Two New Phenylethanoid Glycosides from *Callicarpa longissima*

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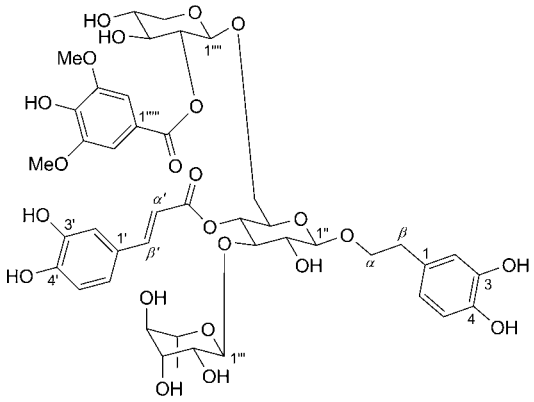
Two new phenylethanoid glycosides, longissimosides A and B (**1** and **2**, resp.), together with eight structurally related known compounds, were isolated from the EtOH extract of leaves and stems of *Callicarpa longissima* (HEMSL.) MERR. The structures of **1** and **2** were elucidated as 2-(3,4-dihydroxyphenyl)ethyl *O*-(α-L-rhamnopyranosyl)-(1→3)-*O*-(2-*O*-syringoyl-β-D-xylopyranosyl)-(1→6)-4-*O*-[(*E*)-caffeoyl]-β-D-glucopyranoside (**1**) and 2-(3-hydroxy-4-methoxyphenyl)ethyl *O*-(α-L-rhamnopyranosyl)-(1→3)-*O*-(β-D-apiofuranosyl)-(1→6)-4-*O*-[(*E*)-isoferuloyl]-β-D-glucopyranoside (**2**) on the basis of spectroscopic data and acid hydrolysis.

Introduction. – The genus *Callicarpa* (Verbenaceae) is a rich source of terpenoids [1–3], lignans [4], phenylethanoid glycosides [5], and flavonoids [6] with various biological features, such as antiplatelet aggregation [2], antibacterial [7], anti-inflammatory [8], and neuroprotective activities [5]. In China, many species of the genus *Callicarpa*, such as *Callicarpa kwangtungensis* CHUN [9] and *Callicarpa formosana* ROLFE [10], which are collected in 'Pharmacopoeia of the People's Republic of China', 2010 edn., Vol. 1, are widely used for the treatment of rheumatism, stomach disorders, and internal or external bleeding. *Callicarpa longissima* (HEMSL.) MERR. is widely distributed in southern China, and extracts of its leaves and stems have been used to treat common cold, cough, arthritis, bleeding, and abdominal pain by a local minority, '*Yao*' people, for thousands of years [11]. In this work, a detailed phytochemical investigation of the extract of leaves and stems of *C. longissima* was carried out, and two new phenylethanoid glycosides, **1** and **2**, were isolated together with eight structurally related known compounds, **3**–**10**, which were found in *C. longissima* for the first time.

Results and Discussion. – The 90%-EtOH extract of air-dried leaves and stems of *C. longissima* was chromatographed repeatedly to afford two new phenylethanoid glycosides, **1** and **2**, along with eight structurally related known compounds, acteoside (**3**) [12], forsythoside B (**4**) [13], alyssonoside (**5**) [14], leucosceptoside A (**6**) [15], poliumoside (**7**) [16], isoacteoside (**8**) [12], peiioside A (**9**) [17], and orobanchoside (**10**) [18] (*Fig. 1*). The known compounds were identified by comparison of their spectroscopic data with those reported in the literature.

Compound **1** was obtained as light-yellowish amorphous powder. Its molecular formula was deduced as $C_{43}H_{52}O_{23}$ from HR-ESI-MS (*m*/*z* 959.2785 ([*M* + Na]$^+$; calc.



