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A new catechin derivative from the fruits of *Rosa sterilis*

S. D. Shi

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ABSTRACT

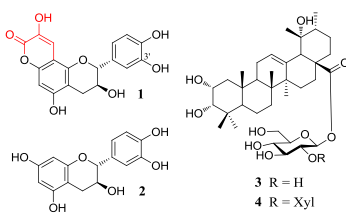
A new catechin derivative named as sterilin A (**1**), and three known compounds, (+)-catechin (**2**), kaji-ichigoside F1 (**3**) and 2 α ,3 α ,19 α -trihydroxyurs-12-en-28-oic acid-28-O- β -D-xylopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside (**4**), was isolated from the fresh fruits of *Rosa sterilis*. Their structures were elucidated by means of extensive spectroscopic analysis and by comparison with data reported in the literatures.

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KEYWORDS


Rosa sterilis; fruits; catechin derivative; sterilin A



1. Introduction

Rosa sterilis S. D. Shi (Rosaceae) is a perennial shrub distributed in the karst areas of Guizhou province, China, which was firstly described by S. D. Shi (1985). It has a very close genetic relationship to *R. roxburghii* Tratt., based on RAPD and AFLP molecular markers (Wen & Deng 2003; Wen et al. 2004; Li et al. 2015), and originates from a hybrid of *R. longicuspis* Bertol. and *R. roxburghii* Tratt. (Deng et al. 2015). As a tonic, the fruits of *R. sterilis* alone or mixed with the fruits of *R. roxburghii* have been used in the food industry to produce fruit wine, beverage and preserved fruits due to their similar taste and production from the same region. To date, some ingredients such as triterpenes (Liang et al. 1989), essential oils (Fu et al. 2012; Jiang et al. 2013; Wu et al. 2014b), nutrition components (Wu et al. 2014a; Zhang et al. 2016a), amino acids (Lu et al. 2015) and trace elements (Zhang et al. 2016b) in *R. sterilis* fruits have been identified. However, the phytochemical studies on *R. sterilis* are very limited (Liang et al. 1989; Liu et al. 2016). In this study, a new catechin derivative named as sterilin A (**1**),

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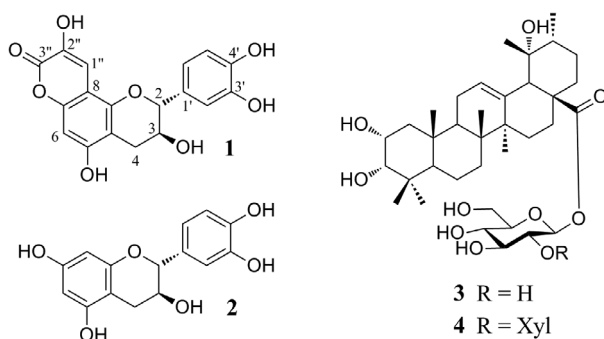


Figure 1. Structures of compounds 1–4 from the fruits of *R. sterilis*.

together with three known compounds (2–4) (Figure 1), has been isolated from the fresh fruits of *R. sterilis* S. D. Shi. Herein, we report the isolation and structure elucidation of these compounds.

2. Results and discussion

Compound **1** was obtained as a pale amorphous powder. It possesses a molecular formula $C_{18}H_{14}O_8$, as established by the negative HR-ESI-MS (m/z 357.0618 calcd for $[M - H]^-$, 357.0616) (Figure S1), corresponding to 12 degrees of hydrogen unsaturation. In the ^{13}C NMR spectrum (Figure S2), 18 carbon signals were observed, referring to 1 aliphatic methylene (δ_c 28.0), 5 aromatic methines (δ_c 119.7, 116.4, 114.9, 113.2, 95.2), 2 aliphatic oxymethines (δ_c 83.2, 68.2) and 10 sp^2 quaternary carbons, with 7 oxygen-bearing ones (δ_c 162.0, 157.9, 151.3, 151.2, 146.6, 146.5, 139.2). In the 1H NMR spectrum (Figure S3) of **1**, an ABX-coupled system [δ_H 6.83 (1H, br s, H-2'), δ_H 6.78 (1H, d, $J = 8.1$ Hz, H-5'), δ_H 6.72 (1H, br d, $J = 8.1$ Hz, H-6')], corresponding to the carbons at δ_c 114.9 (C-2'), δ_c 116.4 (C-5') and δ_c 119.7 (C-6') (Figure S4), indicated the presence of a 1,3,4-trisubstituted benzene ring. Moreover, two aliphatic methylene protons at δ_H 2.86 (1H, dd, $J = 16.8, 4.8$ Hz, H-4b), 2.64 (1H, dd, $J = 16.8, 7.2$ Hz, H-4a), and two oxymethine protons at δ_H 4.83 (1H, d, $J = 6.6$ Hz, H-2), 4.10 (1H, br q, $J = 6.6$ Hz, H-3), suggested **1** to be a catechin derivative. The 1H and ^{13}C NMR spectra of **1** were closely related to those of (+)-catechin (**2**) (Seto et al. 1997), except for the appearance of three additional carbon signals, referring to an ester carbonyl (δ_c 162.0), an oxygen-bearing quaternary carbon (δ_c 139.2) and an olefinic carbon (δ_H 7.20, δ_c 113.2), arising from a $HC=C(OH)-C(=O)$ moiety. In addition, one aromatic methine signal in A-ring of **2** was replaced by an aromatic quaternary carbon (δ_c 103.9) in **1**, suggesting that the additional $HC=C(OH)-C(=O)$ moiety was linked with A-ring of **1**.

