Water-Soluble Constituents from the Liverwort *Marchantia polymorpha*

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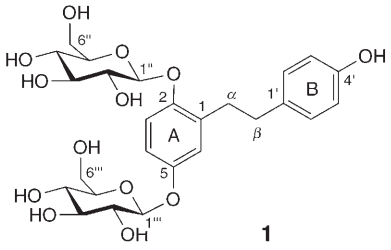
Four new glycosides, the bibenzyl glycoside α,β-dihydrostilbene-2,4′,5-triol 2,5-di-(β-D-glucopyranoside) (**1**), the shikimic acid glycoside shikimic acid 4-(β-D-xylopyranoside) (**2**), and two phenylethanoid glycosides 2-(3,4-dihydroxyphenyl)ethyl *O*-α-L-rhamnopyranosyl-(1→2)-β-D-allopyranoside (**3**) and 2-(3,4-dihydroxyphenyl)ethyl *O*-β-D-xylopyranosyl-(1→6)-β-D-allopyranoside (**4**), together with three known aromatic glycosides were isolated from the H_2O-soluble fraction of the EtOH extract of the liverwort *Marchantia polymorpha*. Their structures were elucidated on the basis of chemical and spectroscopic evidences.

Introduction. – *Marchantia polymorpha* L. (Marchantiaceae), a large thalloid liverwort, is distributed worldwide and shows antihepatic, antimicrobial, and diuretic properties [1]. Samples of *M. polymorpha* from various origins have been chemically investigated previously [2–8], and a series of sesquiterpenoids, diterpenoids, steroids, bibenzyls, flavonoids, and lipids have been isolated from the unpolar fractions of this species [5][8][9]. In this paper, we report the isolation and characterization of four new glycosides, the bibenzyl glycoside α,β-dihydrostilbene-2,4′,5-triol 2,5-di-(β-D-glucopyranoside)[1]) (**1**), the shikimic acid glycoside shikimic acid 4-(β-D-xylopyranoside)[1]) (**2**), and two phenylethanoid glycosides 2-(3,4-dihydroxyphenyl)ethyl *O*-α-L-rhamnopyranosyl-(1→2)-β-D-allopyranoside[1]) (**3**), and 2-(3,4-dihydroxyphenyl)ethyl *O*-β-D-xylopyranosyl-(1→6)-β-D-allopyranoside[1]) (**4**), together with three known constituents, 2-(3,4-dihydroxyphenyl)ethyl β-D-allopyranoside (**5**), 2-(3,4-dihydroxyphenyl)-ethyl β-D-glucopyranoside (**6**), and 3′,4′,5,7-tetrahydroxyisoflavone 7-(β-D-glucopyranoside) (**7**) from the H_2O-soluble portion of *M. polymorpha*.

Results and Discussion. – Compound **1** was obtained as a colorless, amorphous powder. The molecular formula $C_{26}H_{34}O_{13}$ was deduced from the $[M+Na]^+$ peak at *m*/*z* 577.1891 in the HR-ESI-MS. The IR spectrum showed absorptions of OH groups (3355 cm^{-1}) and aromatic rings (1613, 1514, and 1451 cm^{-1}). Two sets of aliphatic protons assignable to two glucose moieties were observed in the ^1H- and ^{13}C-NMR spectra of **1** (*Table 1*), which were similar to those of tyrolobibenzyl E [10]. Acid hydrolysis of **1** afforded glucose (Glc), which confirmed this conclusion. On the basis of

[1]) Arbitrary atom numbering; for systematic names, see *Exper. Part*. The absolute configurations D and L of the sugar moieties are tentative.



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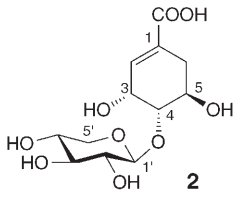

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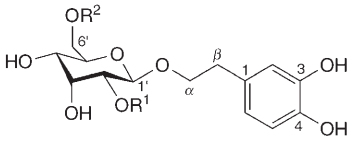
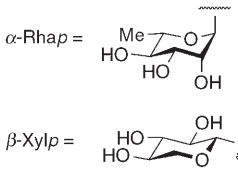
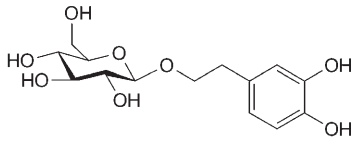


