This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

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

Ether-soluble resin glycosides from the roots of *Ipomoea batatas*

Yong-Qin Yin[a]; Ling-Yi Kong[a]
[a] Department of Natural Medicinal Chemistry, China Pharmaceutical University, Nanjing, China

To cite this Article Yin, Yong-Qin and Kong, Ling-Yi(2008) 'Ether-soluble resin glycosides from the roots of *Ipomoea batatas*', Journal of Asian Natural Products Research, 10: 3, 233 — 238
To link to this Article: DOI: 10.1080/10286020701604839
URL: http://dx.doi.org/10.1080/10286020701604839

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Asian Natural Products Research
Vol. 10, No. 3, March 2008, 233–238

Taylor & Francis
Taylor & Francis Group

Ether-soluble resin glycosides from the roots of *Ipomoea batatas*

Yong-Qin Yin and Ling-Yi Kong*

Department of Natural Medicinal Chemistry, China Pharmaceutical University, Nanjing 210009, China

(*Received 9 November 06; final version received 18 April 07*)

Two new resin glycosides, batataosides I (**1**) and II (**2**), and five known compounds, friedelin (**3**), scopoletin (**4**), octadecyl caffeate (**5**), β-sistosterol (**6**) and daucosterol (**7**), were isolated from the roots of *Ipomoea batatas*. Their structures have been determined based on the chemical and spectral data. Batataosides I and II have novel structures because the core simonic acid B was esterised with cinnamic acid for the first time, and three different substituent esterification groups in one resin glycoside is scarce. The absolute configuration of the aglycone was elucidated to be *S* by Mosher's method.

Keywords: Convolvulaceae; *Ipomoea batatas*; resin glycosides; batataoside I; batataoside II

Downloaded At: 19:01 22 January 2011

1. Introduction

Sweet potatoes are the roots of *Ipomoea batatas* L., usually called Shanyu, Hongshu or Hongshao in China. It is an important edible crop whose production ranks seventh in the global market.[1] As a staple food, it is also popular in many countries.[2] Chinese people have also used it as a food and herb for hundreds of years.[3] It is also known that the glycoresins are an important chemotaxonomic feature of this family and responsible for the purgative properties of some medicinal plants of the family.[4] In this paper, we describe the isolation and characterisation of two novel constituents from the roots of *I. batatas*.

2. Results and discussion

The 95% EtOH extract of the roots of *I. batatas* was partitioned between water and $CHCl_3$. Chromatographic purification over silica gel column and repeated RP-C18 column, followed by HPLC purification of the $CHCl_3$ fraction, afforded two new resin glycosides **1** and **2**.

Batataoside I (**1**), obtained as white powder, has a molecular formula $C_{64}H_{100}O_{25}$ determined from its pseudomolecular ion peak at *m/z* 1267.6418 $[M - H]^-$ in the HRESI-MS. Base hydrolysis of **1** with 5% KOH afforded a fatty acid fraction and glycoside acid fraction. The fatty acids were identified as isobutyric acid, (*S*)-2-methyl butyric acid, and cinnamoyl acid by GC-MS comparison with authentic samples.[5] The glycoside acid was identified as simonic acid B (**8**),[6] which was methylated with CH_2N_2. Acid hydrolysis of **8** yielded **9** (11-hydroxyhexadecanoic acid methyl ester) and sugars. The sugars were identified as D-fucose and L-rhamnose by GC-MS analysis of their derivatives.[6] **9** was derivatized to give **10** (11-(*R*-MPA)-hexadecanoic acid methyl ester) and **11** (11-(*S*-MPA)-hexadecanoic acid methyl ester) with *R*-MPA and *S*-MPA, respectively. The chemical shifts difference of **10** and **11** ($\Delta\delta^{RS}_{H16} = -0.07$ ppm) made it possible to conclude that **1** has the *S*-configuration, the same as the literature.[7] The HMQC spectrum of **1** indicated five anomeric carbons at δ_C 101.7 (C-1 fucose = Fuc), 100.2 (C-1 rhamnose = Rha), 99.1 (C-1-Rha′), 103.8 (C-1-Rha″), and 104.5 (C-1-Rha‴), which showed correlations with the anomeric protons at δ_H 4.80 (d, $J = 7.8$ Hz, H-1-Fuc), 6.31 (d, $J = 1.5$ Hz, H-1-Rha), 5.60 (br s, H-1-Rha′), 5.90 (br s, H-1-Rha″), and 5.63 (br s, H-1-Rha‴), respectively. The HMBC experiment provided evidence for the location of the linkages. The carbonyl group at δ_C 175.4 (C-1-Mba) correlated with H-2-Rha′ (br s, δ_H 5.79), 2′-CH_3-Mba (d, $J = 7.0$ Hz, δ_H 1.11), and H-2-Mba (tq, $J = 7.0, 7.0$ Hz, δ_H 2.38) in HMBC spectrum, which confirmed the presence of the methylbutyroyl moiety at the C-2-Rha′. Further cross-peaks were observed between the methyl groups at δ_H 1.11 (d, $J = 7.0$ Hz, H-3 and H-3′-Iba), the methines at δ_H 2.60 (m, H-2-Iba) and 6.01 (dd, $J = 10.0, 10.0$ Hz, H-4-Rha″) with the carbonyl at δ_C 176.4 (C-1-Iba), indicating the isobutyroyl was at C-4-Rha″. The carbonyl group at δ_C 166.2, assigned to C-1-Cna, exhibited HMBC correlations with H-3-Rha″ (dd, $J = 3.0, 10.0$ Hz, δ_H 5.82), H-2-Cna (d, $J = 15.9$ Hz, δ_H 6.50), and H-3-Cna (d,

