Acylated Stilbene Glucosides and Further Constituents from *Acanthopanax brachypus*

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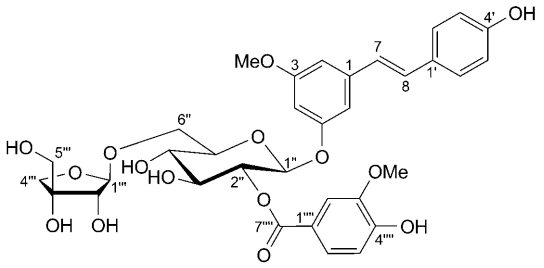
Two new acylated stilbene glucosides, (*E*)-3-*O*-methylresveratrol 5-*O*-*β*-D-apiofuranosyl-(1→6)-*β*-D-(2″-vanilloyl)glucopyranoside (**1**) and (*E*)-3-*O*-methylresveratrol 5-*O*-*α*-L-rhamnopyranosyl-(1→6)-*β*-D-2″-[(*E*)-feruloyl]glucopyranoside (**2**), together with five known compounds 2-methoxyphenyl *β*-D-glucopyranoside, (−)-syringaresinol-4,4′-bis-*O*-*β*-D-glucopyranoside, acantrifoside A, *β*-sitosterol, and daucosterol, were isolated from the EtOH extract of *Acanthopanax brachypus*. Their structures were characterized by means of spectroscopic methods, especially by ^{1}H-, ^{13}C-, 2D-NMR, and HR-MS, as well as by chemical methods and comparison with literature data.

Introduction. – The genus *Acanthopanax* belonging to the Araliaceae family includes 37 species around the world, which are widely distributed in Korea, Japan, China, and the far-eastern region of Russia. 26 Species and 18 varieties grow in mainland China [1][2]. The root and stem bark of these plants have been clinically used for a long time as a tonic and sedative, as well as for the treatment of rheumatism, diabetes, chronic bronchitis, hypertension, anti-stress, ischemic heart disease, and gastric ulcer [3–6]. As an endangered shrub in the wild due to overharvesting and loss of habitat through deforestation, *Acanthopanax brachypus* HARMS is distributed in a narrow geographical area, most in the Loess Plateau of the Northwest of China [7][8]. The seeds of *A. brachypus* have been reported to contain many microelements indispensable to human body, alleviate women menopause syndrome, and exhibit immunostimulating and anticancer activities [9][10]. Rhizome extracts have been used to inhibit the allergic response in China and Korea [11]. Roots, leaves, and flowers possess various therapeutic uses [12–14]. To date, however, the research mainly concentrated on the reproductive biology and ecology, there has been a few studies on the chemical composition and biological activity. Only syringaresinol diglucoside, syringin, sucrose, *β*-sitosterol, and fatty acids have been previously isolated from this plant [15][16]. Further phytochemical investigation led to the isolation of two new acylated stilbene glucosides, (*E*)-3-*O*-methylresveratrol 5-*O*-*β*-D-apiofuranosyl-(1→6)-*β*-D-(2″-vanilloyl)-glucopyranoside[1]) (**1**) and (*E*)-3-*O*-methylresveratrol 5-*O*-*α*-L-rhamnopyranosyl-(1→6)-*β*-D-2″-[(*E*)-feruloyl]glucopyranoside[1]) (**2**), together with five known compounds (2-methoxyphenyl *β*-D-glucopyranoside, (−)-syringaresinol-4,4′-bis-*O*-*β*-D-glucopyranoside, acantrifoside A, *β*-sitosterol, and daucosterol) from

[1]) For systematic names, see *Exper. Part.*

the stem bark of *A. brachypus*. In the present communication, we describe the isolation and structural elucidation of these new compounds.