3 R^1 = α-Rha*p*, R^2 = H
4 R^1 = H, R^2 = β-Xyl*p*
5 R^1 = H, R^2 = H





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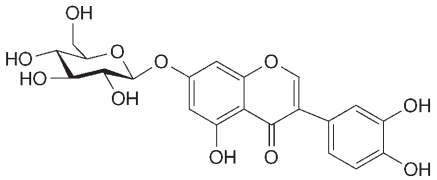

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further spectral evidences, the structure of compound **1** was established as α,β-dihydrostilbene-2,4′,5-triol 2,5-di(β-D-glucopyranoside)[1]) (**1**), which is a new compound. However, the structure assigned here for **1** has ever been misregistered to tyrolobibenzyl E [10] in CA (CAS registry No. 556113-15-6), the molecular formula of which was in fact $C_{28}H_{36}O_{14}$.

The ^{1}H-NMR spectrum of **1** showed two CH_2 signals at δ 2.68–2.71 and 2.77–2.79, three aromatic signals at δ 7.02 (*d*, J = 8.9 Hz, H–C(3)), 6.80 (*dd*, J = 8.9, 2.4 Hz, H–C(4)), and 6.83 (*d*, J = 2.4 Hz, H–C(6)) belonging to a 1,2,4-trisubstituted benzene ring (ring A), as well as two further aromatic signals at δ 7.06 (*d*, J = 8.4 Hz, H–C(2′), H–C(6′)) and 6.65 (*d*, J = 8.4 Hz, H–C(3′), H–C(5′)) assignable to an *AA′BB′* spin system of a 1,4-disubstituted benzene ring (ring B). Rings A and B of **1** were connected *via* the fragment $CH_2(\alpha)$–$CH_2(\beta)$, based on the HMBC correlations (*Fig.*) of $CH_2(\alpha)$ at δ(H) 2.77–2.79 with C(1), C(2), and C(6) at δ(C) 132.3, 150.6, and 118.1, respectively, and correlations of $CH_2(\beta)$ at δ(H) 2.68–2.71 with C(1′), C(2′), and C(6′) at δ(C) 132.4, 125.5, and 125.5, respectively. Thus, the aglycone of **1** was deduced to be bibenzyl-2,4′,5-triol (=2-[2-(4-hydroxyphenyl)ethyl]benzene-1,4-diol). The two glucose anomeric protons at δ(H) 4.69 (H–C(1″), H–C(1‴)) displayed long-range correlations with C(2) (δ(C) 150.6) and C(5) (δ(C) 152.4), respectively, in the HMBC plot, which showed that the glucoses were connected with the bibenzyl moiety at C(2) and C(5). The large coupling constant of the anomeric H-atoms (J = 7.3 Hz) indicated that both sugar units were β-configured.

Compound **2** was obtained as a colorless, amorphous powder. Its molecular formula was determined to be $C_{12}H_{18}O_9$ based on the HR-ESI-MS ($[M + Na]^+$ at m/z 329.0847). The IR spectrum showed absorption bands for OH groups (3403 cm^{-1}). The

Table 1. *^{13}C- and ^{1}H-NMR Data* (150 and 600 MHz, resp., (D_6)DMSO) *of* **1** *and* **2**. δ in ppm, J in Hz.