*Corresponding author. Email: lykong@jlonline.com

ISSN 1028-6020 print/ISSN 1477-2213 online
© 2008 Taylor & Francis
DOI: 10.1080/10286020701604839
http://www.informaworld.com

Downloaded At: 19:01 22 January 2011

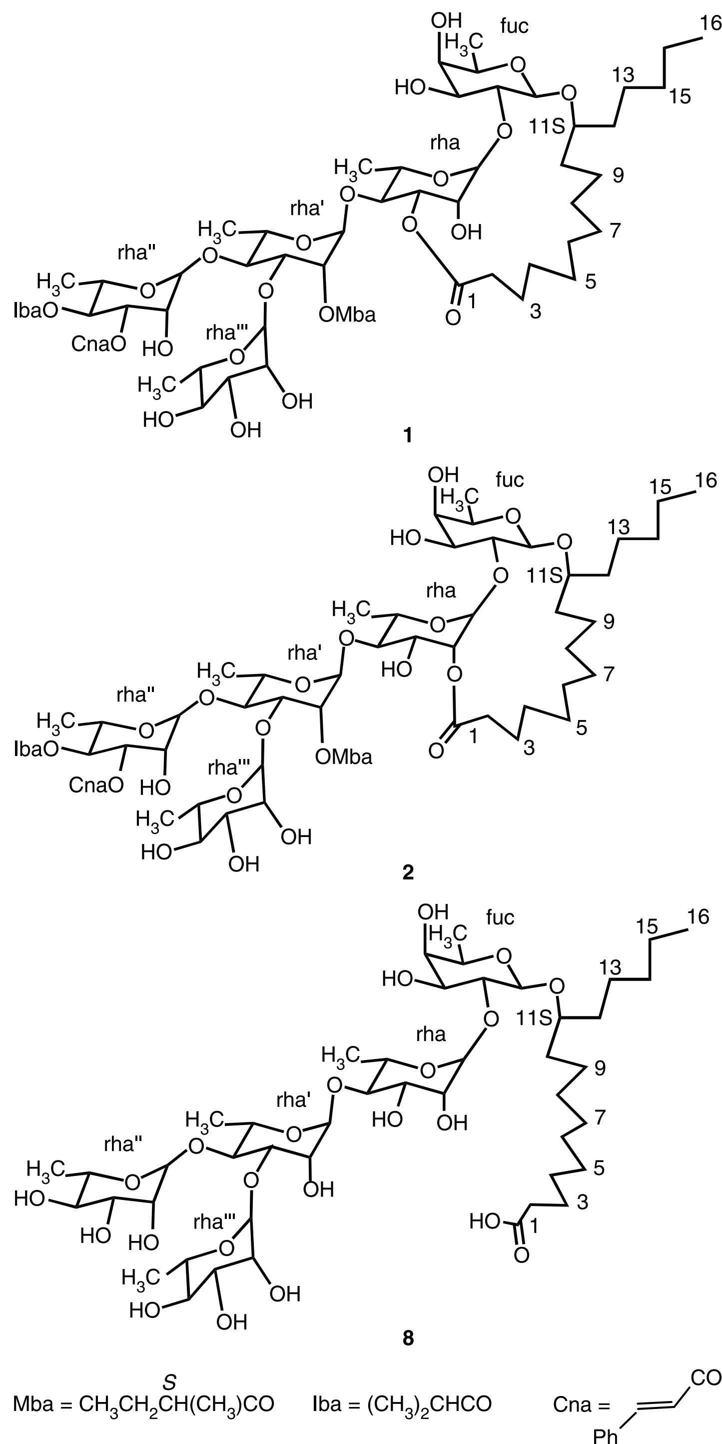

Figure 1. Structures of batataoside I (**1**), batataoside II (**2**), and simonic acid B (**8**).

$J = 15.9$ Hz, δ_H 7.79), which established the acylation position of cinnamoyl group at C-3-Rha″. The site of lactonisation was determined to be at C-3-Rha also by the observing cross-peak in HMBC spectrum. When compared with ^{1}H NMR signals of **8**, 3-H of the first rhamnose (Rha), 2-H of the second rhamnose (Rha′), 3-H and 4-H of the third rhamnose (Rha″) were shifted downfield by 1.00, 0.93, 1.47 and 1.73 ppm, respectively, while two signals at δ_H 2.25 (H-2a-Ag) and δ_H 2.81 (H-2b-Ag) in **1** change to one signal H-2-Ag (δ_H 2.50, 2H, t, $J = 7.3$ Hz) in **8**. Therefore, the ester linkages are located at 3-OH of Rha, 2-OH of Rha′, 3-OH and 4-OH of Rha″,

see Figure 2. Fucose has β-configuration due to the coupling constant of the anomeric proton 7.9 Hz. Four rhamnoses have α-configuration due to the chemical shifts of C-5.[8] Accordingly, the structure of **1** was concluded to be (*S*)-jalapinolic acid 11-*O*-α-L-rhamnopyanosyL-(1 → 3)-*O*-[3-*O*-*trans*-cinnamoyl-4-*O*-isobutyryl-α-L-rhamnopyanosyl-(1 → 4)]-*O*-[2-*O*-(*S*)-2-methylbutyryl]-α-L-rhamnopyranosyl-(1 → 4)-*O*-α-L-rhamnopyranosyl-(1 → 2)-*O*-β-D-fucopyranoside, intramolecular 1, 3″-ester (Figure 1) .

