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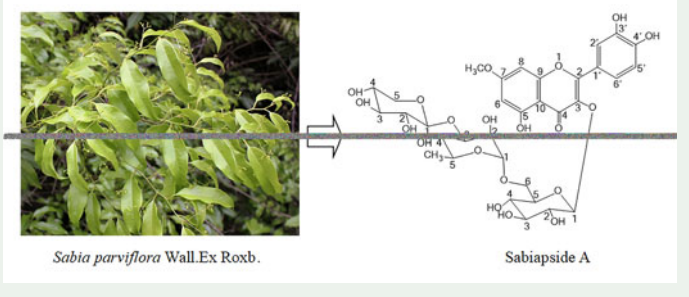
Isolation and structure elucidation of a new flavonol glycoside from *Sabia Parviflora*

Qingwen Sun, Guoji Pan, Wenfen Xu, Xian Lu, Caihong Bai, Mengge Liu and Yinrui Chen

College of Pharmacy, Guizhou University of Traditional Chinese Medicine, Guiyang, China

ABSTRACT

A new flavonol glycoside named Sabiapside A (**1**), along with four known compounds, quercetin-*3*-*O*-gentiobioside (**2**), camelliano-side (**3**), isobariclisin-*3*-*O*- rutinoside (**4**), tsubakioside A (**5**), was isolated from *Sabia parviflora*. Their structures were elucidated by extensive spectroscopic analysis including MS, UV, IR and NMR data. The antioxidant activities of these glycosides evaluated by $ABTS^{+}$ and DPPH radical scavenging reaction was higher than that of vitamin C used as the reference antioxidant.



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KEYWORDS
Sabia parviflora; flavonol glycoside; antioxidant; DPPH; ABTS+

1. Introduction

Sabia parviflora Wall. Ex Roxb. (Sabiaceae) is an evergreen vine widely distributed in Yunnan, Guizhou and Guangxi in China (ECFC 1988) which has been traditionally used as folk medicine to treat icteric hepatitis, rheumatism and inflammation (Wen et al. 2016). Previous studies showed structurally diverse compounds had been isolated from *S. parviflora*, including alkaloids (Fan, Wang, et al. 2018; Sui et al. 2011), flavonoids (Huang et al. 2014) and pentacyclic triterpenes (Chen et al. 2015; Fan, Li, et al. 2018), with flavonoids being the major bioactive phytochemical constitution (Pan et al. 2018). It was reported that *S. parviflora* showed various pharmacological activities such as hepatoprotective (Liu et al. 2008; Yang et al. 2013), antiviral (Qu et al. 2015) and anti-inflammatory (Wang et al. 2018). The investigation on *S. parviflora* by our group

CONTACT Qingwen Sun sqw1978_2006@126.com; Wenfen Xu wenfenxu@126.com
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led to the isolation of a new flavonol glycoside named Sabiapside A (**1**) and four known compounds, quercetin-3-*O*-gentiobioside (**2**) (Liu et al. 2008), camellianoside (**3**) (Onodera et al. 2006), isobariclisin-3-*O*-rutinoside (**4**) (Shen et al. 2013) and tsubakioside A (**5**) (Sato et al. 2017). Herein, we report the isolation, structure identification and antioxidant activities of all isolated compounds.

