Three New Pentasaccharide Resin Glycosides from the Roots of Sweet Potato (*Ipomoea batatas*)

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Three new pentasaccharide resin glycosides, batatosides III—V (1—3), were isolated from the roots of Sweet potato (*Ipomoea batatas*). Saponification of the crude resin glycoside mixture yielded substituents and simonic acid B. The structures of the isolated compounds (1—3) were established through spectroscopic analyses, including high field NMR spectroscopy and HR-ESI-MS, and chemical correlation. The major characteristics of 3 are the presence of three different substituents, especially the substituent of cinnamic acid was seldom. The monosaccharides of 1—3 were proved by GC-MS and the absolute configuration of aglycone was further established as *S* by Mosher's method with *R*-methyloxyphenylacetic acid (MPA) and *S*-MPA.

Key words *Ipomoea batatas*; resin glycoside; pentasaccharide

The genus *Ipomoea* (Convolvulaceae) was shown to be a rich source of "resin glycosides" which exhibited antibacterial,[1] cytotoxic,[2,3] antifugal,[4] and anti-tuberculosis activity.[5] Sweet potato, *I. batatas* (L.) LAM. was an important food crop whose production ranks the seventh in global market.[6] The aerial part of the sweet potato is used as vegetable and the underground part is used as food or raw material in industry.[7] It is known in China as "Shanyu", "Hongshu", "Digua" and "Hongshao" and cultured nationwide. Chinese people used it also as herb to promote the production of body fluid, haemostasis and apocenosis for centuries.[8] Recently, some of resin glycosides were described from *I. batatas*.[9—11] In the present paper, we report the isolation and structure elucidation of three new resin glycosides batatosides III—V (**1**—**3**) from this plant continuously. The major structural characteristics of **3** are the presence of three different substituents, especially the substituent of cinnamic acid (Cna) was seldom. Comparing compounds **1** and **2** with the similar resin glycosides,[9—11] **1** and **2** were hydrophilic.

Results and Discussion

A 95% EtOH extract of the dried roots of *I. batatas* was partitioned between $CHCl_3$ and H_2O to afford a resinous fraction which was chromatographed over Si gel, Rp-18, Sephadex LH-20 and purified by preparative HPLC to afford compounds **1**—**3**.

Batatoside III (**1**) $\{[\alpha]_D^{20} -18.7°$ (c=0.4, MeOH)$\}$ was obtained as white amorphous powder. The molecular formula, $C_{65}H_{102}O_{25}$, was inferred from negative HR-ESI-MS ($[M+Na]^+$ at m/z 1305.6627), and it was supported by ^{13}C-NMR and DEPT spectroscopy. The IR spectrum showed absorptions for hydroxyl (3445 cm^{-1}), methyl (2933, 2859 cm^{-1}), carbonyl (1723 cm^{-1}), and phenyl (1636 cm^{-1}) groups. A pair of *trans*-coupled olefinic protons, five protons of aroma, and many protons of saccharides and pal-chains existed in ^{1}H-NMR spectrum, so compound **1** was possible to be a kind of resin glycoside. Compound **1** was hydrolyzed with alkaline to detect the substituents and acid hydrolysis to determine the absolute configurations of sugars successively, then hydrolysates were proved by GC-MS method, respectively. The configuration of 11*S* was assigned to **1** based on Mosher's method with *S*-methyloxyphenylacetic acid (MPA) and *R*-MPA. Alkaline hydrolysis of compound **1** afforded simonic acid B (**4**)[12] and a mixture which were identified as (*S*)-2-methylbutyric acid (Mba) and *trans*-cinnamic acid (Cna), respectively, by GC-MS, compared of their optical rotations with those of authentic samples. The ^{1}H-NMR spectrum (Table 1) of **1** exhibited a pair of *trans*-coupled olefinic protons at δ 6.53 (d, J=15.9 Hz, H-2 of Cna) and 7.81 (d, J=15.9 Hz, H-3 of Cna), and δ_H 7.27—7.45 (m, C_6H_5) ascribed to five phenyl protons. The ^{13}C-NMR spectrum displayed signals for an α, β-unsaturated lactone unit at δ_C 118.4, 145.5, 166.3. Based on the analysis above, **1** contained a 3-phenylprop-2-enoyl (Cna) moiety. The upfield protons at δ_H 0.82 (t, J=7.0 Hz, H-4 of Mba), 1.07 (d, J=7.0 Hz, CH_3'-2 of Mba), 2.38 (tq, J=7.0, 7.0 Hz, H-2 of Mba) displayed in one spin system in the TOCSY spectra, suggesting the presence of a (*S*)-2-methylbutyryl moiety. Similarly, the protons at δ_H 0.80, 1.14, 2.40 composed the second (*S*)-2-methylbutyryl moiety. The protons in the region of δ_H 4.00—6.4 were assigned by ^{1}H-NMR, ^{13}C-NMR, TOCSY, HSQC, and HMBC spectra. The HMQC spectrum of **1** indicated that anomeric carbons at 104.3, 98.8, 99.4, 103.7, and 104.7 ppm were correlated with the anomeric protons at 4.75 (d, J=7.4 Hz), 5.49 (br s), 6.06 (br s), 5.96 (br s), and 5.68 (br s) ppm, respectively. A combination of one- and two-dimensional NMR techniques allowed all protons to be assigned sequentially within each saccharide system, leading to the identification of one fucopyranosyl and four rhamnopyranosyl units as the monosaccharides present in **1**. The anomeric configuration for the sugar moieties were defined as β for fucopyranosyl, α for rhamnopyranosyl from their coupling constants of 7.4 Hz and C-5 chemical shift,[13] respectively. The connectivities between sugar moieties were determined from the following HMBC correlations: C-1 of fucose (δ_C 104.3) and H-11 of the aglycon (δ_H 3.87), C-2 of fucose (δ_C 80.3) and H-1 of rhamnose (δ_H 5.49), C-1 of rhamnose′ (δ_C 99.4) and H-4 of rhamnose (δ_H 4.25), C-1 of rhamnose″ (δ_C 103.7) and H-4 of (δ_H 4.30) and C-1 of rham-