Batataoside II (**2**), isolated as white powder, has a molecular formula $C_{64}H_{100}O_{25}$, determined from its pseudomolecular ion peak at *m/z* 1267.6421 $[M - H]^-$ in the HRESI-MS. **2** yielded the same components as those of **1** on alkaline hydrolysis, and its negative ESI-MS was the same as that of **1**. Comparing the ^{1}H NMR (Table 1) spectrum of **2** with that of **1**, the signal of H-2 of Rha was shifted by 0.68 ppm downfield, whereas the signal of H-3 of Rha was shifted by 0.59 ppm upfield. In HMBC spectrum, the proton of H-2-Rha (br s, δ_H 5.97) showed correlation with δ_C 173.0 (C-1-Ag). Consequently, **2** was determined to be a regional isomer of **1,** in which the cyclic ester group, at C-3-Rha in **1,** is moved to C-2 in the same sugar unit. The detailed assignments of the ^{1}H NMR and ^{13}C NMR signals for **2** were achieved by TOCSY, HMBC and HMQC experiments. Accordingly, the structure of **2** was concluded to be (*S*)-jalapinolic acid 11-*O*-α-L-rhamnopyanosyl-(1 → 3)-*O*-[3-*O*-*trans*-cinnamoyl-4-*O*-isobutyryl-α-L-rhamnopyanosyl-(1 → 4)]-*O*-[2-*O*-(*S*)-2-methylbutyryl]-α-L-rhamnopyranosyl-(1 → 4)-*O*-α-L-rhamnopyranosyl-(1 → 2)-*O*-β-D-fucopyranoside, intramolecular 1, 2″-ester (Figure 1).