The structure of **1** was further confirmed by the HMBC experiment (Figure S5). In the HMBC spectrum of **1**, correlations of the additional olefinic proton at δ_H 7.20 (H-1'') with C-7 (δ_c 151.3), C-9 (δ_c 151.2), C-2'' (δ_c 139.2) and C-3'' (δ_c 162.0) (Figure S6) indicated that the additional $HC=C(OH)-C(=O)$ moiety linked with C-8 of A-ring and formed a lactone with C-7 hydroxy group in **1**. Moreover, HMBC correlations of H-2 (δ_H 4.83) with C-9, C-1' (δ_c 131.2), C-3 (δ_c 68.2) and C-4 (δ_c 28.0), H-4 (δ_H 2.86, 2.64) with C-9, C-5 (δ_c 157.9), C-10 (δ_c 106.3), C-2 (δ_c 83.2) and C-3 and H-6 (δ_H 6.36) with C-5, C-7, C-8 and C-10 confirmed the planar structure of **1**.

The stereochemistry of **1** was established by the coupling constants observed in the ^1H NMR and circular dichroism (CD) spectra. The values of $J_{2,3}$ (6.6 Hz) and $J_{3,4}$ (7.2, 4.8 Hz) of **1** supported *trans* orientations for H-2 and H-3 (Fan et al. 1999). In CD experiment, compounds **1** and **2** showed the same negative sign at 280 nm ($\Delta\epsilon$ -1.35 for **1**, -1.26 for **2**) supporting the 2*R*,3*S*-configuration in **1** and **2** since flavan-3-ols with a 2*R*-configuration produces a negative Cotton effect at 280 nm while the 2*S*-configuration shows a positive sign (Slade et al. 2005; Tao et al. 2014). Therefore, the structure of compound **1** was established as shown in Figure 1, and named sterilin A.

The known compounds were identified by comparison of their ESI-MS and NMR spectroscopic data with those reported in the literatures as (+)-catechin (**2**) (Seto et al. 1997), kaji-ichigoside F1 (**3**) (Seto et al. 1984) and 2 α ,3 α ,19 α -trihydroxyurs-12-en-28-oic acid-28-*O*- β -D-xylopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside (**4**) (Zhou et al. 2013). All of them were reported from *R. sterilis* for the first time.

3. Experimental

3.1. General

Optical rotations were measured on a P-1020 Polari meter (JASCO, Tokyo, Japan). UV spectra were obtained on a 210A double-beam spectrophotometer (Shimadzu, Kyoto, Japan). 1D and 2D NMR (COSY, HSQC, HMBC) spectra were recorded in CD₃OD with Varian Gemini 300 spectrometers operating at 600 MHz for ^1H , and 150 MHz for ^{13}C , respectively. Coupling constants (J) were expressed in Hz, and chemical shifts were given on a δ (ppm) scale. ESI-MS was recorded on a JEOL JMS DX-303 spectrometer. CD spectra were measured on a Chirascan spectropolarimeter, using 1-mm cell. Column chromatography was performed with MCI-gel CHP20P (Mitsubishi Chemical Corporation), Sephadex LH-20 (GE Healthcare) and Toyopearl WH40F (Beijing). TLC was performed on GF₂₅₄ (Qingdao), and spots were detected by UV illumination and by spraying with 2% ethanolic FeCl₃ and 10% sulphuric acid reagent, followed by heating.

3.2. Plant material

The fresh fruits of *R. sterilis* were collected from Xingren, Guizhou Province, China, in October 2014, and identified by Prof. Yong-He Li. The voucher specimen (SWFU No. 1400792) of the plant used for this study was deposited in the Herbarium of Southwest Forestry University, Kunming City, Yunnan Province, China.

3.3. Extraction and isolation

The fresh fruits of *R. sterilis* (15.4 kg) were exhaustively extracted with 80% EtOH (25 L \times 4) at room temperature by maceration. After filtration, the extract was concentrated under reduced pressure at 45°C until the EtOH was removed, and then the aqueous solution (2.4 L) was partitioned with petroleum ether and EtOAc successively.