2. Results and discussion

2.1. Elucidation of the chemical structure of compounds

Compound **1** was obtained as amorphous yellow powder, positive to Molish reagent. The molecular formula $C_{33}H_{40}O_{20}$ was established on basis of its HR-ESI-MS at *m/z* 755.2043 $[M\text{-}H]^-$, corresponding to fourteen degrees of unsaturation. The IR spectrum clearly indicated the presence of hydroxyl groups (3386 cm^{-1}), aromatic rings (1596 and 1499 cm^{-1}) and carbonyl groups (1653 cm^{-1}). The UV spectrum suggested that it was a flavonoid with absorption maxima at 203, 257 and 356 nm. ^1H NMR spectrum indicated five aromatic protons at δ_H 7.71 (1H, d, $J = 2.2$ Hz), 7.64 (1H, dd, $J = 8.5$, 2.2 Hz), 6.87 (1H, d, $J = 8.5$ Hz), 6.54 (1H, d, $J = 2.2$ Hz) and 6.30 (1H, d, $J = 2.2$ Hz), together with three anomeric protons of saccharide moieties at δ_H 5.13 (1H, d, $J = 7.8$ Hz), 4.52 (1H, d, $J = 1.7$ Hz) and 4.33 (1H, d, $J = 7.6$ Hz), and six methyl protons at δ_H 3.86 (3H, s) and 1.10 (3H, d, $J = 6.0$ Hz). Proton signals of saccharide moieties at δ_H 3.09 to 3.84 were overlapped. ^{13}C NMR and DEPT spectra exhibited 33 carbon signals corresponding to 10 quaternary carbons, 19 methines, two methylenes and two methyls. Among these carbon resonances, 15 of them were assigned to the quercetin skeleton (Onodera et al. 2006) and three carbon signals at δ_C 106.4 (C-1 of the xylose), 104.5 (C-1 of the glucose), 102.3 (C-1 of the rhamnose) were attributed to anomeric carbons of the sugar moieties. Detailed analysis of the spectral data above revealed that compound **1** was similar to compound **3,** camellianoside (Onodera et al. 2006). What **1** differed from **3** was that **1** had one more methoxy than **3**. HMBC Correlation from methoxy protons (δ_H 3.86) to C-7 (δ_C 167.3) suggested that methoxy was substituted at C-7. HMBC correlations of H-6/C-5, C-7, C-8, C-10; H-8/C-7, C-9, C-10; H-2′/C-2; H-5′/C-1′; and H-6′/C-2 indicated that hydroxyl groups were located at C-5, C-7, C-3′ and C-4′, respectively. Acid hydroysis of **1** with 2 $_M$ HCl yielded an aglycone and sugar components. The sugars of **1** were finally identified as D-glucose, L-rhamnose and D-xylose based on specific rotations. Interglycosidic linkages were confirmed by HMBC correlations of H-1-Glc/C-3; H-1-Rha/C-6-Glc and H-1-Xyl/C-3-Rha. The β-glycosidic linkages of the glucopyranoside and xylopyranoside units were determined on the basis of the $J_{1,2}$ values for the anomeric protons of 7.8 and 7.6 Hz, respectively, and the α-linkage of the rhamnopyranoside unit on the basis of the $^1J_{CH}$ value for the anomeric position of 168 Hz calculated from HMBC spectrum (Podlasek et al. 1995). Thus, the structure of compound **1** was identified as 7-methoxy-quercetin-3-*O*-β-*D*-xylopyranosyl (1→3)-*O*-α-*L*-rhamnopyranosyl-(1→6)-*O*-β-*D*-glucopyranoside, to which we gave the trivial name Sabiapside A.

Additionally, the structures of compounds **2–5** were determined by comparison of their spectroscopic data with those reported in the literature.

2.2. Results of the antioxidant assay

All compounds exhibit highter antioxidant activities for $ABTS^+$ and DPPH with IC_{50} values in the range of 2.88 ~ 5.78 μg/mL and 2.41 ~ 7.95 μg/mL, respectively, in comparison with the positive control vitamin C with IC_{50} values of 7.14 μg/mL for $ABTS^+$ and 15.88 μg/mL for DPPH *in vitro*.

3. Experimental

3.1. Apparatus and reagents

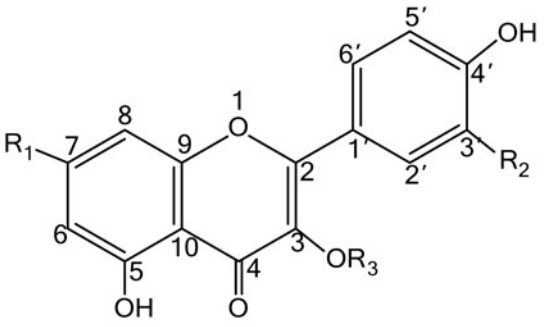
The 1 D and 2 D NMR spectra were recorded on Bruker AM-600 spectrometer with TMS as an internal standard (Bruker, Germany). Mass spectra were collected on a Waters AutoSpec Premier P776 instrument (Waters, USA). IR (KBr) spectra were acquired on a Thermo Antaris II spectrometer (Thermo, USA). Semi-preparative HPLC was carried out on an Agilent 1100 HPLC system with Agilent Eclipse XDB-C18 column (9.4 × 250 mm, 5 μm) (Agilent, USA). Optical Rotations were tested on AUTOPOL1-Digital Automatic Polarimeter (Rudolph, USA). Melting points were determined on a SGW X-4B Microscopic melting point meter (Shanghaijingke, China). Column chromatography was performed on self-packed column with D-101 macroporous (Shanghai, China), polyamide (100-200 mesh, Zhejiang, China), ODS-A-HG (50 μm, 12 nm, MC, Japan) or silica gel (200-300 mesh, Qingdao, China). Antioxidant activity was determined by BioTek Synergy two enzyme standard instrument (BioTek, USA). 2,2′-azinobis (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) and 2,2′-dipheny1(l)-1-picrylhydrazyl (DPPH) were purchased from Sigma (Sigma, USA). Potassium persulfate ($K_2S_2O_8$) was purchased from Pharmacia Fine Chemical (Pharmacia, USA). Vitamin C was purchased from National Institutes for Food and Drug Control (Beijing, China).

