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# New steroidal glycoside ester and aliphatic acid from the fruits of *Lycium chinense*

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Two new compounds stigmast-5-en-3β-ol-3-*O*-β-D-(2′-*n*-triacontanoyl) glucopyranoside (**1**) and 19,21-dimethyl triacont-17,22,24,26,28-pentaene-1-oic acid (**2**), along with the three known compounds *n*-tetracosanyl octadec-9-enoate (**3**), β-sitosterol, and β-sitosterol-3-*O*-β-D-glucoside, have been isolated from the methanol extract of *Lycium chinense* fruits. The structures of these phytoconstituents have been established on the basis of spectral data analysis and chemical reactions.

**Keywords:** *Lycium chinense*; Solanaceae; fruits

## 1. Introduction

*Lycium chinense* Miller fruits (Fructus Lycii) known as 'Gou-Qi-Zi' in Chinese have long history of application as a valuable tonic and health food supplement for improving vision and maintaining good health. It is reputed to have the properties of nourishing the blood, enriching the yin, tonifying the kidney and liver, moistening the lungs [1,2]. Fruits of *L. chinense* (Solanaceae), distributed in northeast Asia, especially China, Japan, Korea, and Taiwan, have been widely used as a tonic in traditional medicine. Potentially isolated constituents were reported to exhibit hypotensive, hypoglycemic, and antipyretic activities [3,4]. Several compounds such as cerebrosides and lyciumamide in this plant are known to display various bioactivities [5,6]. Potentially hepatoprotective glycolipid constituents and determination of betain in *L. chinense* fruits have been reported [7,8]. Antimicrobial compounds have also been reported from *L. chinense* roots [9]. Specific α-galactosidase inhibitors and N-methylcalystegines structure/activity relationship of calystegines from *L. chinense* have been reported [10]. The plant is reported to possess antibacterial, anticancer, and antioxidant properties [9,11,12]. Antihepatotoxic activity and chemical constituents from *L. chinense* fruits have been reported [5,13].

Several compounds such as cyclic peptides, acyclic diterpene glycosides, and other compounds from *L. chinense* [14], and glycoconjugates from *Lycium barbarum* have been reported [15]. Variation in fruit sugar composition of *L. barbarum* and *L. chinense* of different regions and varieties was also reported [16]. Evaluation of antioxidant and other activities of compounds from *L. barbarum* and *L. chinense* has also been reported [17,18]. Due to significance of fruits of this plant in medicinal use, the work in this area has already been done. The aim of the present investigation was to report some of the new findings in the form of natural

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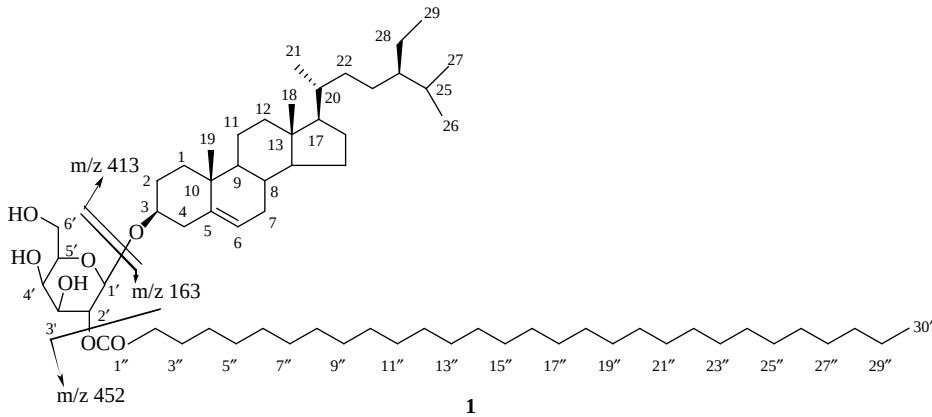
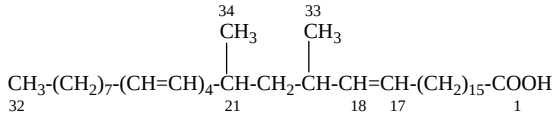



**1**

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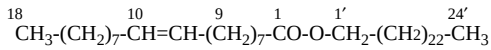


**3**

Figure 1. Chemical structures and fragmentation pattern of compounds **1** and **2**.

products from the fruits of *L. chinense*. This paper describes the isolation and characterization of two new compounds stigmast-5-en-3β-ol-3-*O*-β-D-(2′-*n*-triacontanoyl) glucopyranoside (**1**) and 19,21-dimethyl triacont-17,22,24,26,28-pentaene-1-oic acid (**2**), along with three known compounds *n*-tetracosanyl octadec-9-enoate (**3**), β-sitosterol, and β-sitosterol-3-*O*-β-D-glucoside from the fruits of *L. chinense*. Compound **3** has been reported for the first time in *L. chinense* fruits.