	1[1])			**2**[1])	
	δ(C)	δ(H)		δ(C)	δ(H)
Aglycone:			Aglycone:		
C(1)	132.3		C(1)	136.7	
C(2)	150.6		H–C(2)	129.7	6.20 (br. *s*)
H–C(3)	116.5	7.02 (*d*, *J* = 8.9)	H–C(3)	65.0	4.23 (br. *s*)
H–C(4)	114.5	6.80 (*dd*, *J* = 8.9, 2.4)	H–C(4)	81.6	3.50 (*dd*, *J* = 4.2, 6.6)
C(5)	152.4		H–C(5)	66.0	3.87 (br. *s*)
H–C(6)	118.1	6.83 (*d*, *J* = 2.4)	CH_2(6)	32.6	2.44 (*dd*, *J* = 4.0, 18.0),
CH_2(α)	32.4	2.77–2.79 (*m*)			2.01 (*dd*, *J* = 4.8, 18.0)
CH_2(β)	34.9	2.68–2.71 (*m*)	COOH	171.2	
C(1′)	132.4				
H–C(2′)	125.5	7.06 (*d*, *J* = 8.4)			
H–C(3′)	115.1	6.65 (*d*, *J* = 8.4)			
C(4′)	155.4				
H–C(5′)	115.1	6.65 (*d*, *J* = 8.4)			
H–C(6′)	125.5	7.06 (*d*, *J* = 8.4)			
Glucose I:			Xylose:		
H–C(1″)	102.2	4.69 (*d*, *J* = 7.3)	H–C(1′)	104.5	4.27 (*d*, *J* = 7.7)
H–C(2″)	73.7	3.23–3.26 (*m*)[a])	H–C(2′)	73.6	3.01 (*dd*, *J* = 7.7, 8.2)
H–C(3″)	77.2	3.16–3.18 (*m*)[a])	H–C(3′)	76.6	3.15 (*dd*, *J* = 8.2, 8.7)
H–C(4″)	70.0	3.12–3.14 (*m*)[a])	H–C(4′)	69.7	3.25–3.28 (*m*)[a])
H–C(5″)	77.2	3.16–3.18 (*m*)[a])	CH_2(5′)	66.0	3.68 (*dd*, *J* = 5.2, 11.2),
CH_2(6″)	61.0	3.45–3.46 (*m*)[a])[b]),			3.06 (*dd*, *J* = 10.8, 11.2)
		3.68–3.69 (*m*)[a])[c])			
Glucose II:					
H–C(1‴)	101.4	4.69 (*d*, *J* = 7.3)			
H–C(2‴)	73.4	3.23–3.26 (*m*)[a])			
H–C(3‴)	77.0	3.16–3.18 (*m*)[a])			
H–C(4‴)	69.9	3.12–3.14 (*m*)[a])			
H–C(5‴)	76.8	3.16–3.18 (*m*)[a])			
CH_2(6‴)	60.9	3.45–3.46 (*m*)[a])[b]),			
		3.68–3.69 (*m*)[a])[c])			

[a]) Multiplicity of the signals is unclear due to overlapping. [b])[c]) Signals might be interchangeable in pairs.

^{13}C-NMR spectrum (*Table 1*) showed 12 C-signals. Seven C-atoms were readily attributed to a shikimic acid residue [11]. From further ^{13}C-NMR data and the coupling-constant values of the sugar protons in the ^{1}H-NMR spectrum (*Table 1*), a β-xylopyranose (β-Xyl*p*) was identified [12], and the structure of **2** was assigned as shikimic acid 4-(β-D-xylopyranoside)[1]).

In the ^{13}C-NMR spectrum of **2**, an anomeric C-atom at δ(C) 104.5 (C(1′)) and four other sugar C-signals at δ(C) 73.6 (C(2′)), 76.6 (C(3′)), 69.7 (C(4′)), and 66.0 (C(5′)) were observed. The connectivity of the shikimic acid with the xylose moiety was established by the HMBC experiment (*Fig.*), which revealed the correlation of H–C(4) at δ(H) 3.50 with C(1′) at δ(C) 104.5, indicating that the β-xylopyranose should be linked to C(4). This assignment was further supported by the observation of a *ca.* 15 ppm downfield shift for the C(4) resonance (δ(C) 81.6) [13]. In the ^{1}H-NMR spectrum, the anomeric proton signal at δ(H) 4.27 (*d*, *J* = 7.7 Hz, H–C(1′)) demonstrated the β-configuration of the sugar moiety.