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Table 1. ^{1}H- (600 MHz) and ^{13}C-NMR (150 MHz) Spectral Data of Batatoside III (**1**), Batatoside IV (**2**) in C_5D_5N (δ in ppm, J in Hz)

Position	**1**		**2**	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
Fuc-1	4.75 d (7.4)	104.3	4.78 d (7.8)	101.6
2	4.16 dd (7.4, 9.6)	80.3	4.49 dd (7.8, 9.5)	73.5
3	4.10 d (3.2, 9.6)	73.3	4.17 dd (9.5, 3.4)	76.6
4	3.99 d (3.2)	73.0	3.90 d (3.4)	73.5
5	3.77 br q (6.2)	70.6	3.79 br q (6.4)	71.2
6	1.50 d (6.2)	17.4	1.49 d (6.4)	17.2
Rha-1	5.49 br s	98.8	6.31 br s (1.5)	100.2
2	6.02 br s	73.1	5.27 br s	69.9
3	5.03 dd (3.0, 9.3)	69.8	5.61*	78.1
4	4.25 dd (9.3, 9.3)	80.6	4.65 dd (10.0, 10.0)	76.3
5	4.50 dd (9.3, 6.2)	70.8	4.97 dd (10.0, 6.3)	68.0
6	1.61 d (6.2)	19.5	1.57 d (6.3)	18.8
Rha′-1	6.06 br s	99.4	5.59 br s	98.8
2	5.99 br s	73.4	5.76 br s	72.8
3	4.69 dd (3.1, 9.4)	79.5	4.49 dd (3.0, 9.5)	79.4
4	4.30 dd (9.4, 9.4)	80.2	4.26 dd (9.5, 9.5)	79.6
5	4.36 dd (9.4, 6.2)	68.3	4.29 dd (9.5, 6.1)	68.7
6	1.66 d (6.2)	18.9	1.58 d (6.1)	19.2
Rha″-1	5.96 br s	103.7	5.87 br s	103.8
2	4.94 br s	70.1	4.61 br s	72.7
3	5.92 dd (3.0, 10.0)	73.5	4.34 dd (3.0, 10.0)	72.5
4	6.06 dd (10.0, 10.0)	71.5	4.26 dd (10.0, 10.0)	73.6
5	4.45 dd (10.0, 6.2)	68.5	4.29 dd (10.0, 6.3)	70.7
6	1.43 d (6.2)	17.8	1.39 d (6.3)	18.6
Rha‴-1	5.68 br s	104.7	5.61 br s	104.6
2	4.79 br s	73.9	4.74 br s	72.5
3	4.40 dd (3.1, 9.0)	72.6	4.42 dd (3.4, 9.5)	72.5
4	4.20 dd (9.0, 9.0)	72.5	4.18 dd (9.5, 9.5)	73.5
5	4.27 dd (9.0, 6.2)	68.6	4.29 dd (9.5, 6.1)	70.5
6	1.55 d (6.2)	18.5	1.69 d (6.1)	18.3
Ag-1		173.1		174.6
2	2.19*	34.3	2.25 ddd (4.3, 7.1, 15.5)	33.9
	2.42*		2.81 ddd (4.3, 7.1, 15.5)	
11	3.87*	82.3	3.87 m	79.7
16	0.87 t (6.8)	14.3	0.91 t (6.8)	14.5
Cna-1		166.3		
2	6.53 d (15.9)	118.4		
3	7.81 d (15.9)	145.5		
Mba-1		175.9		175.4
2	2.45 m	41.6	2.35 tq (7.5, 7.5)	41.4
2-Me	1.14 d (7.0)	16.9	1.12 d (7.0)	16.9
4	0.82 t (7.0)	11.8	0.87 t (7.5)	11.8
Mba-1		175.4		
2	2.38 m	41.5		
2-Me	1.07 d (7.0)	16.8		
4	0.83 t (7.0)	11.8		