## 2. Results and discussion

Compound **1** was obtained as colorless crystalline mass from $CHCl_3$:MeOH eluants (9:1). It responded positively to steroidal glycosides. Its IR spectrum showed characteristic absorption bands for hydroxyl groups (3430, 3350 $cm^{-1}$), ester function (1736 $cm^{-1}$), and unsaturated C=C double bond (1645 $cm^{-1}$). On the basis of FAB mass and $^{13}C$ NMR spectra, the molecular ion peak was determined at *m/z* 1011 $[M + H]^+$ consistent with the molecular formula of a steroidal glycosidic ester $C_{65}H_{119}O_7$. The ion fragments generated at *m/z* 452 $[CH_3(CH_2)_{28}\ COOH]^+$ and 413 $[C_{29}H_{49}O]^+$ indicated that *n*-triacontanoic acid was involved in steryl glycoside. The ion peaks arising at *m/z* 180 $[C_6H_{12}O_6]^+$ and 163 $[C_6H_{11}O_5]^+$ supported the attachment of $C_6$-sugar to steroidal skeleton. The fragmentation pattern of compound **1** is shown in Figure 1.

The $^1H$ NMR spectrum of **1** showed one-proton doublets at δ 5.35 ($J = 3.8$ Hz) and 4.49 ($J = 7.5$ Hz) assigned to vinylic H-6 and anomeric H-1′ protons, respectively. A one-proton broad multiplet at δ 4.03 with half-width of 18.5 Hz was ascribed to oxygenated methine H-3α proton. A one-proton multiplet at δ 3.85, three one-proton multiplets at δ 3.70, 3.52, and 4.01, and two one-proton doublets at δ

3.18 ($J = 8.4$ Hz) and 3.15 ($J = 7.8$ Hz) were attributed to the sugar protons H-2′, H-3′, H-4′, H-5′, and $H_2$-6′, respectively. Two one-proton doublets at $\delta$ 2.33 ($J = 7.5$ Hz) and 2.30 ($J = 7.5$ Hz) were due to methylene $H_2$-2″ protons adjacent to the ester group. Two three-proton broad signals at $\delta$ 0.67 and 1.01 and three doublets at $\delta$ 0.92 ($J = 6.2$ Hz), 0.87 ($J = 6.7$ Hz), and 0.85 ($J = 6.5$ Hz) integrating for three protons each were accounted to tertiary C-18 and C-19 and secondary C-21, C-26, and C-27 methyl protons, respectively. Two three-proton triplets at $\delta$ 0.82 ($J = 5.9$ Hz) and 0.80 ($J = 5.4$ Hz) were due to C-29 and C-30″ primary methyl protons. The remaining methine and methylene protons appeared from $\delta$ 2.37 to 1.16. The $^{13}$C NMR spectrum of **1** displayed signals for ester carbon at $\delta$ 175.0 (C-1″), vinylic carbons at $\delta$ 141.2 (C-5) and 122.7 (C-6), oxygenated methine carbon at $\delta$ 77.0 (C-3), anomeric carbon at $\delta$ 102.0 (C-1′), other sugar carbons from $\delta$ 77.5 to 62.5, and methyl carbons between $\delta$ 20.2 and 12.3. The $^{13}$C NMR spectral data of the steroidal nucleus were compared with the reported values of sitosterol and its derivatives [19–22]. The presence of H-2′ signal in the $^1$H NMR spectrum at $\delta$ 3.85 and C-2′ in the $^{13}$C NMR spectrum at $\delta$ 79.7 suggested the attachment of the ester moiety at C-2′. The $^1$H–$^1$H COSY spectrum of **1** showed correlations of H-3 with $H_2$-1, $H_2$-2, $H_2$-4, and H-1′; H-6 with $H_2$-4, $H_2$-7, and H-8; and H-2′ with H-1′, H-3′, H-4′, and $H_2$-2″. The HMBC spectrum of **1** exhibited interactions of C-3 with $H_2$-2, $H_2$-4, and H-1′; C-5 with $H_2$-4, H-3, and H-6; and C-1″ with H-2′ and $H_2$-2″. The HSQC spectrum of **1** showed correlations of C-3 at $\delta$ 77.0 with H-3 at $\delta$ 4.03; C-6 at $\delta$ 122.7 with H-6 at $\delta$ 5.35; C-1′ at $\delta$ 102.0 with H-1′ at $\delta$ 4.49; and C-2′ at $\delta$ 79.7 with H-2′. Alkaline hydrolysis of **1** yielded β-sitosterol (mp 136–137°C, TLC comparable), β-D-glucose and *n*-triacontanoic acid. On the basis of spectral data analysis and chemical reactions, the structure of **1** has been formulated as stigmast-5-en-3β-ol-3-*O*-β-D-(2′-*n*-triacontanoyl) glucopyranoside. This is a new steroidal glycosidic ester.