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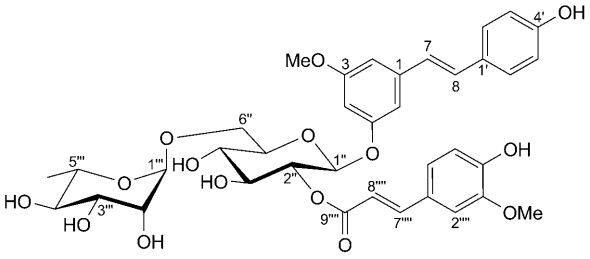

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Results and Discussion. – Compound **1** was obtained as a pale yellowish amorphous powder, and was assigned the molecular formula $C_{34}H_{38}O_{15}$, requiring 16 degrees of unsaturation, based on HR-FAB-MS (*m/z* 687.2296 $[M+H]^+$; calc. 687.2289). The UV spectrum exhibited absorptions at 258, 308, and 326 nm, suggesting the presence of a conjugated aromatic system [17]. The IR spectrum showed the presence of OH (3429 cm^{-1}), aromatic (1600, 1508, 1456 cm^{-1}), and conjugated CO (1715 cm^{-1}) groups.

The ^{1}H-NMR spectrum (*Table 1*) showed the presence of a 1,3,5-trisubstituted aromatic ring at δ(H) 6.70 (br. *s*, 1 H), 6.40 (br. *s*, 1 H), and 6.63 (br. *s*, 1 H), one MeO group at δ(H) 3.81 (*s*, 3 H), a *para*-disubstituted aromatic ring at δ(H) 7.43 (*d*, $J=8.5$, 1 H) and 6.88 (*d*, $J=8.5$, 1 H), and two (*E*)-olefinic H-atoms at δ(H) 6.85 (*d*, $J=16.0$, 1 H) and 7.01 (*d*, $J=16.0$, 1 H) [18]. Moreover, the HMBC and NOESY correlations H−C(7)/C(2) and C(6), H−C(8)/C(2′) and C(6′), and H−C(7)/H−C(2′) and H−C(8)/H−C(6) were observed. These spectra were consistent with those published for (*E*)-resveratrol [19][20] and (*E*)-resveratrol 3-*O*-β-D-glucopyranoside [21][22]. In the NMR and DEPT spectrum of **1**, the signals at δ(H) 4.91 (*d*, $J=7.5$, 1 H) and δ(C) 101.3 (CH), 76.8 (CH), 74.5 (CH), 71.3 (CH), 76.9 (CH), and 68.2 (CH_2) indicated the presence of a β-glucopyranose (Glc) moiety. Likewise, the signals at δ(H) 5.10 (*d*, $J=$ 2.4, 1 H) and δ(C) 109.5 (CH), 78.2 (CH), 80.7 (C), 74.8 (CH_2), and 65.1 (CH_2) indicated the presence of a β-apiofuranose (Api) moiety [23][24]. The remaining signals at δ(H) 7.18 (*d*, $J=2.6$, 1 H), 6.76 (*d*, $J=8.0$, 1 H), 7.25 (*dd*, $J=8.0$, 2.6, 1 H), and 3.75 (*s*, 3 H), and δ(C) 122.8 (C), 110.2 (CH), 147.1 (C), 150.2 (C), 116.9 (CH),

Table 1. *^1H, ^{13}C, and 2D-NMR Data of* **1**. At 400/100 MHz, resp., in CD_3OD; δ in ppm, J in Hz. Arbitrary atom numbering.