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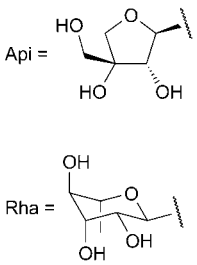
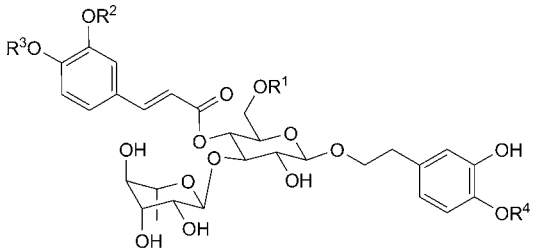
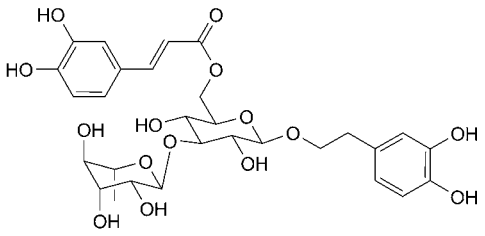




	R^1	R^2	R^3	R^4
2	Api	H	Me	Me
3	H	H	H	H
4	Api	H	H	H
5	Api	H	Me	H
6	H	Me	H	H
7	Rha	H	H	H



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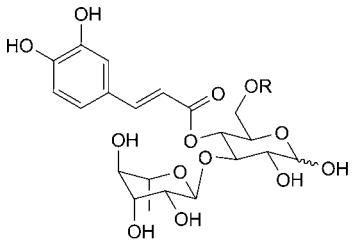

9 R = Api

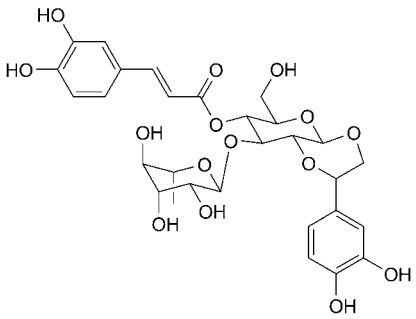

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Fig. 1. *Chemical structures of* **1**–**10**, *isolated from* Callicarpa longissima

959.2792)), which was further confirmed by its ^{1}H- and ^{13}C-NMR data. The ^{1}H-NMR spectrum of **1** (*Table*) displayed three aromatic H-atom signals due to one *ABX* system

Table. *^{1}H- and ^{13}C-NMR Data* (600 and 150 MHz, resp.; in CD_3OD) *of* **1** *and* **2**. δ in ppm, J in Hz.