Compound **2** was obtained as a semi-solid from the eluant system hexane–EtOAc (4:6). It decolorized in bromine water, which indicated the presence of unsaturated linkages. Its IR spectrum displayed characteristic absorption bands for carboxylic group (3010, 2925, 2854, and 1711 cm$^{-1}$) and unsaturation (1463 cm$^{-1}$). On the basis of fast atom bombardment (FAB) mass and $^{13}$C NMR spectra, the molecular ion peak was determined at *m/z* 499 $[M + H]^+$, consistent with the molecular formula of an aliphatic acid $C_{34}H_{59}O_2$. The prominent ion peaks were generated at *m/z* 147, 311 $[C_{21}—C_{22}$ fission$]^+$ and *m/z* 281 $[C_{18}—C_{19}$ fission$]^+$. The fragmentation pattern of compound **2** suggested an aliphatic moiety as shown in Figure 1.

The $^1$H NMR spectrum of **2** displayed two proton multiplets at $\delta$ 5.38 assigned to H-23 and H-24, three-proton multiplets at $\delta$ 5.36 assigned to H-25, H-26, and H-27 and at $\delta$ 5.34 assigned to H-28, H-29, two proton multiplets at $\delta$ 5.33 assigned to H-22, H-17 and at $\delta$ 5.32 to H-18. Several multiplets at $\delta$ 2.80, 2.75, 2.33, 2.07, and 2.04 were assigned for $H_2$-2, H-19, $H_2$-16, H-21, and $H_2$-16. The $^{13}$C NMR spectral data of the aliphatic compounds were compared with the reported values of similar compounds [20,23]. The $^{13}$C NMR spectrum of **2** exhibited important signals for carboxylic carbon at $\delta$ 181.3 (C-1) and vinylic carbons at $\delta$ 129.1 (C-17), 129.3 (C-18), 129.4 (C-22), 133.2 (C-23), 131.5 (C-24), 131.4 (C-25), 131.3 (C-26), 129.6 (C-27), and 128.5 (C-29). The $^1$H–$^1$H COSY spectrum of **2** showed the correlation of vinylic protons H-17 and H-18 with adjacent methylene and methine protons $H_2$-16, H-19, $H_2$-20, and Me-33; Me-32 with the adjacent methylene protons. The HMBC spectrum of **2** showed interaction of C-1 with $H_2$-2 and $H_2$-3; C-17 with $H_2$-16, H-18, H-19, and $H_3$-33; C-32 with $H_2$-31 and $H_2$-30. On the basis

of spectral data analysis, the structure of **2** has been formulated as 19,21-dimethyl triacont-17,22,24,26,28-pentaene-1-oic acid. This is a new aliphatic acid.