	δ(C) (DEPT)	δ(H)	HMBC (H → C)	NOESY
C(1)	141.5 (C)			
H–C(2)	107.3 (CH)	6.70 (br. *s*)	1, 3, 4, 6, 7	9
C(3)	162.1 (C)			
H–C(4)	104.0 (CH)	6.40 (br. *s*)	2, 3, 5, 6	9
C(5)	159.3 (C)			
H–C(6)	107.8 (CH)	6.63 (br. *s*)	1, 2, 4, 5, 7	8, 1″
H–C(7)	126.8 (CH)	6.85 (*d*, *J* = 16.0)	1, 2, 6, 1′, 8	2′
H–C(8)	129.8 (CH)	7.01 (*d*, *J* = 16.0)	1, 2′, 6′, 7	6
Me(9)	55.9 (Me)	3.81 (*s*)	3	2, 4
C(1′)	131.6 (C)			
H–C(2′)	128.7 (CH)	7.43 (*d*, *J* = 8.5)	3′, 4′, 6′, 8	7
H–C(3′)	115.4 (CH)	6.88 (*d*, *J* = 8.5)	1′, 2′, 4′, 5′	OH
C(4′)	158.7 (C)			
H–C(5′)	115.4 (CH)	6.88 (*d*, *J* = 8.5)	1′, 4′, 6′	OH
H–C(6′)	128.7 (CH)	7.43 (*d*, *J* = 8.5)	1′, 4′, 5′, 8	
H–C(1″)	101.3 (CH)	4.91 (*d*, *J* = 7.5)	5, 2″	6, 3″, 5″
H–C(2″)	76.8 (CH)	4.53 (*dd*, *J* = 9.5, 7.5)	7‴, 1″, 3″	4″
H–C(3″)	74.5 (CH)	3.39–3.45 (*m*)[a])	2″, 4″	1″, 5″
H–C(4″)	71.3 (CH)	3.39–3.45 (*m*)[a])	3″, 5″	2″
H–C(5″)	76.9 (CH)	3.39–3.45 (*m*)[a])	4″, 6″	1″, 3″
CH_2(6″)	68.2 (CH_2)	3.98 (*dd*, *J* = 11.5, 1.8), 3.71 (*dd*, *J* = 11.5, 5.0)	1‴, 5″	
H–C(1‴)	109.5 (CH)	5.10 (*d*, *J* = 2.4)	6″, 2‴	
H–C(2‴)	78.2 (CH)	3.74 (*d*, *J* = 2.4)	1‴	
C(3‴)	80.7 (C)			
CH_2(4‴)	74.8 (CH_2)	3.87, 3.61 (2*d*, *J* = 10.0)	2‴, 3‴	
CH_2(5‴)	65.1 (CH_2)	3.39, 3.36 (2*d*, *J* = 11.0)	2‴, 3‴	
C(1⁗)	122.8 (C)			
H–C(2⁗)	110.2 (CH)	7.18 (*d*, *J* = 2.6)	1⁗, 4⁗, 7⁗	8⁗
C(3⁗)	147.1 (C)			
C(4⁗)	150.2 (C)			
H–C(5⁗)	116.9 (CH)	6.76 (*d*, *J* = 8.0)	1⁗, 3⁗	OH
H–C(6⁗)	123.2 (CH)	7.25 (*dd*, *J* = 8.0, 2.6)	2⁗, 4⁗, 7⁗	
C(7⁗)	164.5 (C)			
Me(8⁗)	55.6 (Me)	3.75 (*s*)	3⁗	2⁗

[a]) Overlapping signals.

123.2 (CH), 164.5 (C), and 55.6 (Me) as well as HMBC H–C(6⁗)/C(7⁗) and Me(8⁗)/C(3⁗) (see *Fig. 1*) indicated a vanilloyl moiety in **1**. In the FAB-MS spectrum of **1**, the significant ion peaks at *m*/*z* 555 ($[M+H-132]^+$), 537 ($[M+H-150]^+$), 405 ($[M+H-150-132]^+$), 243 ($[M+H-162-150-132]^+$), and 151 ([vanilloyl]$^+$) also indicated the presence of vanilloyl, glucosyl, and apiosyl groups in **1**. This conclusion was further supported by the detection of vanillic acid, glucose, and apiose (in the ratio of 1:1, determined by *co*-TLC with authentic samples and GC-MS analysis [25]) after acid hydrolysis.