3. Experimental

3.1 General experimental procedures

Optical rotations were obtained using a JASCO P-1020 digital polarimeter (cell length: 1.0 dm). IR spectra were measured on a Shimadzu ftir (FTIR)-8400s spectrophotometer and UV on a Shimadzu UV-2501 PC spectrophotometer. ESI-MS and HRESI-MS experiments were performed on an Agilent 1100 Series LC/MSD Trap mass spectrometer and an Agilent TOF MSD 1946D spectrometer, respectively. NMR spectra were recorded on Bruker DRX-600 spectrometers (^{1}H NMR, TOCSY, HMQC and HMBC at 600 MHz; ^{13}C NMR at 150 MHz) using pyridine-d_5 as solvent with tetramethylsilane (TMS) as internal reference. The chemical shifts were given in δ (ppm) and coupling constants in Hz. Silica gel (200–300 mesh, Qingdao Marine Chemistry Ltd., China), Sephadex LH-20 (20–100 μm, Pharmacia) and RP-C18 (40–63 μm, FuJi) were used for column chromatography. Preparative HPLC was conducted on an Agilent 1100 instrument with a UV detector at 280 nm and with a shim-pack prep-ODS column (20 mm × 250 i.d.). Silica gel GF254 for TLC was produced in Qingdao Marine Chemistry Ltd., and TLC plates were visualised by spraying with 10% sulphuric acid in EtOH followed by heating. GC-MS (Varian 3800 GC, Varian 2200 MS, 70 eV) under the following conditions: capillary column, SE30 (30 m × 0.25 mm × 0.25 μm);

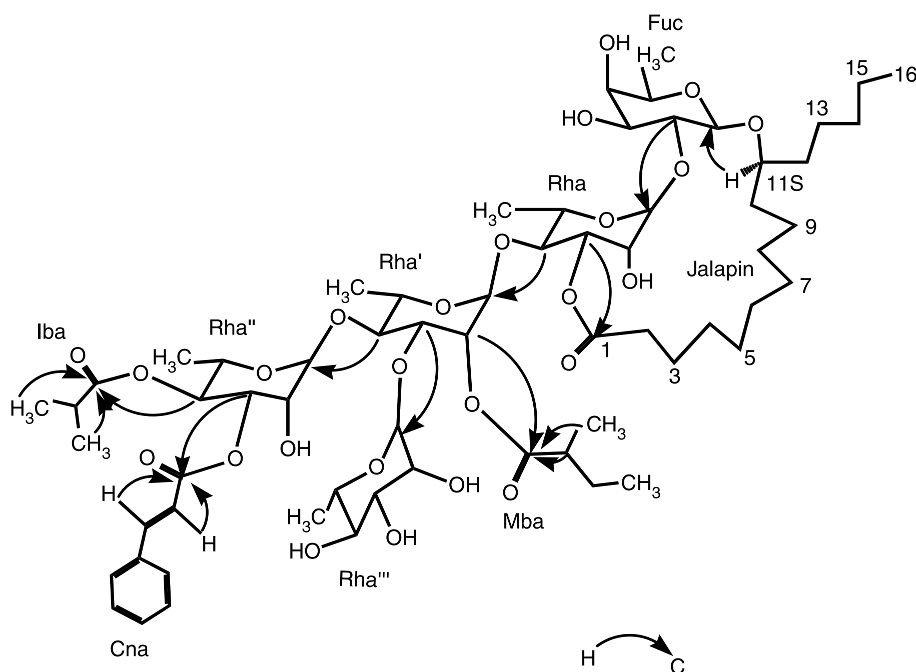

Figure 2. Key HMBC correlations of batataoside I (**1**).

Downloaded At: 19:01 22 January 2011

Table 1. ^{1}H NMR spectral data of compounds **1**, **2**, and **8** (pyridine-d_5, 600 MHz).