## 3. Experimental

### 3.1 General experimental procedures

Optical rotation was measured with an instrument on an AA-10 model polarimeter (Instruments Ltd, Seoul, South Korea). IR spectra were recorded on an Infinity Gold FT-IR (Thermo Mattson, Waltham, MA, USA) spectrophotometer, which was available at Korea Institute of Science and Technology, Seoul, South Korea. Both $^{1}H$ and $^{13}C$ NMR spectra were obtained on a Bruker Avance 600 high resolution spectrometer operating at 600 and 150 MHz, respectively. This NMR machine was available at Seoul National University (SNU), Seoul, South Korea, and all NMR spectra were recorded at SNU (Instrument, Bruker, Bremen, Germany). NMR spectra were obtained in deuterated methanol and chloroform using tetramethylsilane as an internal standard, with chemical shifts expressed in ppm ($\delta$) and coupling constants ($J$) in Hz. FAB/MS data were recorded on a JMS-700 (Jeol, Mitaka, Tokyo, Japan) spectrometer instrument, which was available at SNU, Seoul, South Korea. All chemicals used were of analytical grade. Hexane, ethyl acetate, chloroform, methanol, ethanol, water, sulfuric acid, and vanillin were purchased from Daejung Chemicals and Metals Co. Ltd, Shiheung (Gyeonggi-do) Korea. Pre-coated TLC plates (layer thickness 0.25 mm), silica gel for column chromatography (70–230 mesh American Society Testing Materials) and LiChroprep RP-18 (40—63 μm) were from Merck, Darmstadt, Germany. Authentic standards of β-sitosterol and D-glucose were purchased from Sigma-Aldrich, St Louis, MO, USA. Previously isolated authentic standard of β-sitosterol-3-*O*-β-D-glucoside was available.

### 3.2 Plant material

Fruits of *L. chinense* were purchased from local medicinal plants shop market in Seoul, Korea and were identified by the Head, Department of Pharmacognosy. Voucher specimen No. KU/LC/2010 has been deposited in the Department of Applied Life Science, Konkuk University.

### 3.3 Extraction and isolation

The fruits of *L. chinense* (3.1 kg) were immersed in methanol (8 liters) for 3 days at room temperature and then the supernatant was concentrated under vacuum to yield 230 g of the extract, which was suspended in water and extracted with hexane, ethyl acetate, and *n*-butanol successively to produce 20.0, 10.1, and 40 g extract, respectively.

The entire butanol extract was subjected to normal phase column chromatography over silica gel (600 g) to yield 28 fractions (each of 500 ml) with the following eluants: fractions 1 and 2 with $CHCl_3$, fractions 3 and 4 with $CHCl_3$–MeOH (9.5:0.5, v/v), fractions 5 and 6 with $CHCl_3$–MeOH (9:1, v/v), fractions 7 and 8 with $CHCl_3$–MeOH (8:2, v/v), fractions 9 and 10 with $CHCl_3$–MeOH (7:3, v/v), fractions 11 and 12 with $CHCl_3$–MeOH (6:4, v/v), fractions 13 and 14 with $CHCl_3$–MeOH (1:1, v/v), fractions 15 and 16 with $CHCl_3$–MeOH (4:6, v/v), fractions 17 and 18 with $CHCl_3$–MeOH (3:7, v/v), fractions 19 and 20 with $CHCl_3$–MeOH (2:8, v/v), fractions 21 and 22 with $CHCl_3$–MeOH (1:9, v/v), and fractions 23–28 with MeOH. All fractions were examined by TLC. Fractions 1–4 were not further separated due to the low amount of the substance. Fractions 5 and 6 (0.9 g) were crystallized after the purification by column chromatography, yielding β-sitosterol-3-*O*-β-D-glucoside whose identity was confirmed through the comparison of TLC and spectroscopic data with those of an authentic sample. Fractions 7 and 8

(4.4 g) were re-chromatographed over LiChroprep RP-18 (ODS silica gel; 40–63 μm: 200 g; each fraction 100 ml). The elution was sequentially performed with methanol and water to yield 20 fractions (50 ml each): fractions 1–4 with $H_2O$–MeOH (8:2, v/v), fractions 5–8 with $H_2O$–MeOH (6:4, v/v), fractions 9–12 with $H_2O$–MeOH (4:6, v/v), fractions 13–16 with $H_2O$–MeOH (2:8, v/v), and fractions 17–20 with methanol. Fractions 9–12 (0.56 g) were re-chromatographed over Lichroprep RP18 ODS (80 g, each fraction of 50 ml). The elution was sequentially performed with methanol containing 80%, 60%, 40%, 20%, 10%, and 0% of water to yield new compound **1** (20 mg).