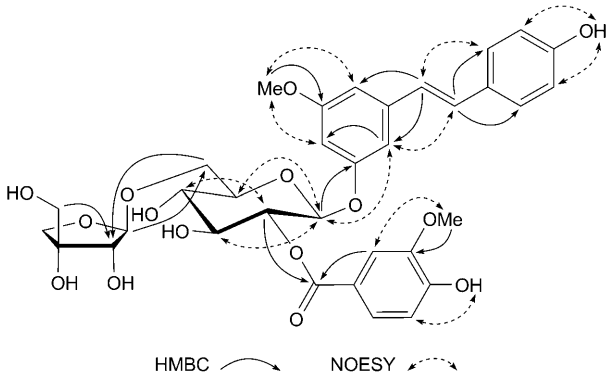

Fig. 1. *Key HMBC* (H → C) *and NOESY* (H ↔ H) *correlations of* **1**

Comparison of the ^{13}C-NMR spectral data of **1** with (*E*)-5-*O*-methylresveratrol 3-*O*-*β*-D-apiofuranosyl-(1 → 6)-*β*-D-glucopyranoside [26] indicated that the vanilloyl moiety was attached to the C(2″) of glucose as this C-atom signal was shifted downfield [27–30], while the C(1″) and C(3″) signals were shifted upfield, respectively. The downfield shift of C(6″) indicated that the terminal apiosyl group was connected to the glucosyl residue through a (1 → 6)-*O*-glycosidic linkage. The downfield shift of C(5) revealed the glycosylation of the aglycone at C(5). These aforementioned conclusions were also supported by the HMBC correlations H–C(2″)/C(7‴″), H–C(1‴)/C(6″), CH_2(6″)/C(1‴), H–C(1″)/C(5), and Me(9)/C(3), along with the NOESY correlations H–C(1″)/H–C(6), H–C(2″)/H–C(4″), H–C(5″)/H–C(3″) and H–C(1″), and Me(9)/H–C(2) and H–C(4) in the HMBC and NOESY spectra.

On the basis of the foregoing studies, the structure of **1** was established as (*E*)-3-*O*-methylresveratrol 5-*O*-*β*-D-apiofuranosyl-(1 → 6)-*β*-D-(2″-vanilloyl)glucopyranoside[1]).

Compound **2** was isolated as a pale yellow amorphous powder. The HR-FAB-MS showed a *quasi*-molecular-ion peak at *m*/*z* 727.2610 ([*M* + H]$^+$; calc. 727.2602), 60 mass units more than that of **1**, indicating the molecular formula as $C_{37}H_{42}O_{15}$, and corresponding to 17 degrees of unsaturation. The UV spectrum exhibited absorptions at 218, 306, and 324 nm. The IR spectrum of **2** showed absorption bands for OH (3431 cm^{-1}), aromatic rings (1600, 1512, 1455 cm^{-1}), and *α*,*β*-unsaturated ester (1701, 1632, 972 cm^{-1}) [31][32] functionalities. Comparison of the NMR and FAB-MS data of **2** with those of **1** suggested that compound **2** differs from **1** in the nature of the acyl and glycosyl substituents.

The ^{1}H-NMR of **2** (*Table 2*) showed the presence of a (*E*)-C=C bond by signals at *δ*(H) 7.48 and 6.25 with a coupling constant of *J* = 15.9 Hz, a typical *ABX* spin system in the aromatic region at *δ*(H) 7.04 (*d*, *J* = 2.0, 1 H), 6.95 (*d*, *J* = 8.0, 1 H), and 7.08 (*dd*, *J* = 2.0, 8.0, 1 H) with *ortho*, *ortho*/*meta*, and *meta* coupling constants, respectively, a *singlet* at *δ*(H) 3.82 (*s*, 3 H) corresponding to a MeO group, and a broad signal exchangeable with D_2O corresponding to a OH group. The ^{13}C-NMR spectrum showed a signal at *δ*(C) 165.5 due to the CO group of an ester function. These data indicated the presence of a (*E*)-feruloyl or (*Z*)-feruloyl unit in **2**. Further evidence came from the mass spectrum of **2**, which showed a significant fragment at *m*/*z* 177 characteristic of a

Table 2. *^1H, ^{13}C, and 2D-NMR Data of* **2**. At 400/100 MHz, resp., in CD_3OD; δ in ppm, J in Hz. Arbitrary atom numbering.