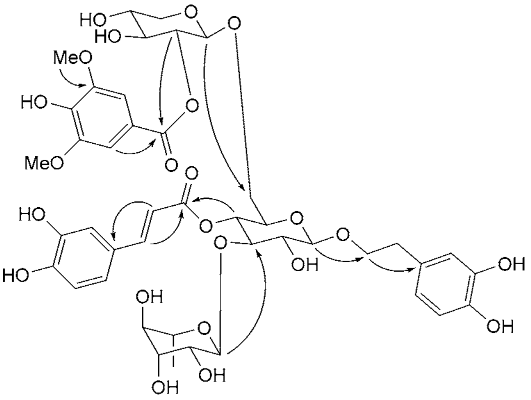
Position	**1**		Position	**2**	
	δ(H)	δ(C)		δ(H)	δ(C)
Aglycone			*Aglycone*		
1		131.8	1		132.7
2	6.66 (d, J = 2.0)	116.3	2	6.74 (d, J = 2.0)	117.1
3		146.0	3		147.5
4		144.6	4		147.4
5	6.67 (d, J = 8.1)	116.3	5	6.81 (d, J = 8.1)	116.5
6	6.51 (dd, J = 8.1, 2.0)	121.3	6	6.70 (dd, J = 8.1, 2.0)	121.2
α	3.68–3.72 (m),	71.6	α	3.98–4.02 (m),	72.2
	3.42–3.46 (m)			3.72–3.76 (m)	
β	2.57 (br. t)	36.6	β	2.83 (br. t)	36.6
Caffeoyl			*Isoferuloyl*		
1′		127.7	1′		127.6
2′	7.06 (d, J = 1.9)	115.2	2′	7.21 (d, J = 1.9)	111.7
3′		149.8	3′		150.8
4′		146.8	4′		149.4
5′	6.78 (d, J = 8.2)	116.5	5′	6.83 (d, J = 8.2)	112.8
6′	6.95 (dd, J = 8.2, 1.9)	123.3	6′	7.09 (dd, J = 8.2, 1.9)	124.4
α′	6.24 (d, J = 15.8)	117.2	α′	6.38 (d, J = 15.8)	115.2
β′	7.53 (d, J = 15.8)	148.0	β′	7.66 (d, J = 15.8)	147.9
C=O		168.1	C=O		168.1
Glucose			*Glucose*		
1″	4.20 (d, J = 7.9)	104.2	1″	4.20 (d, J = 7.9)	104.3
2″	3.12 (dd, J = 8.9, 8.0)	75.9	2″	3.38 (dd, J = 9.1, 7.9)	76.2
3″	3.64–3.67 (m)	81.3	3″	3.78–3.81 (m)	81.5
4″	3.47–3.50 (m)	71.3	4″	3.55–3.58 (m)	70.9
5″	3.55–3.59 (m)	74.6	5″	3.72–3.74 (m)	74.6
6″	3.85–3.87 (m),	69.0	6″	3.70–3.73 (m),	68.5
	3.47–3.50 (m)			3.38 (dd, J = 11.0, 5.8)	
Rhamnose			*Rhamnose*		
1‴	5.11 (d, J = 1.4)	103.0	1‴	5.19 (d, J = 1.7)	103.0
2‴	3.84–3.86 (m)	72.2	2‴	3.91–3.94 (m)	72.3
3‴	3.81–3.85 (m)	72.0	3‴	3.75–3.76 (m)	72.0
4‴	3.24–3.29 (m)	73.7	4‴	3.29 (d, J = 9.5)	73.7
5‴	3.58–3.60 (m)	70.4	5‴	3.56–3.58 (m)	70.4
6‴	1.06 (d, J = 6.2)	18.4	6‴	1.09 (d, J = 6.2)	18.4
Xylose			*Apiose*		
1⁗	4.56 (d, J = 7.7)	103.2	1⁗	4.91 (d, J = 2.3)	111.1
2⁗	4.93 (dd, J = 8.5, 8.0)	75.5	2⁗	3.86 (d, J = 2.3)	78.0
3⁗	3.60–3.63 (m)	75.9	3⁗		80.6
4⁗	3.46–3.49 (m)	70.4	4⁗	3.90 (d, J = 9.5),	75.1
5⁗	3.90–3.93 (m),			3.73 (d, J = 9.5)	
	3.23–3.26 (m)	67.0	5⁗	3.53 (s)	65.6
Syringoyl			4-MeO	3.82 (s)	56.4
1⁗′		121.6	4′-MeO	3.89 (s)	56.5
2⁗′	7.39 (s)	108.5			
3⁗′		148.8			

Table (cont.)

Position	**1**		Position	**2**	
	δ(H)	δ(C)		δ(H)	δ(C)
4‴″		141.8			
5‴″		108.5			
6‴″	7.39 (*s*)	148.8			
7‴″		167.4			
3‴″-MeO	3.83 (*s*)	56.8			
5‴″-MeO	3.83 (*s*)	56.8			