The entire ethyl acetate extract was subjected to normal phase column chromatography over silica gel (500 g) to yield 30 fractions (each of 500 ml) with the following eluants: fractions 1 and 2 with $C_6H_{14}$, fractions 3 and 4 with $C_6H_{14}$–EtOAc (9:1, v/v), fractions 5 and 6 with $C_6H_{14}$–EtOAc (8:2, v/v), fractions 7 and 8 with $C_6H_{14}$–EtOAc (7:3, v/v), fractions 9 and 10 with $C_6H_{14}$–EtOAc (6:4, v/v), fractions 11 and 12 with $C_6H_{14}$–EtOAc (1:1, v/v), fractions 13 and 14 with $C_6H_{14}$–EtOAc (4:6, v/v), fractions 15 and 16 with $C_6H_{14}$–EtOAc (3:7, v/v), fractions 17 and 18 with $C_6H_{14}$–EtOAc (2:8, v/v), fractions 19 and 20 with $C_6H_{14}$–EtOAc (1:9, v/v), fractions 21 and 22 fractions with EtOAc, fractions 23–26 with EtOAc–MeOH (9.5:0.5), and fractions 27 and 30 with EtOAc–MeOH (9:1). All fractions were examined by TLC. Fractions 5 and 6 (0.9 g) were crystallized after purification by column chromatography, yielding β-sitosterol whose identity was confirmed through the comparison of TLC and spectroscopic data with those of an authentic sample. Fractions 17 and 18 (4.4 g) were re-chromatographed over silica gel (100 g, each fraction of 50 ml). The elution was sequentially performed with $C_6H_{14}$–EtOAc to yield one new aliphatic acid (**2**, 19 mg) and known compound (**3**, 22 mg).

### *3.3.1 Stigmast-5-en-3β-ol-3-O-β-D-(2′-n-triacontanoyl) glucopyranoside*

White solid; 20 mg; $R_f$ 0.60 ($CHCl_3$: MeOH: 8.5:1.5); $[\alpha]_D^{20} + 47.1$ ($c = 1$, MeOH); IR $\nu_{max}$ (KBr): 3430, 3350, 2919, 2850, 1736, 1645, 1463, 1377, 1242, and 1020 $cm^{-1}$; $^1H$ and $^{13}C$ NMR spectral data see Table 1; + ve FAB-MS *m/z* (rel. int.): 1011 $[M + H]^+$(1.5), 452 (11.3), 413 (12.6), 183 (9.1), 163 (10.2); HR-FAB-MS: *m/z* 1011.8954 $[M]^+$ (calcd for $C_{65}H_{119}O_7$, 1011.8960).

### *3.3.2 19,21-Dimethyl triacont-17,22,24,26,28-pentaene-1-oic acid (**2**)*

Semi-solid; IR (KBr): $\nu_{max}$ 3010 (COOH), 2925, 2854, 1711 (COOH), 1463, 1282, and 723 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ 5.38 (2H, m, H-23, H-24), 5.36 (3H, m, H-25, H-26, H-27), 5.34 (2H, m, H-28, H-29), 5.33 (2H, m, H-22, H-17), 5.32 (1H, m, H-18), 2.80 (2H, m, $H_2$-2), 2.75 (1H, m, H-19), 2.33 (2H, m, $H_2$-16), 2.07 (1H, m, H-21), 2.04 (2H, m, $H_2$-30), 1.62 (2H, m, $CH_2$), 1.60 (2H, m, $CH_2$), 1.34 (4H, m, $2 \times CH_2$), 1.32 (8H, br s, $4 \times CH_2$), 1.29 (5H, br s, $3 \times CH_2$), 1.26 (10H, br s, $5 \times CH_2$), 0.97 (3H, t, $J = 6.1$ Hz, Me-32), 0.89 (3H, d, $J = 6.5$ Hz, Me-33), 0.86 (3H, d, $J = 6.3$ Hz, Me-34); $^{13}C$ NMR ($CDCl_3$): $\delta$ 181.3 (C-1), 133.2 (C-23), 131.5 (C-24), 131.4 (C-25), 131.3 (C-26), 129.6 (C-27), 129.5 (C-28), 129.4 (C-22), 129.3 (C-18), 129.1 (C-17), 128.5 (C-29), 35.4 (C-2), 32.9 (C-19), 31.1 (C-21), 31.0 (C-20), 30.9 ($CH_2$), 30.8 ($CH_2$), 30.8 ($CH_2$), 30.7 ($CH_2$), 30.7 ($CH_2$), 30.5 ($CH_2$), 30.4 ($CH_2$), 30.4 ($CH_2$), 28.5 ($CH_2$), 27.0 ($CH_2$), 26.9 ($CH_2$), 26.9 ($CH_2$), 26.0 ($CH_2$), 24.1 ($CH_2$), 24.0 ($CH_2$), 21.9 ($CH_2$), 15.6 (Me-33),15.5 (Me-34), 15.4 (Me-32); + ve FAB-MS *m/z* (rel. int.):