	δ(C) (DEPT)	δ(H)	HMBC (H → C)	NOESY
C(1)	141.8 (C)			
H–C(2)	106.9 (CH)	6.72 (br. *s*)	1, 3, 4, 6, 7	9
C(3)	160.4 (C)			
H–C(4)	103.8 (CH)	6.41 (br. *s*)	2, 3, 5, 6	9
C(5)	159.6 (C)			
H–C(6)	108.1 (CH)	6.65 (br. *s*)	1, 2, 4, 5, 7	8, 1″
H–C(7)	126.8 (CH)	6.84 (*d*, *J* = 16.1)	1, 2, 6, 1′, 8	2′
H–C(8)	129.8 (CH)	6.99 (*d*, *J* = 16.1)	1, 2′, 6′, 7	6
Me(9)	56.1 (Me)	3.79 (*s*)	3	2, 4
C(1′)	131.8 (C)			
H–C(2′)	128.5 (CH)	7.45 (*d*, *J* = 8.5)	3′, 4′, 6′, 8	7
H–C(3′)	115.1 (CH)	6.86 (*d*, *J* = 8.5)	1′, 2′, 4′, 5′	OH
C(4′)	160.9 (C)			
H–C(5′)	115.1 (CH)	6.86 (*d*, *J* = 8.5)	1′, 4′, 6′	OH
H–C(6′)	128.5 (CH)	7.45 (*d*, *J* = 8.5)	1′, 4′, 5′, 8	
H–C(1″)	101.5 (CH)	4.89 (*d*, *J* = 7.5)	5, 2″	6, 3″, 5″
H–C(2″)	76.3 (CH)	4.48 (*dd*, *J* = 9.6, 7.5)	9‴″, 1″, 3″	4″
H–C(3″)	75.1 (CH)	3.38–3.44 (*m*)[a])	2″, 4″	1″, 5″
H–C(4″)	71.5 (CH)	3.38–3.44 (*m*)[a])	3″, 5″	2″
H–C(5″)	76.8 (CH)	3.38–3.44 (*m*)[a])	4″, 6″	1″, 3″
CH_2(6″)	67.9 (CH_2)	4.01 (*dd*, *J* = 11.5, 1.9), 3.65 (*dd*, *J* = 11.5, 5.0)	1‴, 5″	
H–C(1‴)	102.1 (CH)	5.08 (*d*, *J* = 1.7)	6″, 2‴	2‴
H–C(2‴)	72.3 (CH)	3.62–3.78 (*m*)[a])		1‴
H–C(3‴)	71.6 (CH)	3.62–3.78 (*m*)[a])		5‴
H–C(4‴)	74.1 (CH)	3.42 (*d*, *J* = 9.6)		
H–C(5‴)	69.8 (CH)	3.62–3.78 (*m*)[a])		3‴
Me(6‴)	18.2 (Me)	1.28 (*d*, *J* = 6.1)	4‴, 5‴	
C(1⁗)	126.8 (C)			
H–C(2⁗)	109.8 (CH)	7.04 (*d*, *J* = 2.0)	4⁗, 6⁗, 7⁗	10⁗
C(3⁗)	148.5 (C)			
C(4⁗)	149.1 (C)			
H–C(5⁗)	114.5 (CH)	6.95 (*d*, *J* = 8.0)	1⁗, 3⁗, 4⁗	OH
H–C(6⁗)	123.8 (CH)	7.08 (*dd*, *J* = 2.0, 8.0)	2⁗, 4⁗, 7⁗	8⁗
H–C(7⁗)	144.8 (CH)	7.48 (*d*, *J* = 15.9)	2⁗, 6⁗, 8⁗, 9⁗	
H–C(8⁗)	115.7 (CH)	6.25 (*d*, *J* = 15.9)	1⁗, 7⁗, 9⁗	6⁗
C(9⁗)	165.5 (C)			
Me(10⁗)	55.7 (Me)	3.82 (*s*)	3⁗	2⁗, 5⁗

[a]) Overlapping signals.