3.2. Plant material

The plants of *S. parviflora* were collected from Zhenning County, Guizhou Province, China, in June 2017, and identified by Prof. Qing-wen Sun, College of Pharmacy, Guizhou University of Traditional Chinese Medicine, where a voucher specimen (No. 170620) was deposited.

3.3. Extraction and isolation

The air-dried and powdered stems and leaves of *S. parviflora* (10.8 kg) were extracted with MeOH (60 L) three times. MeOH was removed under reduced pressure to give 1.2 kg of crude exract, which was suspended in H_2O (2 L), and then subjected to macroporous column chromatography eluted with H_2O/MeOH (100:0→75:25→30:70→0:100) to yield three fractions (A-C). Fr. B (167 g) was subjected to silica gel column chromatography eluted with dichloromethane/MeOH (10:1) to afford Fr. B1 and Fr. B2. Fr. B1 (8.6 g) was chromatographed over silica gel eluting with dichloromethane/MeOH (20:1→20:4) and further purified by Semi-preparative HPLC with H_2O/



	R_1	R_2	R_3
1:	OCH_3	OH	glu-rha-xyl
2:	OH	OH	glu-glu
3:	OH	OH	glu-rha-xyl
4:	OH	OCH_3	glu-rha
5:	OH	H	glu-rha-xyl

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

MeOH (40:60) to afford compound **4** (62 mg). Fr. B2 (1.6 g) was subjected to an ODS-A-HG column (H_2O/MeOH = 3:7) to afford Fr. B2-1 and Fr. B2-2. Fr. B2-1 (310 mg) was further purified by Semi-preparative HPLC with H_2O/MeOH (40:60) to provide compound **5** (89 mg), Fr. B2-2 (790 mg) was further purified by Semi-preparative HPLC with H_2O/MeOH (50:50) to provide compound **1** (210 mg), **2** (59 mg) and **3** (153 mg), (Figure 1).