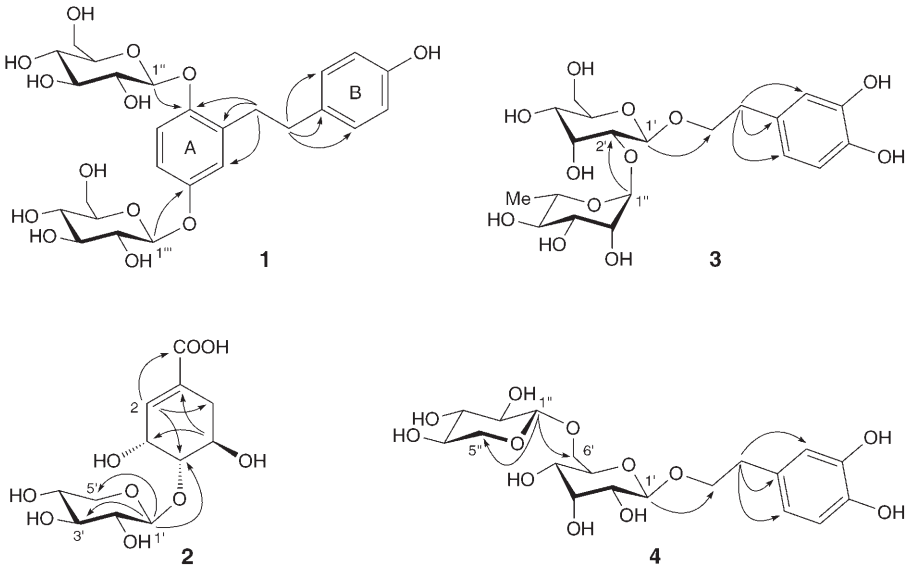

Figure. *Key HMBC correlations* (H → C) *for compounds* **1**–**4**

Compound **3** was obtained as a colorless, amorphous powder, which darkened on exposure to the atmosphere, especially in solution. Its molecular formula was deduced to be $C_{20}H_{30}O_{12}$ from the $[M + Na]^+$ peak at *m*/*z* 485.1632 in the HR-ESI-MS. The IR spectrum showed absorptions of OH groups (3424 cm^{-1}) and aromatic rings (1610, 1522, and 1446 cm^{-1}). In accord with the NMR data (*Table 2*, *Fig.*) compound **3** was established to be 2-(3,4-dihydroxyphenyl)ethyl *O*-*α*-L-rhamnopyranosyl-(1 → 2)-*β*-D-allopyranoside[1].

The ^{13}C-NMR spectrum of **3** displayed 20 signals, of which eight were assigned to the aglycone moiety, including one aromatic ring (δ(C) 131.6 (C(1)), 117.2 (C(2)), 144.6 (C(3)), 146.0 (C(4)), 116.3 (C(5)), and 121.3 (C(6))) and one oxygenated ethyl group (δ(C) 72.2 (C(α)) and 36.7 (C(β))). The remaining 12 signals corresponded to two hexose residues. The ^{1}H-NMR spectrum displayed an *ABX* system assigned to a 1,3,4-trisubstituted aromatic ring at δ(H) 6.60 (*d*, *J* = 2.0 Hz, H–C(2)), 6.58 (*d*, *J* = 8.0 Hz, H–C(5)), and 6.46 (*dd*, *J* = 2.0, 8.0 Hz, H–C(6)); a set of signals assigned to an oxygenated ethyl group at δ(H) 3.90–3.92 (*m*, H_a–C(α)), 3.53–3.55 (*m*, H_b–C(α)), and 2.77 (*t*, *J* = 7.6 Hz, CH_2(β)), together with two anomeric signals at δ(H) 4.64 (*d*, *J* = 8.0 Hz) and 4.79 (*d*, *J* = 1.8 Hz)). These data suggested that **3** should be a phenylethanoid glycoside [14]. The sugar moieties were assigned to be a *β*-allopyranose (*β*-All*p*) and an *α*-rhamnopyranose (*α*-Rha*p*) according to the coupling-constant values of the sugar protons and their ^{13}C-NMR data (*Table 2*) [14][15]. The ESI-MS signals at *m*/*z* 485 ($[M + Na]^+$), 339 ($[M$ – rhamnose + $Na]^+$), and 155 ($[M$ – rhamnose – allose + $H]^+$) further supported this assignment. The sugar sequence within **3** was determined to be (Rha-(1 → 2)-All) with the aid of a ^{1}H,^{13}C long-range correlation (*Fig.*) between H–C(1″) and C(2′) in the HMBC plot. The observation that C(2′) of the inner allose of **3** was downfield shifted by *ca.* 4.0 ppm also supported the above assignment.

Compound **4** was obtained as a colorless, amorphous powder, the solution of which also darkened on exposure to the atmosphere. The HR-ESI-MS showed the $[M + Na]^+$ peak at *m*/*z* 471.1474, consistent with the molecular formula $C_{19}H_{28}O_{12}$. The IR

Table 2. *^{13}C- and ^{1}H-NMR Data* (150 and 600 MHz, resp., D_2O) *of* **3** *and* **4**. δ in ppm, J in Hz.