(*E*)-feruloyl or (*Z*)-feruloyl moiety [33]. The positions occupied by the OH and MeO groups in the aromatic ring were established through the observation of the key HMBC and NOESY correlations Me(10⁗)/C(3⁗), H–C(2⁗), and H–C(5⁗), and H–C(6⁗)/C(4⁗), and H–C(2⁗)/Me(10⁗) (*Fig. 2*). These data confirmed that the MeO and OH groups were attached to C(3⁗) and C(4⁗), respectively, in accordance with a (*E*)-feruloyl residue. The signals for an anomeric CH group at δ(H) 5.08 (*d*, *J* =

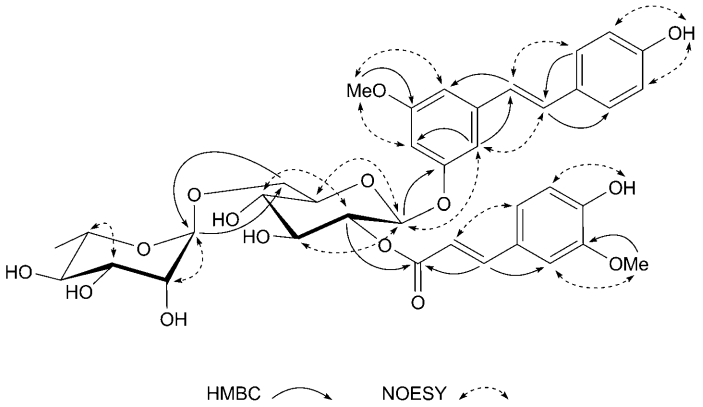

Fig. 2. *Key HMBC* (H → C) *and NOESY* (H ↔ H) *correlations of* **2**

1.7, 1 H) and δ(C) 102.1, together with a Me group at δ(H) 1.28 (*d*, $J = 6.1$, 3 H) and δ(C) 18.2 revealed an α-L-rhamnosyl (Rha) group in **2**. The above conclusions were also verified by the FAB-MS fragment ions at *m/z* 581 ($[M+H-146]^+$), 551 ($[M+H-176]^+$), 405 ($[M+H-176-146]^+$), 243 ($[M+H-162-176-146]^+$), and 177 ([feruloyl]$^+$), as well as the detection of (*E*)-ferulic acid, D-glucose and L-rhamnose (in the ratio of 1:1) after acid hydrolysis of **2**.

As such, the correlations H–C(1″)/C(5), H–C(1‴)/C(6″), CH_2(6″)/C(1‴), H–C(2″)/C(9‴″), and H–C(1″)/H–C(6) in the HMBC and NOESY spectra confirmed that the (*E*)-feruloyl and α-L-rhamnosyl groups were attached to C(2″) and C(6″) of β-D-glucose, respectively, which in turn was located at C(5) of the aglycone. From the above spectroscopic evidence, the structure of **2** was established as (*E*)-3-*O*-methylresveratrol 5-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-2″-[(*E*)-feruloyl]-glucopyranoside[1]).

Finally, the five known compounds were identified as 2-methoxyphenyl β-D-glucopyranoside [34], (−)-syringaresinol-4,4′-bis-*O*-β-D-glucopyranoside [35][36], acantrifoside A [37], β-sitosterol [38] and daucosterol [39], based on comparison of their spectral data with those published.

Besides the new compounds **1** and **2**, 2-methoxyphenyl β-D-glucopyranoside and acantrifoside A were obtained for the first time from *A. brachypus*. This is also the first report on the isolation of (*E*)-resveratrol derivatives from the genus *Acanthopanax*. Numerous interesting biological properties have been described for (*E*)-resveratrol derivatives, including the inhibition of the growth of tumor cell lines *in vitro*, the inhibition of carcinogenesis *in vivo* [40] and the induction of apoptosis [41]. Plants containing stilbenoids may therefore have a potential for the development of new drugs.