Sabiapside A, Yellow amorphous powder, [α]14 D -0.02 ($c = 4.98$, MeOH). Mp. 242 ~ 244 °C. HR-ESI-MS *m/z* 779.1998 $[M + Na]^+$ (calcd for $C_{33}H_{40}O_{20}Na$: 779.2005), 755.2043 $[M\text{-}H]^-$ (calcd for $C_{33}H_{40}O_{20}$: 755.2029). UV (MeOH): λ_{max} 203.33, 257.08 and 355.88 nm. IR (KB) ν_{max} cm^{-1}: 3386, 2931, 1750, 1653, 1596, 1499, 1446, 1303, 1209, 1165, 1042, 885, 809, 612. ^{1}H-NMR (600 MHz, CD_3OD): δ 7.71 (1H, d, $J = 2.2$ Hz, H-2′), 7.64 (1H, dd, $J = 8.5$, 2.2 Hz, H-6′), 6.87 (1H, d, $J = 8.5$ Hz, H-5′), 6.54 (1H, d, $J = 2.2$ Hz, H-8), 6.30 (1H, d, $J = 2.2$ Hz, H-6), 5.13 (1H, d, $J = 7.8$ Hz, H-1-Glc), 4.52 (1H, d, $J = 1.7$ Hz, H-1-Rha), 4.33 (1H, d, $J = 7.6$ Hz, H-1-Xyl), 3.86 (3H, s, OCH_3), 3.82 (1H, overlapped, H-6a-Glc), 3.79 (1H, overlapped, H-2-Rha), 3.75 (1H, overlapped, H-5a-Xyl), 3.56 (1H, overlapped, H-3-Rha), 3.50 (1H, overlapped, H-2-Glc), 3.47 (1H, overlapped, H-5-Rha), 3.47 (1H, overlapped, H-4-Xyl), 3.43 (1H, overlapped, H-3-Glc), 3.42 (1H, overlapped, H-4-Rha), 3.41 (1H, overlapped, H-6b-Glc), 3.39 (1H, overlapped, H-5-Glc), 3.33 (1H, overlapped, H-3-Xyl), 3.24 (1H, overlapped, H-4-Glc), 3.23 (1H, overlapped, H-2-Xyl), 3.12 (1H, overlapped, H-6a-Xyl), 1.10 (3H, d, $J = 6.0$ Hz, H-6-Rha); ^{13}C-NMR (150 MHz, CD_3OD): δ 179.4 (C-4), 167.3 (C-7), 162.6 (C-5), 159.6 (C-2), 158.4 (C-9), 149.9 (C-4′), 145.8 (C-3′), 135.8 (C-3), 123.6 (C-6′), 123.0 (C-1′), 117.9 (C-2′), 116.0 (C-5′), 106.5 (C-10), 106.4 (C-1-Xyl), 104.5 (C-1-Glc), 102.3 (C-1-Rha), 99.2 (C-6), 93.3 (C-8), 82.5 (C-3-Rha),

78.2 (C-3-Glc), 77.5 (C-3-Xyl), 77.2 (C-5-Glc), 75.7 (C-2-Glc), 75.3 (C-2-Xyl), 72.7 (C-4-Rha), 71.7 (C-2-Rha), 71.6 (C-4-Glc), 71.1 (C-4-Xyl), 69.4 (C-5-Rha), 68.9 (C-6-Glc), 66.8 (C-5-Xyl), 56.5 (7-OCH_3), 17.9 (C-6-Rha).

3.4. Hydrolysis experiment

Compound **1** (100 mg) was hydrolyzed by 2 $_M$ HCl solution 5 h under room temperature. The hydrolysate was neutralized by NaOH and then subjected to polyamide column chromatography eluted with EtOAc/EtOH/acetic acid/H_2O (10:5:1:1) to obtain glucose, rhamnose and xylose confirmed by TLC. Configurations of these sugars were determined as D-glucose, L-rhamnose and D-xylose based on the specific rotation values of $+51.5^\circ$, $+8.1^\circ$ and $+18.4^\circ$, respectively.

3.5. Antioxidant activity assay

All compounds were evaluated their ability to scavenge the DPPH radical and $ABTS^+$ radical cation according to previously reported methods (Yang et al. 2014) with some modifications. Vitamin C was used as a positive control. The $ABTS^+$ radical was prepared by mixing equal volume of 7 mM ABTS water solution and 2.45 mM potassium persulfate, and the mixture was reacted in dark at room temperature for 12 h before use. Prior to the assay, the solution was diluted in water to give an absorbance at 734 nm of 0.70 ± 0.02. The DPPH radical solution was diluted with ethanol in dark to an absorbance of 0.70 ± 0.02 at 516 nm. After reacting with the $ABTS^+$ radical solution for 10 min (DPPH radical solution for 30 min), the absorbance value (A_i) of $ABTS^+$ at 734 nm (or A_i of DPPH at 516 nm) was measured. The blank absorbance (A_0) was measured using ethanol. The scavenging activity was determined according to the following equation: $AA(\%) = [A_0 - A_i]/A_0 \times 100\%$.

4. Conclusion

Five flavonol glycosides, Sabiapside A (**1**), quercetin-*3-O*-gentiobioside (**2**), camellianoside (**3**), isobariclisin-*3-O*- rutinoside (**4**) and tsubakioside A (**5**), were isolated from *Sabia parviflora* for the frst time. The antioxidant activities of these glycosides evaluated by $ABTS^+$ and DPPH radical scavenging reaction was higher than that of vitamin C used as the reference antioxidant. The structure-activity relationship of these compounds showed that phenolic hydroxyl could contribute to the antioxidant activity.

Disclosure statement

No potential conflict of interest was reported by the authors.

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