at δ(H) 7.06 (*d*, $J = 1.9$, H–C(2′)), 6.95 (*dd*, $J = 8.2$, 1.9, H–C(6′)), and 6.78 (*d*, $J = 8.2$, H–C(5′)) and two (*E*)-positioned olefinic H-atom signals due to one *AX* system at δ(H) 7.53 (*d*, $J = 15.8$, H–C(β')) and 6.24 (*d*, $J = 15.8$, H–C(α')). The HMBC spectrum of **1** revealed correlations of H–C(α') with C(β') (δ(C) 148.0), C(1′) (127.7), and C(α')–*C*=*O* (168.1), of H–C(β') with C(1′), C(α') (117.2), and C(α')–*C*=*O*, of H–C(2′) (δ(H) 7.06) with C(β'), and of H–C(6′) with C(β'), which indicated the presence of an (*E*)-caffeoyl moiety. Further, the ^{1}H-NMR spectrum of **1** (*Table*) also showed three aromatic H-atom signals for another *ABX* system at δ(H) 6.67 (*d*, $J = 8.1$, H–C(5)), 6.66 (*d*, $J = 2.0$, H–C(2)), and 6.51 (*dd*, $J = 8.1$, 2.0, H–(6)), a broad *triplet* at 2.57 ($CH_2(\beta)$), and two nonequivalent H-atom signals at 3.68 – 3.72 and 3.42 – 3.46 ($CH_2(\alpha)$). The HMBCs of $CH_2(\alpha)$ (δ(H) 3.68 – 3.72) with C(β) (δ(C) 36.6) and C(1) (131.8), of $CH_2(\beta)$ (δ(H) 2.57) with C(1) (δ(C) 131.8) and C(α) (71.6), of H–C(2) (δ(H) 6.66) with C(β), and of H–C(6) (δ(H) 6.51) with C(β) indicated the presence of one (3,4-dihydroxyphenyl)ethyl moiety. In addition, there were two equivalent aromatic H-atom signals at δ(H) 7.39 (*s*, H–C(2‴″,6‴″)) and a signal for two MeO groups at 3.83 (*s*, *Me*O–C(3‴″,5‴″)) in the ^{1}H-NMR spectrum of **1**. The HMBCs between H–C(2‴″,6‴″) (δ(H) 7.39) and C(7‴″)=O (δ(C) 167.4) confirmed the presence of a syringoyl moiety. Acid hydrolysis of **1** evidenced the presence of L-rhamnose, D-xylose, and D-glucose moieties, in a ratio of 1:1:1, as determined by HPLC analysis [19]. Furthermore, the ^{1}H-NMR spectrum showed signals for three anomeric H-atoms at δ(H) 5.11 (*d*, $J = 1.4$, H–C(1‴)), 4.56 (*d*, $J = 7.7$, H–C(1⁗)), and 4.20 (*d*, $J = 7.9$, H–C(1″)), which showed HSQCs with the anomeric C-atom signals at δ(C) 103.0 (C(1‴)), 103.2 (C(1⁗)), and 104.2 (C(1″)), respectively. The coupling constant ($J = 7.9$) of the anomeric H-atom of the glucose residue and the coupling constant ($J = 7.7$) of the anomeric H-atom of the xylose residue suggested that both sugar residues were β-forms. The configuration of the rhamnose residue was determined as α by comparing the ^{13}C-NMR data of C(3‴) (δ(C) 72.0) and C(5‴) (70.4) with those reported in the literature (α-form: 72.5 and 69.0; β-form: 73.8 and 73.1 [20][21]).

The HMBC spectrum of **1** revealed the connectivities between the different moieties (*Fig. 2*). The HMBCs between H–C(1⁗) (δ(H) 4.56) and C(6″) (δ(C) 69.0) suggested that the xylose and glucose units were connected by a (1 → 6) linkage. The HMBCs between H–C(1‴) (δ(H) 5.11) and C(3″) (δ(C) 81.3) indicated that the rhamnose and glucose units were connected by a (1 → 3) linkage. Furthermore, the HMBCs between H–C(1″) (δ(H) 4.20) and C(α) (δ(C) 71.6), and between $CH_2(\alpha)$