Chemical shifts (δ) are in ppm relative to TMS. The spin coupling (J) is given in parentheses (Hz). All assignments are based on ^{1}H–^{1}H TOCSY, HSQC, and HMBC experiments. Chemical shifts marked with an asterisk (*) indicate overlapped signals. Spin-coupled patterns are designated as follows: s=singlet, br s=broad singlet, d=doublet, t=triplet, m=multiplet, q=quartet. Abbreviations: Fuc=fucose; Rha=rhamnose; Ag=11-hydroxyhex-adecanoyl; Cna=*trans*-cinnamoyl; Mba=(*S*)-2-methylbutanoyl.

nose‴ (δ_C 104.7) and H-3 of rhamnose′ (δ_H 4.69). The HMBC spectrum of **1** also permitted the unambiguous assignment of the esterified positions of the oligosaccharide core by the correlations between the carbonyl ester group with their corresponding vicinal proton ($^2J_{CH}$) and the pyranose ring proton ($^3J_{CH}$). In **1**, (*S*)-2-methylbutanoyl was placed at C-2 of rhamnose′, as shown by the correlation between the carbonyl at δ_C 175.9 and H-2 of rhamnose′ at δ_H 5.99; a *trans*-cinnamoyl residue was located at C-3 of rhamnose″, as shown by the correlation between the carbonyl at δ_C 166.3 with H-3 of rhamnose″ at δ_H 5.92, and another (*S*)-2-methylbutanoyl was placed at C-4 of rhamnose″, as shown by the correlation between the carbonyl at δ_C 175.4 with H-4 of rhamnose″ at δ_H 6.06. The position of the jalapinolic acid unit was determined by the long-range correlations with the lactone carbonyl at δ_C 173.1 with the H-2 of rhamnose (δ_H 6.02). Based on these results, batatoside III (**1**) was elucidated as (*S*)-jalapinolic acid 11-*O*-α-L-rhamnopyranosyl-(1→3)-*O*-[3-*O*-*trans*-4-*O*-(*S*)-2-methylbutyryl-α-L-rhamnopyranosyl-(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 (Fig. 1).

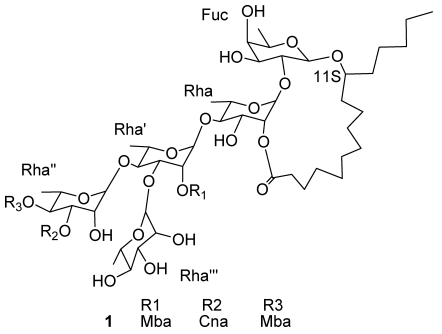

Fig. 1. Structure of Batatoside III (**1**)

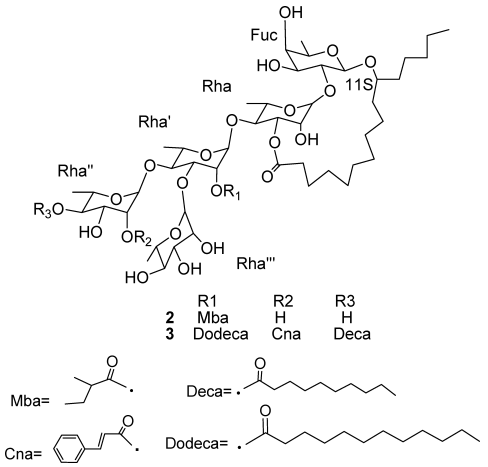

Fig. 2. Structures of Batatoside IV (**2**), Batatoside V (**3**)

