company, Qingdao, China) and RP-18 (50 μm, YMC, Kyoto, Japan) were used for column chromatography and silica gel GF-254

(Qingdao Marine Chemical Company, Qingdao, China) for TLC.

3.2 Plant material

The roots of *Symplocos caudata* were collected from Jiangxi province of China in July 2002. The plant material was identified by Prof. Lin Ma. A voucher specimen (No. 0201) has been deposited in the Herbarium of the Department of Medicinal Plants, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing, China.

3.3 Extraction and isolation

The dried roots of *Symplocos caudata* (7.8 kg) were exhaustively extracted with 95% EtOH at reflux. The EtOH extract was then concentrated under reduced pressure to give a residue (333 g) which was suspended in H_2O, and the suspension was then extracted with petroleum ether, EtOAc, and *n*-BuOH. The *n*-BuOH extract was evaporated *in vacuo* to give a residue (122 g) which was chromatographed over silica gel column eluting with $CHCl_3$–MeOH (in gradient) to yield 20 fractions (Frs 1–20). Fraction 5 (0.3 g) was chromatographed over repeated RP-18 column and eluted with H_2O–MeOH (50:50) to give the mixture of compounds **4** and **5**. Fraction 6 (0.5 g) was chromatographed over repeated RP-18 column and eluted with H_2O–MeOH (50:50) to give the mixture of compounds **2** and **3**. Fraction 4 (0.3 g) was chromatographed over repeated RP-18 column and eluted with H_2O–MeOH (70:30) to give compound **1** (12 mg).

*3.3.1 3β,17β-Dihydroxy-28-nor-12-oleanen-16-one 3-O-β-D-galacto-pyranosyl (1 → 2)-{α-L-arabinopyranosyl (1 → 3)-[α-L-arabinofuranosyl (1 → 4)-β-D-glucuronopyranoside]} (**1**)*

White powder; $[\alpha]_D^{25}$ −33.3 ($c = 0.06$, MeOH); IR (KBr) ν_{max}: 3371, 2945, 1707, 1655, 1606, 1421, 1390, 1365, 1078, 1049, 783 cm^{-1}; ^1H NMR (500 MHz, pyridine-d_5) and ^{13}C NMR (125 MHz, pyridine-d_5) spectral data: see Table 1; ESI-MS: *m/z* 1067 $[M + Na]^+$; HR-FAB-MS: *m/z* 1089.4887 $[M + 2Na - H]^+$ (calcd for $C_{51}H_{79}O_{22}Na_2$, 1089.4858).

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References

[1] Editor Committee of Quan Guo Zhong Cao Yao Hui Bian, *Quan Guo Zhong Cao Yao Hui Bian* (People's Health Press, Beijing, 1992), Vol. 2, p. 801.
[2] J.S. Jiang, Z.M. Feng, Y.H. Wang, and P.C. Zhang, *Chem. Pharm. Bull.* **53**, 110 (2005).
[3] A.K. Nandy, G. Podder, N.P. Sahu, and S.B. Mahato, *Phytochemistry* **28**, 2769 (1989).
[4] T. Seto, T. Tanaka, O. Tanaka, and N. Naruhashi, *Phytochemistry* **23**, 2829 (1984).
[5] F. Abe and T. Yamauchi, *Chem. Pharm. Bull.* **35**, 1833 (1987).
[6] S.B. Mahato and A.P. Kundu, *Phytochemistry* **37**, 1517 (1994).
[7] Y. Masayuki, M. Toshio, F. Emi, O. Teruki, A. Yasunobu, and M. Hisashi, *Heterocycles* **55**, 1653 (2001).