New Phenylpropanoid Esters of Sucrose from *Polygonum lapathifolium*

Midori Takasaki, Satoshi Kuroki, Mutsuo Kozuka, and Takao Konoshima*

Kyoto Pharmaceutical University, Misasagi, Yamashina-ku, Kyoto 607-8414, Japan

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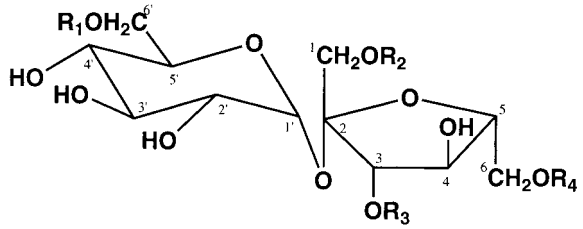
Four new phenylpropanoid esters of sucrose, lapathosides A (**1**), B (**2**), C (**3**), and D (**4**), were isolated from the aerial parts of *Polygonum lapathifolium* together with known esters, vanicoside B (**5**) and hydropiperoside (**6**). The structures of **1**−**4** were determined by spectral (1D and 2D NMR and MS) analysis. Lapathoside A (**1**) and vanicoside B (**2**) showed significant inhibitory effects on the Epstein−Barr virus early antigen activation by tumor-promoters.

To search for cancer chemopreventive agents from natural products, many North American plants have been screened using the in vitro synergistic assay indicated by the inhibitory effects on the induction of Epstein−Barr virus early antigen (EBV-EA) by 12-*O*-tetradecanoylphorbol-13-acetate (TPA). Several plants that are distributed throughout the desert area of Northwestern America showed significant inhibitory effects on EBV-EA induction, and several compounds isolated from these plants exhibited remarkable inhibitory effects on mouse two-stage skin carcinogenesis.[1−3] Of these plants, the aerial part of *Polygonum lapathifolium* and several plants belonging to the same genus have been used as folk medicines for the treatment of dysentery or articular pain and inflammation reduction in China.[4] In the course of our continuing chemical and biological studies on anti-tumor-promoters (cancer chemopreventive agents),[5−7] we investigated the constituents of the aerial part of *P. lapathifolium*. Four new phenylpropanoid esters of sucrose, lapathosides A (**1**), B (**2**), C (**3**), and D (**4**), were isolated from the EtOAc and *n*-BuOH soluble fractions of MeOH extracts together with two known phenylpropanoid esters of sucrose, vanicoside B (**5**)[8] and hydropiperoside (**6**).[9] Herein we report the structural elucidation and biological evaluation of **1**−**4**.



1. R_1 = R_2 = feruloyl , R_3 = R_4 = *p*-coumaroyl
2. R_1 = R_2 = R_4 = feruloyl , R_3 = *p*-coumaroyl
3. R_1 = feruloyl , R_2 = H , R_3 = R_4 = *p*-coumaroyl
4. R_1 = R_2 = H , R_3 = R_4 = *p*-coumaroyl.
5. R_1 = feruloyl , R_2 = R_3 = R_4 = *p*-coumaroyl
6. R_1 = H , R_2 = R_3 = R_4 = *p*-coumaroyl.

Results and Discussion

Lapathoside A (**1**) was obtained as a colorless amorphous powder. Its molecular formula was determined to be $C_{50}H_{50}O_{21}$ by HRFABMS. The UV and IR spectra of **1** showed the presence of hydroxyl and α,β-unsaturated aromatic ester groups. In the positive FABMS of **1**, quasi-molecular ion peaks were observed at *m*/*z* 1009 $[M + Na]^+$ and 987 $[M + H]^+$. Alkaline hydrolysis of **1** with 0.5% NaOH yielded *p*-coumaric acid, ferulic acid, and sucrose. The ^1H NMR spectrum of **1** showed the anomeric proton at δ 5.57, O-Me signals at δ 3.84 and 3.83, and typical proton signals of two *p*-coumaroyl moieties indicating that **1** was sucrose acylated by two *p*-coumaric acids and two ferulic acids. Characteristic fragment ion peaks in the positive FABMS were observed at *m*/*z* 631, 485, 455, and 339, indicating that one feruloyl moiety is located on the glucopyranose ring and one feruloyl and two *p*-coumaroyl moieties are located on the fructofuranose ring. In the ^{13}C NMR spectrum of **1**, the sucrose moiety signals of C-1, C-6 of fructose and C-6′ of glucose were shifted to lower field (+2 to +3 ppm) and the signals of C-2, C-5 of fructose and C-5′ of glucose were shifted to higher field (−2 to −3 ppm) compared with those of sucrose.[10] The HMBC spectrum of **1** showed long-range correlations from phenyl protons to olefinic carbons, correlations from each olefinic proton to each ester carbonyl carbon, and correlations from H-6′ of glucose to the C-9″ carbonyl of the feruloyl group, and from H-1, H-3, and H-6 of fructose to the C-9‴, C-9⁗, and C-9⁗′ carbonyls, respectively. These reslts suggested that the positions of phenylpropanoid esters are C-1, C-3, and C-6 of fructose and C-6′ of glucose. On the basis of these data, compound **1** was characterized as 1,6′-diferuloyl-3,6-di-*p*-coumaroyl sucrose.