Batatoside IV (**2**) {$[\alpha]_D^{20}$ −38.1° (c=0.5, MeOH)} was obtained as white amorphous powder, giving the molecular formula $C_{51}H_{88}O_{23}$ from HR-ESI-MS spectrometric analyses ($[M+Na]^+$ at m/z 1091.5616). The IR spectrum showed absorptions for hydroxyl (3448 cm^{-1}), methyl (2929, 2856 cm^{-1}), carbonyl (1736 cm^{-1}), and phenyl (1636 cm^{-1}) groups. The ^{1}H-NMR spectrum of compound **2** was similar to **1**. Compound **2** was hydrolyzed with base and acid, then the hydrolysates were detected with authentic samples by GC-MS. Alkaline hydrolysis of **2** afforded (*S*)-2-methylbutyric acid and simonic acid B. Acylation sites of substituent and aglycone were identified by HMBC correlations between the H-2 of rhamnose′ (δ_H 5.76) and δ_C 175.4, and between the H-3 of rhamnose (δ_H 5.61) and δ_C 174.6. From the above results, the structure of **2** was elucidated as (*S*)-jalapinolic acid 11-*O*-α-L-rhamnopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-

Table 2. ^{1}H- (600 MHz) and ^{13}C-NMR (150 MHz) Spectral Data of Batatoside V (**3**), Simonic Acid B (**4**) in C_5D_5N (δ in ppm, J in Hz)

Position	**3**		**4**	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
Fuc-1	4.79 d (7.8)	101.5	4.78 d (7.3)	101.2
2	4.52 dd (7.8, 9.5)	73.6	4.46 dd (7.3, 9.7)	74.9
3	4.18 dd (9.5, 3.4)	76.6	4.13 dd (9.7, 3.1)	76.7
4	3.90 d (3.4)	73.6	3.91 d (3.1)	73.5
5	3.80 br q (6.4)	71.3	3.77 br q (6.2)	71.2
6	1.49 d (6.4)	17.1	1.49 d (6.2)	17.2
Rha-1	6.33 br s	100.2	6.22 br s	101.3
2	5.31 br s	69.9	4.63*	73.2
3	5.62*	78.0	4.63*	72.7
4	4.62 dd (10.0, 10.0)	77.3	4.20 dd (9.5, 9.5)	80.4
5	5.02 dd (10.0, 5.9)	68.2	4.86*	67.1
6	1.58 d (5.9)	19.1	1.55 d (6.6)	19.1
Rha′-1	5.67 br s	99.0	6.15 br s	102.9
2	5.79 br s	72.8	4.86*	72.0
3	4.58 dd (3.0, 9.5)	79.6	4.52 dd (2.6, 9.1)	82.6
4	4.24 dd (9.5, 9.5)	79.0	4.46 dd (9.1, 8.6)	78.7
5	4.36 dd (9.5, 5.8)	68.2	4.28 dd (8.6, 6.1)	68.7
6	1.60 d (5.8)	18.7	1.58 d (6.1)	18.3
Rha″-1	5.81 br s	100.2	5.66 br s	104.5
2	5.99 br s	73.8	4.66 br s	72.6
3	4.55 dd (3.0, 10.0)	67.8	4.35 dd (2.6, 9.6)	72.7
4	5.77 dd (10.0, 10.0)	75.0	4.28 dd (9.6, 9.6)	73.7
5	4.67 dd (10.0, 6.4)	68.0	4.32 dd (9.6, 6.1)	70.1
6	1.52 d (6.4)	17.9	1.52 d (6.1)	18.9
Rha‴-1	5.59 br s	104.2	5.92 br s	103.3
2	4.90 br s	72.6	4.95 br s	72.7
3	4.40 dd (3.4, 9.5)	72.7	4.52 dd (2.6, 9.5)	72.8
4	4.18 dd (9.5, 9.5)	73.6	4.20 dd (9.5, 9.5)	74.0
5	4.25 dd (9.5, 6.0)	70.9	4.71 dd (9.5, 6.5)	70.4
6	1.69 d (6.0)	18.7	1.53 d (6.5)	18.6
Ag-1		174.7	2.50 t (7.3)	176.3
2	2.26 m	33.5		35.7
	2.97 m			
11	3.87 m	79.2	3.90 br s	77.9
16	0.99 t (6.8)	14.4	0.90 t (6.3)	14.4
Cna-1		166.6		
2	6.49 d (15.9)	118.3		
3	7.84 d (15.9)	145.5		
Deca-1		173.4		
2	2.39 m	34.3		
10	0.84 m	14.2		
Dodeca-1		172.8		
2	2.47 m	34.5		
12	0.84 t (7.0)	14.2		