The EtOAc extract (48.5 g) was separated to 10 fractions (Fr.1-Fr.10) by Sephadex LH-20 column chromatography (CC, 4.5 \times 70 cm), eluted with a stepwise gradient solvent system of H₂O/MeOH (1:0–0:1, v/v). Fr.4 (1.2 g) was further fractionated on Sephadex LH-20 CC

(3 × 60 cm) eluting with H₂O/MeOH (1:0–0:1, v/v) to give six fractions (Fr.4-1–Fr.4-6). Fr.4-1 (230.7 mg) was purified repeatedly by MCI gel CHP20P CC (2 × 50 cm) eluted with H₂O/MeOH (1:0–0:1, v/v) to yield **3** (11 mg) and **4** (1.5 mg). Fr. 5 (3.6 g) was subjected to Sephadex LH-20 column (3 × 60 cm) eluted with H₂O/MeOH (1:0–0:1, v/v) to give seven fractions (Fr.5-1–Fr.5-7), and then Fr.5-6 (73 mg) was further chromatographed over Sephadex LH-20 (1 × 40 cm) eluted with H₂O/MeOH (1:0–0:1, v/v), and Fraction 5-6-3 (66 mg) was further purified on a MCI-gel CHP20P (1 × 40 cm) eluting with H₂O/MeOH (1:0–0:1, v/v) to give **1** (1.1 mg). Fr.6 (3.7 g) was subjected to Sephadex LH-20 (4 × 50 cm) eluted with 100% EtOH to give seven fractions (Fr.6-1–Fr.6-7), and then Fr.6-3 (661 mg) was further purified by MCI-gel CHP20P (3 × 50 cm) and Toyopearl HW40F (3 × 40 cm) CC, eluting with H₂O/MeOH (1:0–0:1, v/v) to give **2** (60 mg).

3.4. Spectroscopic data

Compound **1**: a pale amorphous powder, $[\alpha]_D^{19.5} = -91.6$ ($c = 0.0015$, MeOH); UV (MeOH) λ_{\max} (log ϵ) 207 (4.68), 272 (3.92), 356 (3.85) nm; CD (MeOH) nm ($\Delta\epsilon$): 200 (+22.99), 219 (–12.13), 280 (–1.35); ESI⁺-MS m/z : 358 [M]⁺; ESI[–]-MS m/z : 357 [M – H][–], HR-ESI[–]-MS m/z : 357.0618 [M (C₁₈H₁₄O₈) – H][–] (calcd 357.0616). ¹H NMR (600 MHz, CD₃OD): δ_H 7.20 (1H, s, H-1''), 6.83 (1H, br s, H-2'), 6.78 (1H, d, $J = 8.1$ Hz, H-5'), 6.72 (1H, br d, $J = 8.1$ Hz, H-6'), 6.36 (1H, s, H-6), 4.83 (1H, d, $J = 6.6$ Hz, H-2), 4.10 (1H, br q, $J = 6.6$ Hz, H-3), 2.86 (1H, dd, $J = 16.8, 4.8$ Hz, H-4b), 2.64 (1H, dd, $J = 16.8, 7.2$ Hz, H-4a). ¹³C NMR (150 MHz, CD₃OD): δ_C 162 (s, C-3''), 157.9 (s, C-5), 151.3 (s, C-7), 151.2 (s, C-9), 146.6 (s, C-4'), 146.5 (s, C-3'), 139.2 (s, C-2''), 131.2 (s, C-1'), 119.7 (d, C-6'), 116.4 (d, C-5'), 114.9 (d, C-2'), 113.2 (d, C-1''), 106.3 (s, C-10), 103.9 (s, C-8), 95.2 (d, C-6), 83.2 (d, C-2), 68.2 (d, C-3), 28.0 (t, C-4).

4. Conclusion

In this study, a new catechin derivative named sterilin A (**1**), together with three known compounds, (+)-catechin (**2**), kaji-ichigoside F1 (**3**) and 2 α ,3 α ,19 α -trihydroxyurs-12-en-28-oic acid-28-O- β -D-xylopyranosyl-(1 → 2)- β -D-glucopyranoside (**4**), has been isolated from the fresh fruits of *R. sterilis* for the first time. Compound **1** was supposed to be biosynthesised by the complex condensation of (+)-catechin (**2**) with lactic acid contained in the fruits (Liu et al. 2016), and its formation mechanism is great of interest. (+)-Catechin (**2**) was reported as one of the major phenolic constituents in green tea, and showed various significant bio-activities, e.g. neuroprotection, anti-oxidant, anti-inflammatory, antitumor and antihepatitis activities (Syed Hussein et al., 2015). The known ursane-type triterpene 28-O-monoglycosyl ester, kaji-ichigoside F1 (**3**), showed *in vivo* hepatoprotective effect by the reduction in cytotoxicity caused by D-galactosamine (Morikawa et al., 2014). Both compounds in the fruits of *R. sterilis* indicated that the fruit is a good material for food industry and supported local uses.

Supplementary material

Supplementary materials relating to this article are available online, alongside Figures S1–S6.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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