The structures of compounds **2**−**4** were deduced from the comparisons of physicochemical properties of **2**−**4** with those of compound **1** and reported data of similar compounds as follows.[11−14]

Lapathoside B (**2**) was isolated as a colorless amorphous powder, and its molecular formula was determined to be $C_{51}H_{52}O_{22}$ by HRFABMS. The IR and UV spectra of **2** were similar to those of **1**, and quasimolecular ion peaks were observed at *m*/*z* 1039 $[M + Na]^+$ and 1017 $[M + H]^+$ in the positive FABMS. Characteristic fragment ion peaks in the positive FABMS were observed at *m*/*z* 661, 515, 485, and 339 to indicate that one feruloyl moiety is located on the glucopyranose ring and two feruloyl and one *p*-coumaroyl moieties are located on the fructofuranose ring in compound **2**. From the results of HMBC, compound **2** was characterized as 1,6,6′-triferuloyl-3-*p*-coumaroyl sucrose.

Lapathosides C (**3**) and D (**4**) were isolated as colorless amorphous powders and their molecular formulas were determined to be $C_{40}H_{42}O_{18}$ and $C_{30}H_{34}O_{15}$ by HRFABMS, respectively. The IR and UV spectra of **3** and **4** were also similar to those of **1** or **2**. The quasimolecular ion peaks of

* Corresponding author. Tel: +81-75-595-4645. Fax: +81-75-595-4754. E-mail: konosima@mb.kyoto-phu.ac.jp.

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Table 1. NMR (CD_3OD, 400MHz) Data for Lapathosides A, B, C, and D