Chemical shifts (δ) are in ppm relative to TMS. The spin coupling (J) is given in parentheses (Hz). All assignments are based on ^{1}H–^{1}H TOCSY, HSQC, and HMBC experiments. Chemical shifts marked with an asterisk (*) indicate overlapped signals. Spin-coupled patterns are designated as follows: s=singlet, br s=broad singlet, d=doublet, t=triplet, m=multiplet, q=quartet. Abbreviations: Fuc=fucose; Rha=rhamnose; Ag=11-hydroxyhex-adecanoyl; Cna=*trans*-cinnamoyl; Deca=*n*-decanoyl; Dodeca=*n*-dodecanoyl.

(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 (Fig. 2).

Batatoside V (**3**) {$[\alpha]_D^{20}$ −28.1° (c=0.4, MeOH)} was obtained as white amorphous powder, giving the molecular formula $C_{77}H_{126}O_{25}$ from HR-ESI-MS spectrometric analyses ($[M+Na]^+$ at m/z 1473.8423). The IR spectrum exhibited absorptions for hydroxyl (3443 cm^{-1}), methyl (2929, 2857 cm^{-1}), carbonyl (1736 cm^{-1}), and phenyl (1631 cm^{-1}) groups. Alkline hydrolysis of **3** afforded decanoic acid, dodenoic acid, *trans*-cinnamic and simonic acid B. From ^{1}H-, ^{13}C-NMR, HMQC, and TOCSY (Table 2), signals were assigned

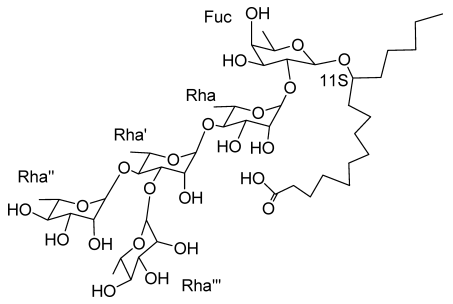

Fig. 3. Structure of Simonic Acid B (**4**)

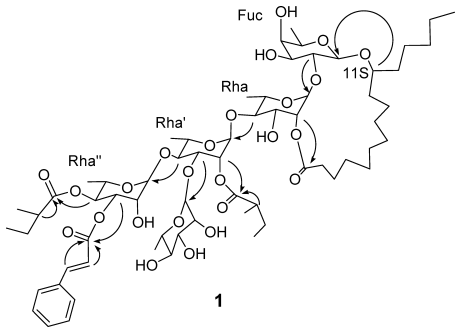

Fig. 4. Key HMBC Correlations from H to C for Compound **1**

to each spin-system. The connections sites were determined by HMBC experiment. In **3**, dodecanoic residue was placed at C-2 of rhamnose′, as shown by the correlation between the carbonyl at δ_C 172.8 and H-2 rhamnose′ at δ_H 5.79; a *trans*-cinnamoyl residue was located at C-2 of rhamnose″, as shown by the correlation between the carbonyl at δ_C 166.6 with H-2 of rhamnose″ at δ_H 5.99, and decanoic was placed at C-4 of rhamnose″, as shown by the correlation between the carbonyl at δ_C 173.4 with H-4 of rhamnose″ at δ_H 5.77. From the above results, the structure of **3** was established as (*S*)-jalapinolic acid 11-*O*-α-L-rhamnopyranosyl-(1→3)-*O*-[2-*O*-*trans*-cinnamoyl-4-*O*-*n*-decanoyl-α-L-rhamnopyranosyl-(1→4)]-*O*-[2-*O*-*n*-dodecanoyl]-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-β-D-fucopyranoside, intramolecular 1,3″-ester (Fig. 2).