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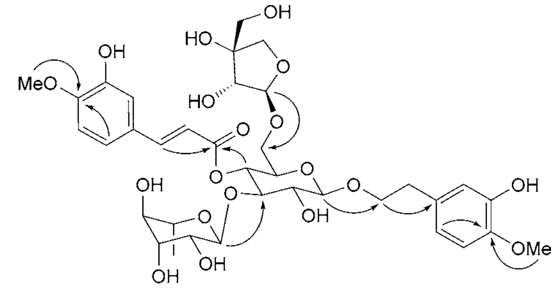

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Fig. 2. *Key HMBCs* (H → C) *of* **1** *and* **2**

(δ(H) 3.68–3.72) and C(1″) (δ(C) 104.2) confirmed the linkage between the (3,4-dihydroxyphenyl)ethyl and the glucose residue. The HMBCs between H–C(4″) (δ(H) 3.47–3.50) and C(α')–*C*=O (δ(C) 168.1) evidenced that the (*E*)-caffeoyl moiety was linked to C(4) of the glucose unit. The HMBCs between H–C(2⁗) (δ(H) 4.93) and C(7‴″)=O (δ(C) 167.4) indicated that the syringoyl unit was at C(2) of the xylose unit. The ^{1}H- and ^{13}C-NMR assignments for **1** were accomplished unambiguously based on HSQC, HMBC, and COSY data. Consequently, **1** was identified as 2-(3,4-dihydroxyphenyl)ethyl *O*-(α-L-rhamnopyranosyl)-(1 → 3)-*O*-(2-*O*-syringoyl-β-D-xylopyranosyl)-(1 → 6)-4-*O*-[(*E*)-caffeoyl]-β-D-glucopyranoside (*Fig. 1*) and named longissimoside A.

Compound **2** was obtained as white amorphous powder with a molecular formula of $C_{36}H_{48}O_{19}$ determined by HR-ESI-MS (*m/z* 783.2720 ([*M* − H]$^{-}$; calc. 783.2717)). The ^{1}H-NMR spectrum of **2** (*Table*) showed six aromatic H-atom signals indicating the presence of two *ABX* systems. The signals at δ(H) 7.21 (*d*, *J* = 1.9, H–C(2′)), 7.09 (*dd*, *J* = 8.2, 1.9, H–C(6′)), and 6.83 (*d*, *J* = 8.2, H–C(5′)) belonged to one *ABX* system, and the signals at 6.74 (*d*, *J* = 2.0, H–C(2)), 6.81 (*d*, *J* = 8.1, H–C(5)), and 6.70 (*dd*, *J* = 8.1, 2.0, H–C(6)) were ascribed to the other. Additionally, two signals of (*E*)-positioned olefinic H-atoms for one *AX* system at δ(H) 7.66 (*d*, *J* = 15.8, H–C(β')) and 6.38 (*d*,

$J = 15.8$, H–C(α')), two MeO groups at 3.89 (*s*, *Me*O–C(4′)) and 3.82 (*s*, *Me*O–C(4)), a broad *triplet* at 2.83 ($CH_2(\beta)$), and two nonequivalent H-atom signals at 3.98 – 4.02 and 3.72 – 3.76 ($CH_2(\alpha)$) were also detected in the ^{1}H-NMR spectrum of **2** (*Table*). The HMBCs of H–C(α') (δ(H) 6.38) with C(β') (δ(C) 147.9), C(1′) (127.6), and C=O (168.1), of H–C(β') (δ(H) 7.66) with C(1′), C(α') (115.2), and C=O, of H–C(2′) (δ(H) 7.21) with C(β'), of H–C(6′) (δ(H) 7.09) with C(β') and C(4′) (δ(C) 149.4), and of *Me*O–C(4′) (δ(H) 3.89) with C(4′) suggested the existence of an (*E*)-isoferuloyl moiety (*Fig. 2*). The HMBCs of $CH_2(\alpha)$ (δ(H) 3.98 – 4.02) with C(β) (δ(C) 36.6) and C(1) (132.7), of $CH_2(\beta)$ (δ(H) 2.83) with C(1) and C(α) (72.2), of H–C(2) (δ(H) 6.74) with C(β), of H–C(6) (δ(H) 6.70) with C(β) and C(4) (147.4), and of *Me*O–C(4) (δ(H) 3.82) with C(4) indicated the presence of a (3-hydroxy-4-methoxyphenyl)ethyl moiety (*Fig. 2*).