	lapathosideA (**1**)		lapathoside B (**2**)		lapathoside C (**3**)		lapathoside D(**4**)	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
fructose								
1	4.33 (2H, m)	66.2	4.32 (2H, m)	66.3	3.61 (2H, m)	65.4	3.62 (2H, m)	65.1
2		103.4		103.4		104.9		105.1
3	5.65 (d, 8.4)	79.1	5.64 (d, 8.4)	79.1	5.53 (d, 8.1)	79.0	5.49 (d, 8.1)	79.2
4	4.74 (m)	74.0	4.74 (m)	73.9	4.67 (m)	75.0	4.43 (dd, 8.1, 8.0)	75.0
5	4.20 (m)	81.0	4.21 (m)	81.0	4.17 (m)	81.1	4.16 (m)	81.2
6	4.56, 4.58 (m)	65.5	4.54−4.59 (m)	65.5	4.55 (2H, m)	65.8	4.54 (2H, m)	66.4
glucose								
1'	5.57 (d, 4.0)	92.9	5.56 (d, 3.9)	92.9	5.51 (d, 4.0)	92.5	5.44 (d, 4.0)	93.2
2'	3.47 (dd, 9.6, 4.0)	72.9	3.47 (dd, 9.8, 3.9)	72.9	3.47 (dd, 9.6, 4.0)	73.1	3.43 (dd, 9.7, 4.0)	73.2
3'	3.65 (dd, 9.6, 9.0)	74.9	3.65 (dd, 9.8, 9.2)	74.9	3.64 (dd, 9.6, 9.0)	74.8	3.63 (dd, 9.7, 9.5)	75.0
4'	3.30 (m)	72.2	3.30 (m)	72.3	3.29 (m)	72.2	3.41 (m)	71.5
5'	3.30 (m)	72.4	3.32 (m)	72.4	3.30 (m)	72.4	3.98 (m)	74.5
6'	4.72 (m), 4.20 (m)	65.8	4.73 (m), 4.22 (m)	65.7	4.70 (m), 4.24 (m)	65.8	3.92 (m), 3.82 (m)	62.6
phenylpropanoids								
(glc-6′)	feruloyl		feruloyl		feruloyl			
9″		169.3		169.3		169.3		
8″	6.48 (d, 16.0)	115.3	6.46 (d, 15.9)	115.3	6.48 (d, 16.1)	115.3		
7″	7.62 (d, 16.0)	147.2	7.61 (d, 15.9)	147.2	7.61 (d, 16.1)	147.2		
1″		127.7		127.7		127.7		
2″	7.20 (d, 2.0)	111.5	7.19 (d, 1.9)	111.5	7.21 (d, 1.9)	111.5		
3″		148.3		149.3		149.3		
4″		150.6		150.6		150.6		
5″	6.76 (d, 8.4)	116.4	6.74−6.80	116.4	6.75 (d, 8.2)	116.3		
6″	7.01 (dd, 8.4, 2.0)	124.5	6.99 (dd, 8.3, 1.9)	124.5	7.01 (dd, 8.2, 1.9)	124.6		
O-Me	3.84 (3H, s)	56.4	3.84 (3H, s)	56.4	3.84 (3H, s)	56.4		
(fruc-1)	feruloyl		feruloyl					
9‴		168.5		168.5				
8‴	6.39 (d, 16.0)	115.0	6.39 (d, 15.9)	114.9				
7‴	7.65 (d, 16.0)	147.4	7.65 (d, 15.9)	147.5				
1‴		127.6		127.6				
2‴	7.15 (d, 2.0)	111.6	7.14 (d, 1.9)	111.6				
3‴		149.3		149.4				
4‴		150.7		150.8				
5‴	6.75 (d, 8.4)	116.3	6.74−6.80	116.3				
6‴	7.04 (dd, 8.4, 2.0)	124.4	7.04 (dd, 8.3, 1.9)	124.4				
O-Me	3.83 (3H, s)	56.4	3.83 (3H, s)	56.4				
(fruc-3)	*p*-coumaroyl		*p*-coumaroyl		*p*-coumaroyl		*p*-coumaroyl	
9⁗		168.5		168.5		168.4		168.4
8⁗	6.44 (d, 16.0)	114.3	6.44 (d, 15.9)	114.3	6.43 (d, 16.0)	114.6	6.41 (d, 15.9)	114.7
7⁗	7.70 (d, 16.0)	147.9	7.70 (d, 15.9)	147.9	7.71 (d, 16.0)	147.6	7.71 (d, 15.9)	147.5
1⁗		127.1		127.0		127.1		127.1
2⁗, 6⁗	7.47 (d, 8.8)	131.5	7.47 (d, 8.8)	131.5	7.51 (d, 8.7)	131.5	7.51 (d, 8.6)	131.5
3⁗, 5⁗	6.78 (d, 8.8)	116.8	6.74−6.80	116.8	6.80 (d, 8.7)	116.8	6.80 (d, 8.6)	116.9
4⁗		161.5		161.4		161.4		161.6
(fruc-6)	*p*-coumaroyl		feruloyl		*p*-coumaroyl		*p*-coumaroyl	
9⁗′		168.9		168.9		168.9		169.1
8⁗′	6.26 (d, 16.0)	114.8	6.31 (d, 15.9)	115.1	6.24 (d, 16.0)	114.8	6.36 (d, 15.9)	114.8
7⁗′	7.58 (d, 16.0)	146.8	7.65 (d, 15.9)	147.1	7.57 (d, 16.0)	146.8	7.66 (d, 15.9)	147.0
1⁗′		127.1		127.6		127.1		127.1
2⁗′, 6⁗′ (2⁗′)	7.33 (d, 8.8)	131.2	7.08 (d, 1.9)	111.6	7.33 (d, 8.7)	131.2	7.48 (d, 8.6)	131.3
3⁗′, 5⁗′ (3⁗′)	6.76 (d, 8.8)	116.8		149.4	6.76 (d, 8.7)	116.8	6.80 (d, 8.6)	116.9
4⁗′		161.3		150.7		161.3		161.5
(5⁗′)			6.74−6.80	116.4				
(6⁗′)			6.97 (dd, 8.3, 1.9)	124.2				
(O-Me)			3.84 (3H, s)	56.4				