Proton	1	2	8
Fuc-1	4.80 d (7.8)	4.76 d (7.8)	4.78 d (7.3)
2	4.51 dd (7.8, 9.5)	4.18 dd (7.8, 10.0)	4.46 dd(7.3, 9.7)
3	4.16 (9.5, 3.4)	4.11 dd (10.0, 3.5)	4.13 dd (9.7, 3.1)
4	3.90 d (3.4)	3.99 d (3.5)	3.91 d (3.1)
5	3.79 br q (6.4)	3.78 br q (6.3)	3.77 br q (6.2)
6	1.49 d (6.4)	1.49 d (6.3)	1.49 d (6.2)
Rha-1	6.31 d (1.5)	5.49 br s	6.22 br s
2	5.29 br s	5.97 br s	4.63[a]
3	5.63[a]	5.03 dd (3.1, 10.5)	4.63[a]
4	4.66 dd (10.0, 10.0)	4.22 dd (10.5, 10.5)	4.20 dd (9.5, 9.5)
5	5.01 dq (10.0, 6.3)	4.27 dq (10.5, 6.1)	4.86[a]
6	1.57 d (6.3)	1.61 d (6.1)	1.55 d (6.6)
Rha′-1	5.60 br s	6.09 br s	6.15 br s
2	5.79 br s	5.99 br s	4.86[a]
3	4.59 dd (3.0, 9.5)	4.68 dd (2.9, 9.4)	4.52 dd (2.6, 9.1)
4	4.24 dd (9.5, 9.5)	4.30 dd (9.4, 9.4)	4.46 dd (9.1, 8.6)
5	4.36 dd (9.5, 6.1)	4.36 dd (6.0)	4.28 dd (8.6, 6.1)
6	1.58 d (6.1)	1.63 d (6.0)	1.58 d (6.1)
Rha″-1	5.90 br s	5.96 br s	5.66 br s
2	4.87 br s	4.98 br s	4.66 br s
3	5.82 dd (3.0, 10.0)	5.92 dd (2.3, 10.0)	4.35 dd (2.6, 9.6)
4	6.01 dd (10.0, 10.0)	6.05 dd (10.0, 10.0)	4.28 dd (9.6, 9.6)
5	4.45 dd (10.0, 6.3)	4.48 dd (10.0, 6.0)	4.32 dd (9.6, 6.1)
6	1.39 d (6.3)	1.40 d (6.0)	1.52 d (6.1)
Rha″-1	5.63 br s	5.71 br s	5.92 br s
2	4.74 br s	4.81 br s	4.95 br s
3	4.40 dd (3.4, 9.5)	4.41 dd (3.1,9.0)	4.52 dd (2.6, 9.5)
4	4.18 dd (9.5, 9.5)	4.22 dd (9.0, 9.0)	4.20 dd (9.5, 9.5)
5	4.25 dd (9.5, 6.1)	4.50 dd (9.0, 6.3)	4.71 dd (9.5, 6.5)
6	1.69 d (6.1)	1.54 d (6.0)	1.53 d (6.5)
Ag-2	2.81 ddd (4.3, 7.1, 15.5)	2.62 ddd (3.8, 7.0, 14.0)	2.50 t (7.3)
	2.25 ddd (4.3, 7.1, 15.5)	2.22 ddd (3.8, 7.0, 14.0)	
11	3.87 m	3.86 m	3.90 br s
16	0.96 t (6.8)	0.85 t (6.7)	0.90 t (6.3)
Cna-2	6.50 d (15.9)	6.53 d (16.0)	
3	7.79 d (15.9)	7.80 d (16.0)	
2′ and 6′	7.43 m	7.44 m	
3′ and 5′	7.32 m	7.32 m	
4′	7.32 m	7.32 m	
Iba-2	2.60 m	2.38 m	
3	1.11 d (7.0)	1.04 d (7.0)	
3′	1.11 d (7.0)	1.11 t (7.2)	
Mba-2	2.38 tq (7.0,7.0)	2.34 tq (7.0, 7.0)	
2-CH_3	1.11 d (7.0)	1.11 t (7.2)	
4	0.86 t (7.4)	0.81 t (7.4)	

All assignments were based on TOCSY, HMQC and HMBC experiments. Chemical shifts marked with superscript a indicate overlapped signals. Abbreviations: s, singlet; br s, broad singlet; d, doublet; t, triplet; m, multiplet; q, quartet; Fuc, fucose; Rha, rhamnose; Ag, aglycone = (*S*)-11-hydroxyhexadecanoyl; Cna cinnamoyl; Iba, isobutanoyl; Mba, (*S*)-2-methylbutanoyl.

the column temperature, 170–250°C with the rate of 5°C/min; carrier gas, N_2 (30 ml/min).