Experimental

General Procedure Optical rotations were measured with a JASCO P-1020 polarimeter. IR spectra and UV spectra were recorded on a Nicolet Impact-410 spectrometer and Shimadzu UV-2501PC. 1D and 2D NMR spectra were carried out with a Bruker ACF-600 NMR spectrometer (^{1}H: 600 MHz, ^{13}C: 150 MHz) in pyridine-d_5. Chemical shifts are reported in ppm as δ values and TMS was used as internal standard. Mass spectra were obtained on a MS Agilent 1100 series LC/MSD ion trap mass spectrometer (ESI-MS), an Agilent TOF-MSD 1946D spectrometer, and a Micro Q-TOF-MS. TLC was performed on pre-coated silica gel 60 F_{254} (Qingdao Haiyang Chemical Co., Ltd.) and detected by spraying with 10% H_2SO_4–EtOH. Silica gel H (Qingdao Haiyang Chemical Co., Ltd.), sephadex LH-20 (Pharmacia), and Rp-C_{18} (40—63 μm, Fuji) were used for column chromatography. Preparative HPLC was carried out using Agilent 1100 series instrument with a Shimpark Rp-C_{18} column (200×20 mm i.d.).

Plant Material The roots of *I. batatas* were collected in Yanlin Country, Hunan Province, People's Republic of China in September, 2004 and identified by Prof. 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.

Extraction and Isolation Roots (18 kg) of *I. batatas* were pulverized and dried in the shade for one week, and were extracted with 95% EtOH

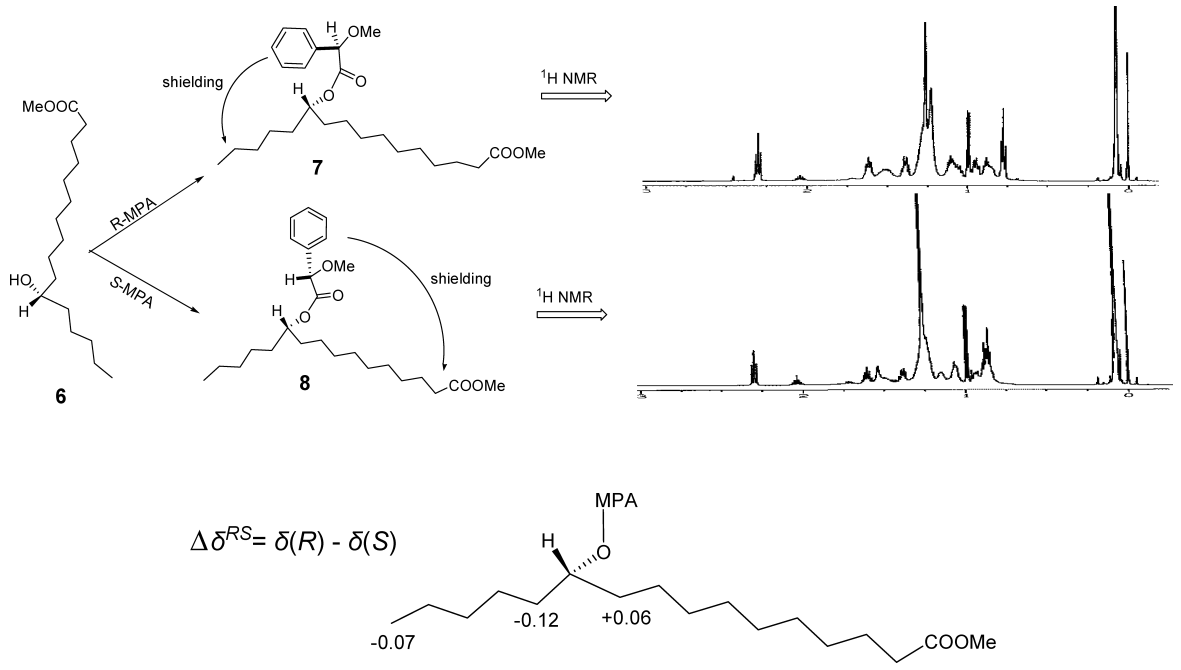

Fig. 5. Structures of **6**—**8** and $\Delta\delta^{RS}$ Values of the MPA Esters

(3×20 l×2 h) at 80 °C, concentrated under a vacuum, and stood 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 of extract, respectively. The $CHCl_3$ extract was subjected to silica column chromatography (Φ5×60 cm, 200—300 mesh, 300 g), eluted with $CHCl_3$–MeOH (100 : 3→100 : 50). Fractions of 245 to 272 (1.8 g) eluted with $CHCl_3$–MeOH (100 : 10) was further submitted to Rp-C_{18} column chromatography (Φ1.5×30, 40 g) and eluted with MeOH–H_2O (90 : 10→100 : 0) to afford fraction 1 by 90 : 10 MeOH/H_2O, fraction 2 by 95 : 5 MeOH/H_2O and fraction 3 by MeOH, respectively. Fraction 1 was further purified by successive Rp-18 preparative HPLC (UV detection at 210 and 280 nm) with 80% MeOH/H_2O to afford batatoside IV (**2**, 45 mg, t_R 8.34 min), and 90% MeOH/H_2O to afford batatoside III (**1**, 4.1 mg, t_R 6.43 min) and batatoside V (**3**, 3.4 mg, t_R 10.16 min), respectively.