3 were observed at *m*/*z* 833 $[M + Na]^+$ and 811 $[M + H]^+$, and the quasimolecular ion peaks of **4** were observed at *m*/*z* 657 $[M + Na]^+$ and 635 $[M + H]^+$ in the positive FABMS spectra. Further, in the positive FABMS of **3**, characteristic fragment ion peaks were observed at *m*/*z* 455, 339, and 309 to indicate that one feruloyl moiety is located on the glucopyranose ring as in compound **1** or **2**, and two *p*-coumaroyl moieties are located on the fructofuranose ring. In the positive FABMS of compound **4**, the characteristic fragment ion peaks were observed at *m*/*z* 455 and 309 to indicate that two *p*-coumaroyl moieties are located on the fructofuranose ring. From these MS results, ^{13}C NMR chemical shifts and $^1H-^{13}C$ long-range correlation of HMBC spectra of **3** and **4**, the structures of **3** and **4** were characterized as 6′-feruloyl-3,6-di-*p*-coumaroyl sucrose and 3,6-di-*p*-coumaroyl sucrose, respectively.

Compounds **5** and **6** were identified as vanicoside B, previously isolated from *P. pensilvanicum*,[8] and hydropiperoside isolated from *P. hydropiperitum*.[9]

The inhibitory effects of the constituents isolated from *P. lapathifolium* on EBV-EA induction by TPA were also examined via a primary screening for anti-tumor-promoting activity,[3−6] and the results are shown in Table 2. Lapathoside A (**1**), lapathoside D (**4**), vanicoside B (**5**), and hydropiperoside (**6**) exhibited inhibitory effects (more than 85%, 60%, and 30% inhibition of activation at 1000, 500, and 100 mol ratio to TPA, respectively) on EBV-EA induction. These results strongly suggested that these

Table 2. Percentages of EBV-EA Induction in the Presence of Compounds **1**−**6** with Respect to Positive Control (100%)

sample	concentration[a]			
	1000	500	100	10
lapathoside A (**1**)	10.0[b] (70)[c]	37.2 (>80)	70.9 (>80)	95.0 (>80)
lapathoside B (**2**)	26.8 (60)	51.6 (>80)	77.9 (>80)	100 (>80)
lapathoside C (**3**)	33.6 (70)	59.0 (>80)	83.5 (>80)	100 (>80)
lapathoside D (**4**)	10.5 (70)	38.3 (>80)	71.4 (>80)	100 (>80)
vanicoside B (**5**)	11.8 (70)	40.9 (>80)	70.0 (>80)	100 (>80)
hydropiperoside (**6**)	10.6 (70)	39.6 (>80)	71.5 (>80)	100 (>80)
7-oxo-β-sitosterol[d]	11.5 (60)	42.8 (>80)	71.5 (>80)	100 (>80)
β-sitosterol-3-glucoside[d]	14.8 (60)	45.7 (>80)	73.9 (>80)	100 (>80)
methyl-*p*-coumarate[d]	15.7 (70)	42.6 (>80)	77.5 (>80)	100 (>80)
(−)-catechin[d]	11.3 (70)	41.3 (>80)	75.8 (>80)	100 (>80)

[a] Mol ratio/TPA (20 ng = 32 pmol/mL). [b] Values represent relative percentages to the positive control values (100%). [c] Values in parentheses represent viability percentages of Raji cells. [d] These compounds were also isolated from *P. lapathifolium* together with **1**−**6**.

compounds might be valuable anti-tumor-promoters for cancer chemoprevention.

Experimental Section

General Experimental Procedures. Optical rotations were measured on a JASCO DIP-370 digital polarimeter at 25 °C. IR spectra were recorded in KBr on a Shimadzu FT-IR-8100A spectrometer, and UV spectra were recorded in MeOH on a Shimadzu UV-1600 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained in CD_3OD on a Varian XL-300 spectrometer or on a Varian unity INOVA 400NB spectrometer with tetramethylsilane as internal standard. FABMS were obtained on a JEOL JMS-SX102 mass spectrometer.