Acid hydrolysis of **2** confirmed the presence of L-rhamnose, D-apiose, and D-glucose moieties, in a ratio of 1:1:1, as determined by HPLC analysis [19]. The three anomeric H-atom signals at δ(H) 5.19 (*d*, $J = 1.7$, H–C(1‴)), 4.91 (*d*, $J = 2.3$, H–C(1⁗)), and 4.20 (*d*, $J = 7.9$, H–C(1″)) showed HSQCs with the C-atom signals at δ(C) 103.0 (C(1‴)), 111.1 (C(1⁗)), and 104.3 (C(1″)), respectively, indicating the presence of three sugar units. The coupling constants of the anomeric H-atoms of the glucose and apiose residues were 7.9 and 2.3, respectively, suggesting β-configurations for both sugar residues. The configuration of the rhamnose residue was determined to be α from its ^{13}C-NMR data [20][21].

The linkages between different moieties were confirmed through the HMBC spectrum (*Fig. 2*). The HMBC between H–C(1⁗) (δ(H) 4.91) and C(6″) (δ(C) 68.5) suggested that the apiose and glucose units were connected by a (1 → 6) linkage. The HMBC between H–C(1‴) (δ(H) 5.19) and C(3″) (δ(C) 81.5) indicated that the rhamnose and glucose units were connected by a (1 → 3) linkage. The HMBCs between H–C(1″) (δ(H) 4.20) and C(α) (δ(C) 72.2), and between $CH_2(\alpha)$ (δ(H) 3.98 – 4.02) and C(1″) (δ(C) 104.3) confirmed the linkage between the (3-hydroxy-4-methoxyphenyl)ethyl and the glucose residues. The HMBC between H–C(4″) (δ(H) 3.55 – 3.58) and C=O (δ(C) 168.1) established that the (*E*)-isoferuloyl moiety was linked to C(4) of the glucose unit. The ^{1}H- and ^{13}C-NMR assignments for **2** were accomplished unambiguously based on HSQC, HMBC, and COSY data. Thus, **2** was elucidated as 2-(3-hydroxy-4-methoxyphenyl)ethyl *O*-(α-L-rhamnopyranosyl)-(1 → 3)-*O*-(β-D-apiofuranosyl)-(1 → 6)-4-*O*-[(*E*)-isoferuloyl]-β-D-glucopyranoside and named longissimoside B.

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Experimental Part

General. TLC: Polyamide film plates (10 × 10 cm; *Taizhou Luqiao Sijia Biochemical Plastics Company*, Zhejiang, P. R. China); visualization with UV light at 254 nm. Column chromatography (CC): macroporous resin (*D101*; *Cangzhou Bon Adsorber Technology Co., Ltd.*, P. R. China), *Sephadex LH-20* (*Amersham Biosciences*, Germany), polyamide (40 – 60 mesh; *Sinopharm Chemical Reagent Co., Ltd.*,

P. R. China), *MCI* gel (*CHP20P*; 75–150 μm; *Mitsubishi Chemical Corporation*, Japan), and silica gel *G* (SiO_2; 100–200 mesh; *Qingdao Marine Chemical Factory*, P. R. China). MPLC: *Eyela Ceramic VSP 3050* pump, *Eyela* glass column (300 × 10 mm). Sugar anal. HPLC: *Dionex UltiMate 3000* HPLC system, *Gemini* C_{18} column (5 μm, 250 × 4.6 mm i.d., *Phenomenex*, USA); flow rate 0.8 ml min^{-1}; detection, at 250 nm. Prep. HPLC: *Shimadzu LC-6AD* pump, *Shimadzu SPD-20A* UV detector, *YMC ODS-A* column (20 × 250 mm, 10 μm); flow rate 8.0 ml min^{-1}; detection, at 330 nm. Optical rotations: *JASCO P1020* digital polarimeter (*JASCO*, Tokyo, Japan). UV Spectra: *Shimadzu UV mini-1240* UV/VIS spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *PerkinElmer Spectrum One* FT-IR spectrometer (*PerkinElmer*, Norwalk, CT, USA); $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker ARX-600* spectrometer; in CD_3OD; δ in ppm rel. to Me_4Si as internal standard: *J* in Hz. ESI-MS: *Agilent 1100-LC/MS D Trap SL*; in *m*/*z*. HR-ESI-MS: *Waters API QSTAR Pular-1* mass spectrometer and *Waters Synapt G2 MS* mass spectrometer; in *m*/*z*.