3.2 Plant material

Roots of *Ipomoea batatas* (18 kg) were collected in September 2004 from Hunan province of China and identified by Professor Min-jian Qin, Department of Medicinal Plants, China Pharmaceutical University. A voucher specimen (No. 040912) is deposited in the Department of Natural Medicinal Chemistry, China Pharmaceutical University.

3.3 Extraction and isolation

Roots of *I. batatas* (18 kg) were crushed to pieces and dried in shade for one week. The pieces were extracted with 95% EtOH ($3 \times 20\,L \times 2\,h$) at 80°C, then

Downloaded At: 19:01 22 January 2011

Table 2. ^{13}C NMR spectral data of compounds **1**, **2**, and **8** (pyridine-d_5, 150 MHz).

Carbon	**1**	**2**	**8**	Carbon	**1**	**2**	**8**
Fuc-1	101.7	104.2	101.2	Rha″-2	72.7	72.6	72.7
2	73.6	80.4	74.9	3	72.6	72.4	72.8
3	76.6	73.3	76.7	4	73.6	73.2	74.0
4	73.6	73.0	73.5	5	70.7	68.5	70.4
5	71.3	70.5	71.2	6	18.9	18.5	18.6
6	17.2	17.3	17.2	Ag-1	174.7	173.0	176.3
Rha-1	100.2	98.7	101.3	2	33.9	34.3	35.7
2	69.9	73.3	73.2	11	79.6	82.2	77.9
3	78.0	69.7	72.7	16	14.5	14.2	14.4
4	77.3	80.2	80.4	Can-1	166.2	166.3	
5	68.2	70.7	67.1	2	118.4	118.4	
6	18.8	19.0	19.1	3	145.4	145.4	
Rha′-1	99.1	99.3	102.9	1′	134.7	134.5	
2	72.8	72.9	72.0	2′ and 6′	128.5	128.5	
3	79.6	79.3	82.6	3′ and 5′	129.3	128.9	
4	80.7	80.0	78.7	4′	130.8	130.4	
5	68.5	68.2	68.7	Iba-1	176.4	176.3	
6	19.2	18.7	18.3	2	34.4	34.1	
Rha″-1	103.8	103.6	104.5	3	18.8	18.8	
2	70.1	70.0	72.6	3′	19.3	19.4	
3	73.3	73.8	72.7	Mba-1	175.4	175.4	
4	71.6	71.5	73.7	2	41.5	41.3	
5	68.2	68.3	70.1	2-CH_3	17.0	16.7	
6	17.7	17.6	18.9	4	11.9	11.7	
Rha″-1	104.5	104.8	103.3				

All assignments were based on TOCSY, HMQC and HMBC experiments. Abbreviations: Fuc, fucose; Rha, rhamnose; Ag, aglycone = (*S*)-11-hydroxyhexadecanoyl; Cna cinnamoyl; Iba, isobutanoyl; Mba, (*S*)-2-methylbutanoyl.

concentrated under vacuum and kept overnight. The solution was further concentrated to produce a residue, which was partitioned with $CHCl_3$ (5 × 0.5 L) and water (0.5 L) to give 45 g and 18 g extract, respectively. The $CHCl_3$ fraction was subjected to silica gel column chromatography (Ø 5 × 60 cm, 200–300 mesh, 300 g), eluted with $CHCl_3$/MeOH (100:3 → 100:50). The elution of 217 to 273 fractions (2 g) was submitted to RP-C18 column chromatography (Ø 1.5 × 30 cm, 40 g) eluted with MeOH/H_2O (85:15) to afford fraction I (96 mg), eluted with MeOH/H_2O (90:10) to afford fraction II (580 mg), and eluted with MeOH/H_2O (95:5) to afford fraction III (1280 mg). Two peaks from fraction I were collected by preparative HPLC over C18 using 87% MeOH/H_2O to give batataoside I (52 mg, t_R 22.6 min) and batataoside II (23 mg, t_R 34.0 min). The elution of 57 to 102 fractions (6 g) was eluted with petroleum/ethyl acetate (100:4, 100:10, 100:30 and 100:80) to afford **3** (80 mg), **4** (73 mg), **5** (75 mg), **6** (50.8 mg), and **7** (500 mg).