Plant Material. The aerial part of *Polygonum lapathifolium* L. was collected in Oklahoma in July 1991. A voucher specimen (#010701) verified by Dr. James R. Estes of the Department of Botany, the University of Oklahoma at Norman, is deposited in the herbarium of Kyoto Pharmaceutical University.

Inhibition of EBV-EA Activation Assay. The inhibition of EBV-EA activation was assayed using Raji cells (virus nonproducer type) as described previously.[3−6] The indicator cells (Raji, 1×10^6/mL) were incubated at 37 °C for 48 h in 1 mL of medium containing *n*-butyric acid (4 mmol), TPA (32 pmol = 20 ng in dimethyl sulfoxide (DMSO), 2 μL) as inducer, and various amounts of test compounds in 5 μL of DMSO. Smears were made from the cell suspension, and the activated cells which were stained by EBV-EA positive serum from NPC patients were detected by an indirect immunofluorescence technique. Assays were performed in triplicate. The average EBV-EA induction of the test compounds was expressed as a relative ratio to the control experiment (100%) which was carried out only with *n*-butyric acid plus TPA. The viability of treated Raji cells was assayed by the Trypan Blue staining method.

Extraction and Isolation. Chopped and dried aerial parts of *P. lapathifolium* (3.45 kg) were extracted with hot MeOH (20 L). After the solvent was removed in vacuo, a dark green residue (579 g) was obtained. The residue was suspended in H_2O and extracted with *n*-hexane, $CHCl_3$, EtOAc, and *n*-BuOH saturated with H_2O, successively. Each organic layer was evaporated in vacuo to afford the residue (35.6, 23.6, 35.1, and 191.8 g). The EtOAc extract (17.6 g portion) was subjected to column chromatography on silica gel eluted with $CHCl_3$ containing increasing amounts of MeOH to provide fractions 1−7. Fractions 2−5 (eluted with 10% MeOH in $CHCl_3$) were each subjected to column chromatography on silica gel [solvent system: $CHCl_3$−MeOH−H_2O (9:1:0.1, lower layer)] repeatedly and on Sephadex LH-20 (solvent: MeOH). Lapathosides A (**1**, 102 mg) and B (**2**, 12 mg) were obtained from fractions 2 and 3, vanicoside B (**5**, 135 mg) and lapathoside C (**3**, 44 mg) were obtained from fractions 3 and 4, and hydropiperoside (**6**, 39 mg) and lapathoside D (**4**, 20 mg) were obtained from fractions 4 and 5. The *n*-BuOH extract (10 g portion) was also subjected to column chromatography on silica gel eluted with a solution of MeOH in $CHCl_3$ to provide fractions 1−5. Fractions 3 and 4 eluted with 8% and 15% MeOH in $CHCl_3$ were rechromatographed on Si gel [solvent system: $CHCl_3$−MeOH−H_2O (9:1:0.1, lower layer)] repeatedly to afford compounds **1** (7 mg), **3** (3 mg), **5** (10 mg), and **6** (2 mg). Compounds **5** and **6** were identified by comparison with reported data.[8,9]

Lapathoside A (1): amorphous powder; $[\alpha]_D$ 22.68° (*c* 0.26, MeOH); UV (MeOH) λ_{max} (log ϵ) 235 (4.35), 319 (4.60) nm; IR (KBr) ν_{max} 3400, 1700, 1630, 1605, 1514, 1271, 1167 cm^{-1}; ^{1}H and ^{13}C NMR see Table 2; FAB-MS (positive) *m*/*z* 1009 [M + Na]$^+$, 987 [M + H] $^+$, 631, 485 [631 − *p*-coumaryl ketene]$^+$, 455 [631 − ferulyl ketene]$^+$, 339; HRFABMS *m*/*z* 1009.2757 (calcd for $C_{50}H_{50}O_{21}Na$, 1009.2747).

Lapathoside B (2): amorphous powder; $[\alpha]_D$ 18.56° (*c* 0.20, MeOH); UV (MeOH) λ_{max} (log ϵ) 218 (4.29), 235 (4.24), 319 (4.50) nm; IR (KBr) ν_{max} 3400, 1698, 1632, 1605, 1514, 1275, 1165 cm^{-1}; ^{1}H and ^{13}C NMR, see Table 2; FAB-MS (positive) *m*/*z* 1039 [M + Na]$^+$, 1017 [M + H] $^+$, 661, 515 [661 − *p*-coumaryl ketene]$^+$, 485 [661 − ferulyl ketene]$^+$, 339; HR-FABMS *m*/*z* 1039.2853 (calcd for $C_{51}H_{52}O_{22}Na$, 1039.2848).