Plant Material. Stems and leaves of *C. longissima* were collected at Laibin, Guangxi Zhuang Autonomous Region, P. R. China, in April 2012. The plant was identified by traditional Chinese medicine pharmacist *Bin Dai*, Guangxi Institute of Minority Medicine. A voucher specimen (No. 20120401) has been deposited with the Laboratory of Natural Products of the College of Pharmacy, Guangxi Medical University.

Extraction and Isolation. Powder of air-dried stems and leaves (22.0 kg) of *C. longissima* was extracted two times with 220 l of 90% EtOH/H_2O (each 2 h) under reflux. After evaporation, the residue (1.9 kg) was suspended in H_2O (5 l) and partitioned successively with AcOEt (3 × 5 l). The aq. layer was subjected to CC (*D101*; EtOH/H_2O 0:100, 20:80, 60:40, and 95:5). The fraction (320.0 g) eluted with 60% EtOH was resubjected to CC (*D101*; EtOH/H_2O 0:100, 10:90, 30:70, 50:50, 70:30, and 95:5) to yield six fractions, *Frs. 1–6*. *Fr. 2* (10.0 g) was submitted to CC (*Sephadex LH-20*; MeOH/H_2O 30:70) to yield three subfractions, *Frs. 2.1–2.3*. *Fr. 2.1* (0.2 g) was separated by prep. HPLC (MeOH/H_2O 15:85) to afford **9** (t_R 15.26 min; 20 mg). *Fr. 3* (110.0 g) was dissolved in H_2O and subjected to CC (polyamide; EtOH/H_2O 0:100 → 90:10) to yield five subfractions, *Frs. 3.1–3.5*. *Fr. 3.1* (24.0 g) was purified by CC (*Sephadex LH-20*; MeOH/H_2O 1:1) to afford four subfractions, *Frs. 3.1.1–3.1.4*. *Fr. 3.1.3* (4.0 g) was subjected to MPLC (*MCI* gel; MeOH/H_2O 0:100 → 100:0) to yield three subfractions, *Frs. 3.1.3.1–3.1.3.3*. *Fr. 3.1.3.3* (0.9 g) was purified by CC (*Sephadex LH-20*; MeOH/H_2O 70:30) and prep. HPLC (MeOH/H_2O 45:55) to afford **2** (t_R 18.47 min; 100 mg). *Fr. 3.1.4* (4.0 g) was separated by prep. HPLC (MeOH/H_2O 35:65) to yield **4** (2.8 g) and *Fr. 3.1.4.1*. *Fr. 3.1.4.1* (1.1 g) was subjected to CC (SiO_2; CH_2Cl_2/MeOH 6:1) to afford **5** (50 mg) and **7** (820 mg). *Fr. 3.3* (26.0 g) was separated by CC (*Sephadex LH-20*; MeOH/H_2O 4:1) to afford four subfractions, *Frs. 3.3.1–3.3.4*. *Fr. 3.3.2* (0.1 g) was purified by prep. HPLC (MeOH/H_2O 35:65) to afford **1** (t_R 59.81 min; 30 mg). *Fr. 3.3.3* (9.0 g) was submitted to CC (*Sephadex LH-20*; MeOH/H_2O 1:1) to give **3** (2.5 g) and *Fr. 3.3.3.1* (6.0 g). A part of *Fr. 3.3.3.1* (1.1 g) was separated by prep. HPLC (MeOH/H_2O 35:65) to afford **6** (t_R 40.35 min; 30 mg) and **10** (t_R 51.94 min; 32 mg). *Fr. 3.3.4* (6.0 g) was repeatedly subjected to CC (*Sephadex LH-20*; MeOH/H_2O 4:1) to yield **8** (1.3 g).