	3[1])			**4**[1])	
	δ(C)	δ(H)		δ(C)	δ(H)
Aglycone:			Aglycone:		
C(1)	131.6		C(1)	132.0	
H–C(2)	117.2	6.60 (*d*, *J* = 2.0)	H–C(2)	117.3	6.76 (*d*, *J* = 2.0)
C(3)	144.6		C(3)	142.9	
C(4)	146.0		C(4)	144.5	
H–C(5)	116.3	6.58 (*d*, *J* = 8.0)	H–C(5)	116.8	6.90 (*d*, *J* = 8.0)
H–C(6)	121.3	6.46 (*dd*, *J* = 2.0, 8.0)	H–C(6)	121.8	6.86 (*dd*, *J* = 2.0, 8.0)
$CH_2(\alpha)$	72.2	3.90–3.92 (*m*), 3.53–3.55 (*m*)	$CH_2(\alpha)$	71.5	4.02–4.04 (*m*), 3.83–3.85 (*m*)
$CH_2(\beta)$	36.7	2.77 (*t*, *J* = 7.6)	$CH_2(\beta)$	35.0	2.83 (*t*, *J* = 7.6)
Allose:			Allose:		
H–C(1′)	100.3	4.64 (*d*, *J* = 8.0)	H–C(1′)	100.6	4.68 (*d*, *J* = 8.2)
H–C(2′)	74.8	3.47 (*dd*, *J* = 3.3, 8.0)	H–C(2′)	70.7	3.40–3.42 (*m*)[a])
H–C(3′)	68.8	4.12 (*t*, *J* = 3.3)	H–C(3′)	71.5	4.12 (*t*, *J* = 2.6)
H–C(4′)	68.7	3.50 (*dd*, *J* = 3.3, 9.8)	H–C(4′)	67.2	3.65 (*dd*, *J* = 2.6, 10.2)
H–C(5′)	75.2	3.71–3.72 (*m*)	H–C(5′)	73.2	3.85–3.86 (*m*)
$CH_2(6')$	63.0	3.74 (*dd*, *J* = 2.3, 11.7), 3.56 (*dd*, *J* = 5.7, 11.7)	$CH_2(6')$	69.6	4.05 (*dd*, *J* = 2.5, 11.7), 3.79 (*dd*, *J* = 6.0, 11.7)
Rhamnose:			Xylose:		
H–C(1″)	97.7	4.79 (*d*, *J* = 1.8)	H–C(1″)	104.1	4.43 (*d*, *J* = 7.8)
H–C(2″)	72.2	3.81 (*dd*, *J* = 1.8, 3.4)	H–C(2″)	73.5	3.29–3.31 (*m*)[a])
H–C(3″)	72.3	3.63 (*dd*, *J* = 3.4, 9.5)	H–C(3″)	76.2	3.41–3.42 (*m*)[a])
H–C(4″)	74.0	3.42 (*t*, *J* = 9.5)	H–C(4″)	69.8	3.60–6.62 (*m*)
H–C(5″)	69.8	3.87–3.88 (*m*)	$CH_2(5'')$	65.7	3.96 (*dd*, *J* = 5.3, 11.6), 3.32 (*dd*, *J* = 7.8, 11.6)
Me(6″)	18.0	1.26 (*d*, *J* = 6.2)			

[a]) Multiplicity of the signals is unclear due to overlapping.

spectrum also showed absorption bands of OH groups (3423 cm^{-1}) and aromatic rings (1609, 1521, and 1446 cm^{-1}). The ^{1}H- and ^{13}C-NMR spectra of **4** (*Table 2*) were very similar to those of **3**, revealing the same aglycone as in **3**, but a different sugar moiety. Compound **4** was determined to be 2-(3,4-dihydroxyphenyl)ethyl *O*-β-D-xylopyranosyl-(1 → 6)-*O*-β-D-allopyranoside[1]).