Batatoside III (**1**): White amorphous power, $[\alpha]_D^{25}$ −18.7° (c=0.4, MeOH). IR ν_{max} (KBr) 3445, 2933, 2859, 1723, 1636 cm^{-1}; UV (MeOH) λ_{max} (log ε): 280 (4.33), 217 (4.25), 204 (4.28) nm. ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) see Table 1. ESI-MS 1281 $[M-H]^-$; HR-ESI-MS 1305.6627 $[M+Na]^+$ ($C_{65}H_{102}O_{25}Na$, Calcd 1305.6602).

Batatoside IV (**2**): White amorphous power, $[\alpha]_D^{25}$ −38.1° (c=0.5, MeOH). IR ν_{max} (KBr) 3448, 2929, 2856, 1736, 1636 cm^{-1}; ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) see Table 1. ESI-MS m/z 1067 $[M-H]^-$; HR-ESI-MS 1091.5616 $[M+Na]^+$ ($C_{51}H_{88}O_{23}Na$, Calcd 1091.5608).

Batatoside V (**3**): White amorphous power, $[\alpha]_D^{25}$ −28.1° (c=0.5, MeOH). IR ν_{max} (KBr) 3443, 2929, 2857, 1736, 1631 cm^{-1}; UV (MeOH) λ_{max} (log ε): 280 (4.18), 217 (4.07), 204 (4.06) nm. ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) see Table 2. ESI-MS m/z 1450 $[M-H]^-$; HR-ESI-MS 1473.8423 $[M+Na]^+$ ($C_{77}H_{126}O_{25}Na$, Calcd 1473.8480).

Alkaline Hydrolysis of 1—3 Compounds **1**—**3** (3 mg each) in 5% KOH (3 ml) were refluxed at 90 °C for 2 h, separately. The reaction mixtures were acidified to pH 4 and extracted with ether (30 ml) and n-BuOH (30 ml). The ether layer was washed with H_2O, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was methylated with CH_3OH/0.5 N H_2SO_4 to afford methyl ester, which was analyzed by GC-MS (Varian 3800 GC, Varian 2200 MS, 70 eV) under the following conditions: capillary column, SE-30 (30 m×0.25 mm×0.25 μm); column temperature, 160—250 °C temperature programmed at with of 5 °C/min; carrier gas, N_2 (30 ml/min). Five different peaks were detected from compounds **1**—**3** and identified by comparing with authentic samples as *trans*-cinnamoic acid methyl ester (t_R 12.498 min): m/z $[M]^+$ 162 (45), 131 (100), 103 (76), 77 (35) from **1** and **3**; n-decanoic acid methyl ester (t_R 11.422 min): m/z $[M]^+$ 116 (10), 143 (45), 87 (64), 74 (100), 55 (55), 43 (80) and n-dodecanoic acid methyl ester (t_R 14.020 min): m/z $[M]^+$ 215 (23), 171 (31), 143 (55), 87 (85), 74 (100), 55 (86), 43 (96), 41 (56) from **3**; 2-methylbutyric acid methyl ester (t_R 3.593 min): m/z $[M+H]^+$ 117 (5), 101 (23), 88 (87), 57 (100), 41 (57) from **1** and **2**. The 2-methylbutyric acid prepared from the crude resin glycoside was proved *S*-configuration by comparing the optical rotation with that of authentic (*S*)-2-methylbutyric acid ($[\alpha]_D^{25}$ +19.0°).