Longissimoside A (=*2-(3,4-Dihydroxyphenyl)ethyl* O-*(α-*L*-Rhamnopyranosyl)-(1 → 3)*-O-*(2*-O-*syringoyl-β-*D*-xylopyranosyl)-(1 → 6)-4*-O-*[(*E*)-caffeoyl]-β-*D*-glucopyranoside* =*2-(3,4-Dihydroxyphenyl)ethyl 6-Deoxy-α-*L*-mannopyranosyl-(1 → 3)-[2*-O-*(4-hydroxy-3,5-dimethoxybenzoyl)-β-*D*-xylopyranosyl-(1 → 6)]-4*-O-*[(2*E*)-3-(3,4-dihydroxyphenyl)prop-2-enoyl]-β-*D*-glucopyranoside*; **1**). Light-yellowish amorphous powder. $[\alpha]_D^{22} = -51.0$ ($c = 0.50$, MeOH). UV (MeOH): 332 (4.24), 290 (4.23). IR (KBr): 3443, 3130, 1705, 1610, 1519, 1120. ^{1}H- and ^{13}C-NMR: *Table*. HR-ESI-MS: 959.2785 ($[M+Na]^+$, $C_{43}H_{52}NaO_{23}^+$; calc. 959.2792).

Longissimoside B (=*2-(3-Hydroxy-4-methoxyphenyl)ethyl* O-*(α-*L*-Rhamnopyranosyl)-(1 → 3)*-O-*(β-*D*-apiofuranosyl)-(1 → 6)-4*-O-*[(*E*)-isoferuloyl]-β-*D*-glucopyranoside* =*2-(3-Hydroxy-4-methoxyphenyl)ethyl 3*-O-*(6-Deoxy-α-*L*-mannopyranosyl)-6*-O-*(β-*D*-apiofuranosyl)-4*-O-*[(2*E*)-3-(3-hydroxy-4-methoxyphenyl)prop-2-enoyl]-β-*D*-glucopyranoside*; **2**). White amorphous powder. $[\alpha]_D^{22} = -85.2$ ($c =$ 0.50, MeOH). UV (MeOH): 329 (4.34). IR (KBr): 3442, 3134, 1703, 1631, 1591, 1515, 1271, 1131, 1067. ^{1}H- and ^{13}C-NMR: *Table*. HR-ESI-MS: 783.2720 ($[M-H]^-$, $C_{36}H_{47}O_{19}^-$; calc. 783.2717).

Acid Hydrolysis and Sugar Analysis [19] *of* **1** *and* **2**. Each compound (1 mg) was hydrolyzed with 1 ml of 2M HCl at 85° for 1 h. The mixture was extracted with AcOEt (2 × 1 ml), and the aq. phase was

evaporated under reduced pressure. Then, the residue was dissolved in pyridine (1 ml) containing L-cysteine methyl ester hydrochloride (1 mg) and heated at 60° for 1 h. *o*-Tolyl isothiocyanate (20 µl) was added to the mixture, which was heated at 60° for 1 h. The mixture was directly analyzed by reversed-phase (RP) HPLC. Anal. HPLC was performed on a *RP-18* column at 35° with isocratic MeCN/H_2O/HCOOH 25 : 75 : 1 for 40 min. The peaks at t_R 22.48, 26.23, 37.48, and 38.28 min were coincided with those of the derivatives of D-glucose, D-xylose, D-apiose, and L-rhamnose.

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