In the ^{1}H-NMR spectrum of **4**, two sugar moieties with the anomeric protons at δ(H) 4.68 (*d*, *J* = 8.2 Hz, H–C(1′)) and 4.43 (*d*, *J* = 7.8 Hz, H–C(1″)) were observed. The coupling-constant values of the sugar protons and the corresponding ^{13}C-NMR data indicated the presence of an allopyranose and a xylopyranose moiety [12][14]. In the HMBC plot, H–C(1″) showed long-range correlations with C(5″), also indicating the presence of the xylopyranose unit; H–C(1″) showed a cross-peak with C(6′), and H–C(1′) showed a cross-peak with C(α), suggesting that the xylopyranose residue was linked to the C(6′) position of the allose and that the allose residue was attached to C(α). The large coupling constants of H–C(1′) (*J* = 8.2 Hz) and H–C(1″) (*J* = 7.8 Hz) indicated that both sugar units were β-configured.

The three known compounds were identified as 2-(3,4-dihydroxyphenyl)ethyl β-D-allopyranoside (**5**) [15], 2-(3,4-dihydroxyphenyl)ethyl β-D-glucopyranoside (**6**) [16],

and 3′,4′,5,7-tetrahydroxyisoflavone 7-(β-D-glucopyranoside) (**7**) [17], based on comparison of their ^{1}H- and ^{13}C-NMR and MS data with those reported. They were all obtained for the first time from this plant species.

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Experimental Part

General. All solvents used were of anal. grade (*Tianjin No. 1 Chemical Reagent Factory*). Column chromatography (CC): silica gel (200–300 mesh; *Qingdao Marine Chemical Industry*), *Sephadex LH-20* gel (*Pharmacia Biotek*), *MCI* gel (*CHP20P*, 75–150 μm, *Mitsubishi Chemical Industries Ltd.*), and polyamide resin (*Luqiaosijia Biochemistry Plastic Plant*). TLC: pre-coated silica gel *GF254* plates (*Qingdao Marine Chemical Industry*). Semi-prep. HPLC: *YMC-Pack ODS-A* column (250 × 20 mm, S-10 μm, 12 nm), with *Agilent 1100-G1310A* isopump and *Agilent 1100-G1314* detector (280 nm); MeOH/H_2O 11:89 as mobile phase, flow rate 3.0 ml/min. Optical rotations: *Perkin-Elmer 241MC* polarimeter. UV Spectra. *Shimadzu UV-2450* spectrophotometer; λ_{max} (log ε) in nm. IR spectra: *Thermo-Nicolet 670* spectrophotometer; KBr disks; $\tilde{\nu}_{max}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker Avance-DRX-600* spectrometer; at 600 (^{1}H) or 150 MHz (^{13}C), in (D_6)DMSO or D_2O; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz; 2D spectra recorded with standard pulse programs and acquisition parameters. MS: *API-4000* triple-stage quadrupole instrument for electrospray ionization (ESI) and *Finnigan LC-Q^{DECA}* mass spectrometer for HR-ESI; in *m*/*z* (rel. %).

Plant Material. The whole plant of *M. polymorpha* was collected from Leshan Mountain, Sichuan Province, P. R. China, in October 2002, and was identified by Prof. *Qian Gao* (Shenyang Institute of Applied Ecology, Chinese Academy of Sciences, P. R. China). A voucher specimen (No. 20021002) was deposited at the Department of Natural Products, School of Pharmaceutical Sciences, Shandong University.

Extraction and Isolation. The powder of *M. polymorpha* (8.95 kg) was first extracted with Et_2O (15 l) and then with 95% EtOH (15 l) under reflux for 2.5 h. The process was repeated three times, and the combined EtOH extract was concentrated: crude extract (63 g). The crude extract was partitioned between Et_2O (0.2 l) and H_2O (0.4 l). The aq. portion (54 g) was purified further by CC (*MCI* gel, $H_2O \rightarrow$ MeOH) to give fractions eluted with H_2O (34 g) and MeOH (20 g). A portion (19 g) of the MeOH fraction was subjected to CC (*Sephadex LH-20*, MeOH); *Fractions 1–6*). *Fr. 2* (1.3 g) was applied to CC (silica gel, $CHCl_3$/MeOH 8:1): **7** (10 mg) and **2** (5 mg). *Fr. 3* (2.0 g) was subjected to CC (silica gel, $CHCl_3$/MeOH 8.5:1.5, then polyamide resin, H_2O/MeOH 10:1): **1** (15 mg). *Fr. 4* (1.0 g) was purified by CC (silica gel, $CHCl_3$/MeOH 8:2): **6** (20 mg). *Fr. 5* (4.3 g) was subjected to CC (silica gel, $CHCl_3$/MeOH 10:1 → 9:1 → 8:2 → 0:1): *Fr. 5.1–5.10*. *Fr. 5.6* (240 mg) was further fractionated by semi-prep. HPLC (see *General*): **3** (10 mg) and **4** (4 mg). *Fr. 5.7* (150 mg) was subjected to semi-prep. HPLC (see *General*): **5** (15 mg).