Lapathoside C (3): amorphous powder; $[\alpha]_D$ −14.66° (*c* 0.23, MeOH); UV (MeOH) λ_{max} (log ϵ) 230 (4.19), 316 (4.45) nm; IR (KBr) ν_{max} 3400, 1695, 1630, 1605, 1516, 1267, 1169 cm^{-1}; ^{1}H and ^{13}C NMR, see Table 2; FAB-MS (positive) *m*/*z* 833 [M + Na]$^+$, 811 [M + H]$^+$, 455, 339, 309 [455 − *p*-coumaryl ketene]$^+$; HRFABMS *m*/*z* 833.2283 (calcd for $C_{40}H_{42}O_{18}Na$, 833.2269).

Lapathoside D (4): amorphous powder; $[\alpha]_D$ 10.30° (*c* 0.15, MeOH); UV (MeOH) λ_{max} (log ϵ) 230 (4.15), 316 (4.46) nm; IR (KBr) ν_{max} 3400, 1695, 1655, 1605, 1516, 1264, 1169 cm^{-1}; ^{1}H and ^{13}C NMR, see Table 2; FAB-MS (positive) *m*/*z* 657 [M + Na]$^+$, 635 [M + H] $^+$, 455, 309 [455 − *p*-coumaryl ketene]$^+$; HRFABMS *m*/*z* 657.1790 (calcd for $C_{30}H_{34}O_{15}Na$, 657.1796).

Vanicoside B (5): amorphous powder; $[\alpha]_D$ 29.47° (*c* 0.54, MeOH); UV (MeOH) λ_{max} (log ϵ) 212 (4.31), 231 (4.31), 317 (4.59) nm; IR (KBr) ν_{max} 3400, 1695, 1632, 1605, 1514, 1266, 1169 cm^{-1}; FAB-MS (positive) *m*/*z* 979 [M + Na]$^+$, 957 [M + H] $^+$, 601, 455[601 − *p*-coumaryl ketene]$^+$, 339; HRFABMS *m*/*z* 979.2648 (calcd for $C_{49}H_{48}O_{20}Na$, 979.2637). Compound **5** was identified as vanicoside B by comparison with NMR data previously reported.[8]

Hydropiperoside (6): amorphous powder; $[\alpha]_D$ 61.86° (*c* 0.31, MeOH); UV (MeOH) λ_{max} (log ϵ) 230 (4.16), 314 (4.45) nm; IR (KBr) ν_{max} 3400, 1695, 1632, 1605, 1514, 1264, 1169 cm^{-1}; FAB-MS (positive) *m*/*z* 803 [M + Na]$^+$, 781 [M + H]$^+$, 601, 455[601 − *p*-coumaryl ketene]$^+$; HRFABMS *m*/*z* 803.2159 (calcd for $C_{39}H_{40}O_{17}Na$, 803.2163). Compound **6** was identified as hydropiperoside by comparison with NMR data previously reported.[9]

Alkaline Hydrolysis of 1−6. Each compound (**1**−**6**) was treated with 0.5% NaOH (0.5 mL) in MeOH (3 mL) at room temperature for 18 h. The reaction mixture was neutralized with 1 N HCl and extracted with $CHCl_3$. The organic layer was concentrated under reduced pressure. From compounds (**1**, **2**, **3**, and **5**), ferulic acid, *p*-coumaric acid, methyl ferulate, and methyl *p*-coumarate were identified, and from compounds **4** and **6**, *p*-coumaric acid and methyl *p*-coumarate were identified, respectively, by comparison with authentic samples and by TLC behavior [silica gel (Merck precoated), solvent:

$CHCl_3$−MeOH−H_2O (8:3:1, lower layer)]. Sucrose was obtained from each H_2O layer, identified as sucrose by its TLC behavior.

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Supporting Information Available: Figures of postitive-FABMS fragmentations of lapathoside A (**1**) and $^1H-^{13}C$ long-range correlations from HMBC of **1** are available free of charge via the Internet at http://pubs.acs.org.

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