Acid Hydrolysis The ether-insoluble layer of alkaline hydrolysis was extracted with n-BuOH (30.0 ml) to afford **4**, which was methylated with CH_3OH/0.5 N H_2SO_4 to give **5** (simonic acid B methyl ester). Compound **5** was hydrolyzed with 1 N H_2SO_4, then the product was extracted with ether (30.0 ml) to yield **6** (11-hydroxyhexadecanoic acid methyl ester) and extracted with BuOH to afford mixture of saccharides. The solution of (*R*)-MPA (12.0 mg, MPA=methyloxyphenylacetic acid) and DMAP (10.0 mg, DMAP=4-dimethylaminopyridine) in CH_2Cl_2 (1.0 ml) was added to CH_2Cl_2 (1.5 ml) containing **6** (2.0 mg), followed by DCC (10.0 mg, DCC=*N*,*N*-dicyclohexylcarbodiimide), and the solution was stirred for 17.0 h at 25.0 °C. Then EtOAc (30.0 ml) was added to quench the reaction and filtrated.[2] The filtrate was concentrated and purified by silica gel chromatography eluted with cyclohexane/ethyl acetate (95 : 5) to give **7** (2.6 mg, 94%, 11-(*R*-MPA)-hexadecanoic acid methyl ester) (Fig. 5). Treatment of **6** with (*S*)-MPA by the same procedure yielded **8** (2.3 mg, 85%, 11-(*S*-MPA)-hexadecanoic acid methylester). The sbustituents phenyl in *R*-MPA and *S*-MPA could shield different sites, so the values in **7** and **8** were variance, which $\Delta\delta^{RS}$ ($\Delta\delta^{RS}_{H10}$= 0.06, $\Delta\delta^{RS}_{H12}$=−0.13, $\Delta\delta^{RS}_{H16}$=−0.07 ppm)[14—18] made it possible to assign 11*S* to **6**, same as that in the literature.[2] The mixture of saccharides was neutralized by passing through an ion-exchange resin (Amberlite MB-3) column and concentrated to yield saccharides residue, which was treated with water (0.05 ml) and pyridine (0.03 ml) at 60 °C for 1 h under stirring. After the solvent was evaporated and the reaction mixture was dried, pyridine (0.5 ml), hexamethyldisilazane (0.8 ml), and trimethylsilyl chloride (0.4 ml) were added to the residue. The reaction mixture was heated at 60 °C for 30 min. Under the same condition as above, the supernatant was applied to GC-MS to afford D-fucose [t_R 4.57 min, $[\alpha]_D^{25}$ +66.4° (c=0.8, H_2O)], L-rhamnose [t_R 5.09 min, $[\alpha]_D^{25}$ −9.7° (c=1.0, H_2O)].

Simonic Acid B (**4**) White amorphous power, $[\alpha]_D^{25}$ −82.0° (c=0.8, MeOH). IR ν_{max} (KBr) 3425, 2931, 2858, 1713, 1043 cm^{-1}. ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) see Table 2. ESI-MS m/z: 1001 $[M-H]^-$, 855 $[M-H-146]^-$, 709 $[855-146]^-$, 563 $[709-146]^-$, 417 $[563-146]^-$, 271 $[417-146]^-$.

11-Hydroxyhexadecanoic Acid Methyl Ester (**6**): Colorless oil ($CHCl_3$), $[\alpha]_D^{25}$ +1.1° (c=0.2, $CHCl_3$); IR ν_{max} (KBr): 3333, 2920, 2850, 1207 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H: 3.67 (s, OCH_3), 3.58 (m, OCH-11), 2.30 (t, J=7.5 Hz, $OCOCH_2$-2), 1.62 (t, J=7.0 Hz, CH_2-10), 1.44 (m, CH_2-12), 0.89

(t, J=6.9 Hz, CH_3-16); TOF-MS m/z: 309 $[M+Na]^+$.

11-(*R*-MPA)-hydroxyhexadecanoic Acid Methyl Ester (**7**): Colorless oil ($CHCl_3$), $[\alpha]_D^{25}$ −2.0° (c=0.1, $CHCl_3$); IR ν_{max} (KBr): 3442, 2927, 2855, 1743, 1261, 802 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H: 7.44 (m, C_6H_2), 7.34 (m, C_6H_3), 4.90 (m, OCH-11), 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, $OCOCH_2$-2), 1.67 (m, CH_2-10), 1.41 (m, CH_2-12), 0.77 (3H, J=7.1 Hz, CH_3-16); TOF-MS m/z: 457 $[M+Na]^+$; 435 $[M+H]^+$.

11-(*S*-MPA)-hydroxyhexadecanoic Acid Methyl Ester (**8**): Colorless oil ($CHCl_3$), $[\alpha]_D^{25}$ +1.4° (c=0.2, $CHCl_3$); IR ν_{max} (KBr): 3453, 2961, 2926, 2852, 1742, 1261 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H: 7.44 (m, C_6H_2), 7.34 (m, C_6H_3), 4.90 (m, OCH-11), 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, $OCOCH_2$-2), 1.61 (m, CH_2-10), 1.54 (m, CH_2-12), 0.84 (t, J=7.1 Hz, CH_3-16); TOF-MS m/z: 457 $[M+Na]^+$.

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