3.3.1 Batataoside I (1)

A white powder (MeOH); mp 123.0–125.0°C; $[\alpha]_D^{25}$ − 26.9 (*c* 0.4, MeOH); UV (MeOH) λ_{max} (log ε) 280 (3.34) nm; IR (KBr): ν_{max} 3451, 2976, 2935, 2860, 1737, 1638, 1137, and 1060 cm^{-1}; ^1H NMR and ^{13}C NMR spectral data, see Tables 1 and 2; HRESI-MS *m/z* 1267.6418 $[M - H]^-$ (calcd for $C_{64}H_{99}O_{25}$, 1267.6475).

3.3.2 Batataoside II (2)

A white powder (MeOH); mp 115.0–117.0°C; $[\alpha]_D^{25}$ − 31.5 (*c* 0.5, MeOH); UV (MeOH) λ_{max} (log ε) 280 (3.47) nm; IR (KBr): ν_{max} 3441, 2932, 2858, 1728, 1636, 1137, and 1061 cm^{-1}; ^1H NMR and ^{13}C NMR spectral data, see Tables 1 and 2; HRESI-MS *m/z* 1267.6421 $[M - H]^-$ (calcd for $C_{64}H_{99}O_{25}$, 1267.6475).

3.4 Hydrolysis of resin glycoside

Compound **1** (10.0 mg) was refluxed in 5% KOH (2.0 ml) for 2.0 h. The reaction mixture was acidified to pH 4 and extracted with ether (30.0 ml). The organic layer was washed with H_2O, dried with anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was directly analysed by GC-MS. Three peaks were detected and identified, by comparing with authentic samples, as isobutyric acid (t_R 2.8 min): *m/z* 87 (58) $[M - H]^-$, 73 (100), 60 (93), 55 (98); (*S*)-2-methylbutyric acid (t_R 4.2 min): *m/z* 101 (25) $[M - H]^-$, 87 (65), 73 (100), 60

Downloaded At: 19:01 22 January 2011

(81), 55 (82), 41 (70); cinnamic acid (t_R 5.6 min): *m/z* 147 (22) $[M - H]^-$, 73 (100), 45 (35).

The aqueous layer was extracted with *n*-butanol to afford simonic acid B (**8**), which was methylated with CH_2N_2. The product was dissolved in 1 N HCl (2.0 ml) refluxing at 90°C for 2.0 h. The reaction was cooled to room temperature and diluted to 5.0 ml. This solution was extracted with ether (30.0 ml) to afford aglycone ester (11-hydroxyhexadecanoic acid methyl ester = aglycone, **9**).[9] The aqueous layer was neutralized with ion exchange resin (Amberlite MB-3), concentrated and dissolved in pyridine (1.0 ml). The pyridine solution was treated with hexamethyldisilazane ($CH_3SiNHSi(CH_3)_3$, 0.8 ml) and trimethylsilylmethyl chloride ($(CH_3)_3SiCl$, 0.4 ml) at room temperature for 30 min, then added to water (2.0 ml). The upper layer was analysed by GC-MS comparing with authentic samples and identified as D-fucose and L-rhamnose.

3.5 Determination of the absolute configuration

The solution of (*R*)-MPA (12.0 mg, MPA = methoxyphenyl acetic acid) and DMAP (5.0 mg, DMAP = 4-dimethylaminopyridine) in CH_2Cl_2 (0.5 ml) was added to CH_2Cl_2 (1.5 ml) containing **9** (1.0 mg), followed by DCC (10.0 mg, DCC = *N*,*N*-dicyclohexyl-carbodiimide), and the mixture was stirred for 17.0 h at 25.0°C. EtOAc (30.0 ml) was added,[10] and the filtrate was concentrated and purified by silica gel eluted with cyclohexane/ethyl acetate (95:5) to give **10** (1.3 mg, 94%). Treatment of **9** with (*S*)-MPA by the same procedure yielded **11** (1.1 mg, 85%).