Table 1. $^{1}$H NMR and $^{13}$C NMR spectral data of compound **1** (600 and 150 MHz, MeOD solvent).

| Position | $\delta_H$ | δc |
|---|---|---|
| 1 | 1.41 m, 2.41 m | 37.5 |
| 2 | 2.37 m, 2.05 m | 32.7 |
| 3 | 4.03 br m ($w1/2 = 18.5$) | 77.0 |
| 4 | 1.72 m, 1.65 m | 43.1 |
| 5 | – | 141.2 |
| 6 | 5.35 d (3.8) | 122.7 |
| 7 | 2.40 m, 2.03 dd (3.8, 6.1) | 30.1 |
| 8 | 1.30 m | 34.7 |
| 9 | 1.49 m | 51.1 |
| 10 | – | 38.1 |
| 11 | 1.98 m, 1.48 m | 23.4 |
| 12 | 1.18 m, 1.85 m | 39.4 |
| 13 | – | 40.6 |
| 14 | 1.56 m | 56.9 |
| 15 | 1.21 m, 1.52 m | 23.8 |
| 16 | 1.72 m, 1.49 m | 26.8 |
| 17 | 1.41 m | 57.6 |
| 18 | 0.67 br s | 12.3 |
| 19 | 1.01 br s | 19.4 |
| 20 | 2.03 m | 36.9 |
| 21 | 0.92 d (6.2) | 19.3 |
| 22 | 1.27 m, 1.50 m | 32.7 |
| 23 | 1.77 m, 1.31 m | 25.0 |
| 24 | 1.67 m | 27.3 |
| 25 | 1.38 m | 46.7 |
| 26 | 0.87 d (6.7) | 19.8 |
| 27 | 0.85 d (6.5) | 20.2 |
| 28 | 1.50 m, 1.61 m | 21.8 |
| 29 | 0.82 t (5.9) | 12.3 |
| 1′ | 4.49 d (7.5) | 102.0 |
| 2′ | 3.85 m | 79.7 |
| 3′ | 3.70 m | 74.5 |
| 4′ | 3.52 m | 71.2 |
| 5′ | 4.01 m | 77.5 |
| 6′ | 3.18 d (8.4), 3.15 d (7.8) | 62.5 |
| 1″ | – | 175.0 |
| 2″ | 2.33 d (7.5), 2.30 d (7.5) | 44.3 |
| 3″ | 1.52 m | 34.7 |
| 4″–26″ | 1.29 br s | 30.4 |
| 27″ | 1.25 m | 29.9 |
| 28″ | 1.19 m | 29.0 |
| 29″ | 1.16 m | 25.7 |
| 30″ | 0.80 t (5.4) | 14.4 |

Note: Coupling constants in Hz are provided in parentheses.

499 $[M + H]^+$(4.8), 311 (7.3), 281 (22.5), 221 (29.6), 147 (100); HR-FAB-MS: *m/z* 499.4512 $[M]^+$ (calcd for $C_{34}H_{59}O_2$, 499.4517).

### *3.4 Alkaline hydrolysis of compound 1*

The solution of compound **1** (5 mg) in 5% KOH–$H_2O$ was heated under reflux for 2 h. The reaction mixture was acidified to pH 7.0 and extracted with chloroform. The organic layer was washed with water and dried over anhydrous sodium sulfate. The chloroform extract containing the aglycone portion was separated through small column chromatography, while the water extract (glycone potion) co-chromatographed on TLC ($CHCl_3$:$CH_3OH$:$H_2O$:AcOH at 16:9:2:2) was separated with authentic sample.

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