α,β-Dihydrostilbene-2,4′,5-triol 2,5-Di(β-D-glucopyranoside)[1]) (=*2-[2-(4-Hydroxyphenyl)ethyl]-1,4-phenylene Bis(β-D-glucopyranoside)*; **1**): Colorless, amorphous powder. $[\alpha]_D^{20} = -114$ ($c = 1.0$, H_2O). UV (H_2O): 220 (4.12), 277 (3.55). IR (KBr): 3355, 1613, 1514, 1451. ^{1}H- and ^{13}C-NMR: *Table 1*. ESI-MS (pos.): 577 ($[M+Na]^+$). HR-ESI-MS: 577.1891 ($[M+Na]^+$, $C_{26}H_{34}O_{13}Na^+$; calc. 577.1899).

Shikimic Acid 4-(β-D-Xylopyranoside)[1]) (=(*3*R,*4*S,*5*S)*-3,5-Dihydroxy-4-(β-D-xylopyranasyloxy)cyclohex-1-ene-1-carboxylic Acid*; **2**): Colorless, amorphous powder. $[\alpha]_D^{20} = -255$ ($c = 0.8$, H_2O). UV (H_2O): 205 (3.96). IR (KBr): 3403, 3138, 1664, 1586. ^{1}H- and ^{13}C-NMR: *Table 1*. ESI-MS (neg.): 305 ($[M-H]^-$). HR-ESI-MS: 329.0847 ($[M+Na]^+$, $C_{12}H_{18}O_9Na^+$; calc. 329.0849).

2-(3,4-Dihydroxyphenyl)ethyl O-α-L-*Rhamnopyranosyl-(1 → 2)-β-D-allopyranoside*[1]) (=*2-(3,4-Dihydroxyphenyl)ethyl 2*-O*-(6-Deoxy-α-L-mannopyranosyl)-β-D-allopyranoside*; **3**): Colorless, amorphous powder. $[\alpha]_D^{20} = -76$ ($c = 0.5$, H_2O). UV (H_2O): 202 (3.80), 274 (3.17). IR (KBr): 3424, 1610, 1522, 1446.

^{1}H- and ^{13}C-NMR: *Table 2*. ESI-MS (pos.): 485 (100, $[M+Na]^+$), 339 (30, $[M-$rhamnose$+Na]^+$), 155 (5, $[M-$rhamnose$-$allose$+H]^+$). HR-ESI-MS: 485.1632 ($[M+Na]^+$, $C_{20}H_{30}O_{12}Na^+$; calc. 485.1635).

2-(3,4-Dihydroxyphenyl)ethyl O-*β*-D-*Xylopyranosyl-(1→6)*-O-*β*-D-*allopyranoside*[1]) (=*2-(3,4-Dihydroxyphenyl)ethyl 6*-O-*β*-D-*Xylopyranosyl-β*-D-*allopyranoside*; **4**): Colorless, amorphous powder. $[\alpha]_D^{20}=-70$ ($c=0.2$, H_2O). UV (H_2O): 202 (3.98), 274 (3.14). IR (KBr): 3423, 1609, 1521, 1446. ^{1}H- and ^{13}C-NMR: *Table 2*. ESI-MS (neg.): 447 ($[M-H]^-$). HR-ESI-MS: 471.1474 ($[M+Na]^+$, $C_{19}H_{28}O_{12}Na^+$; calc. 471.1478).

Acid Hydrolysis of **1**. Compound **1** (2 mg) was hydrolyzed with 2N aq. CF_3COOH (5 ml) by heating on a water bath (90°) for 3 h in a sealed tube. The mixture was diluted with H_2O (15 ml) and extracted with CH_2Cl_2 (3×5 ml). The aq. layer was repeatedly evaporated with MeOH until neutral [18]. The sugar was identified by co-TLC with an authentic sample TLC (silica gel, $CHCl_3$/MeOH/H_2O 8:5:1, detection by spraying with anisaldehyde/H_2SO_4, followed by heating): R_f value of glucose 0.31.

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