Absolute configuration of sugars and aglycone from **2** was determined by the same procedures as **1**.

3.5.1 11-(R-MPA)-hydroxyhexadecanoic acid methyl ester (10)

Colourless oil ($CHCl_3$); $[\alpha]_D^{25}$ −2.0 (*c* 0.1, $CHCl_3$); IR (KBr): ν_{max} 3442, 2927, 2855, 1743, 1261, and 802 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ_H 7.44 (m, C_6H_2), 7.34 (m, C_6H_3), 4.90 (m, OCH), 4.73 (s, OCH), 3.67 (s, OCH_3), 3.41 (t, $J = 1.7$ Hz, 1-OCH_3), 2.30 (t, $J = 7.4$ Hz, $OCOCH_2$), 0.77 (3H, $J = 7.1$ Hz, CH_3); TOF-MS *m/z:* 457 $[M + Na]^+$; 435 $[M + H]^+$.

3.5.2 11-(S-MPA)-hydroxyhexadecanoic acid methyl ester (11)

Colourless oil ($CHCl_3$); $[\alpha]_D^{25}$ + 1.4 (*c* 0.2, $CHCl_3$); IR (KBr): ν_{max} 3453, 2961, 2926, 2852, 1742, and 1261 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ_H 7.44 (m, C_6H_2), 7.34 (m, C_6H_3), 4.90 (m, OCH), 4.73 (s, OCH), 3.67 (s, OCH_3), 3.41 (t, $J = 1.7$ Hz, 1-OCH_3), 2.30 (t, $J = 7.6$ Hz, $OCOCH_2$), 0.84 (t, $J = 7.1$ Hz, CH_3); TOF-MS *m/z*: 457 $[M + Na]^+$.

3.6 Cytotoxicity assay

Preliminary biological activity screening revealed that the two compounds are not active against the growth of a limited panel of cancer cell lines, including A549, MCF-7, MAD-MB-435, and HO-8910. The results of further biological activity screening will be reported elsewhere in the future.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 30472144). This support is gratefully acknowledged. We also thank Dr Bing Ma for measuring the TOCSY, HMQC, and HMBC spectra.

References

[1] S. Rajapakse, S.D. Nilmagoda, M. Molna, R.E. Ballard, D.F. Austin, and J.R. Bohac. *Mol. Phylogenet. Evol.* **30**, 623 (2004).
[2] L.V. An, B.E. Frank-Lindberg, and J.E. Lindberg. *Field Crops Res.* **82**, 49 (2003).
[3] S.Z. Li. *(Min dynasty) Compendium of Materia Medica* ((midst volume), People's Medical Publishing House, Beijing, 1999), p. 150.
[4] K. Umehaara, K. Nemoto, T. Ohkubo, T. Miyase, M. Degawa, and H. Noguchi. *Planta Med.* **70**, 299 (2004).
[5] I. Leon, R.G. Enriquez, D. Gnecco, M.L. Villarreal, D.A. Cortes, W.F. Reynolds, and M. Yu. *J. Nat. Prod.* **67**, 1552 (2004).
[6] N. Noda, S. Yoda, T. Kawasaki, and K. Miyahara. *Chem. Pharm. Bull.* **40**, 3163 (1992).
[7] M. Ono, F. Yamada, N. Noda, T. Kawasaki, and K. Miyahara. *Chem. Pharm. Bull.* **41**, 1023 (1993).
[8] S.M. Sang, A.N. Lao, Y. Leng, Z.P. Gu, Z.L. Chen, J. Uzawa, and Y. Fujimoto. *Tetrahedron Lett.* **41**, 9205 (2000).
[9] M. Ono, K. Kubo, and K. Miyahara, T. Kawasaki. *Chem. Pharm. Bull.* **37**, 241 (1989).
[10] S.G. Cao, R.C. Guza, H.J. Wisse, J.S. Miller, R. Evans, and D.G.I. Kingston. *J. Nat. Prod.* **68**, 487 (2005).

Downloaded At: 19:01 22 January 2011