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Experimental Part

General. All solvents were distilled before use. Thin-layer chromatography (TLC): precoated silica-gel GF_{254} plates (*Qingdao Haiyang Chemical Plant*, P. R. China). Column Chromatography (CC): silica gel (SiO_2; 100–200, 200–300 mesh; *Qingdao*) and *Sephadex LH-20* gel (*Amersham Biosciences*). GC-MS: *GC6890N-MSD5973N* (*Agilent*); *HP-5* MS fused silica capillary column (30 m × 0.25 mm, film thinkness 0.25 μm). Optical rotations: *Perkin-Elmer 341* digital polarimeter. UV Spectra: *Shimadzu UV-300* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Perkin-Elmer 577* spectrometer with KBr pellets; in cm^{-1}. 1D- and 2D-NMR Spectra: *Bruker DRX-400* spectrometer; in $CDCl_3$, CD_3OD or (D_6)acetone soln.; δ in ppm rel. to Me_4Si, *J* in Hz. FAB-MS: *VG Auto-Spec-3000* mass spectrometer; in *m/z*, glycerol matrix.

Plant Material. The stem bark of *A. brachypus* was collected from Qingyang of Gansu Province, P. R. China, in August 2007, and identified by Prof. *Xiao-Qiang Guo* (Department of Life Sciences, Longdong University, P. R. China). A voucher specimen (No. 2007-18) was deposited with the Herbarium of the Department of Life Sciences, Longdong University.

Extraction and Isolation. The air-dried and pulverized stem barks of *A. brachypus* (5.0 kg) were extracted three times with 95% aq. EtOH at r.t. (15 l × 7 d, each time), and then the extracts were combined and concentrated under reduced pressure at 60° to yield 242 g of a brown viscous residue. The EtOH extract was suspended in distilled H_2O (1500 ml) and partitioned successively with hexane (500 ml), AcOEt (500 ml), and BuOH (sat. with H_2O, 500 ml). The concentrated AcOEt-soluble extract (188 g) was subjected to CC (SiO_2 (480 g; 100–200 mesh), polarity gradient with hexane, $CHCl_3$, Me_2CO, and MeOH, pure or in mixtures): *Fractions* A_1–A_{18} (TLC control). *Fr.* A_2 (2.0 g, $CHCl_3$/Me_2CO 1:2) was rechromatographed on *Sephadex LH-20* with MeOH as eluent to give (−)-syringaresinol-4,4′-bis-*O*-β-D-glucopyranoside (12 mg). *Fr.* A_5 (1.5 g, Me_2CO/MeOH 5:2) was rechromatographed over SiO_2 (50 g; 200–300 mesh, $CHCl_3$/MeOH 3:7), and further purified by prep. TLC (MeOH/$CHCl_3$/hexane, 1:5:2) to afford 2-methoxyphenyl β-D-glucopyranoside (24 mg). *Fr.* A_8 (13.0 g, Me_2CO/MeOH 3:8) was rechromatographed over SiO_2 (120 g; 200–300 mesh) with a gradient mixture of $CHCl_3$/MeOH (from 2:1 to 1:4) to give seven subfractions (*Fr.* A_{801}–A_{807}). *Subfr.* A_{802} (1.3 g) was chromatographed on *Sephadex LH-20* with MeOH/H_2O (1:1) to afford compound **1** (19 mg). *Subfr.* A_{804} (870 mg) was separated in the same way as *Subfr.* A_{802} to afford compound **2** (23 mg). *Fr.* A_{12} (13.9 g) was rechromatographed over SiO_2 (130 g; 200–300 mesh) with a gradient mixture of AcOEt/MeOH (from 8:1 to 1:7) to yield crude acanitrifoside A, which was repeatedly subjected to SiO_2 column (113 g; 200–300 mesh) with a gradient mixture of $CHCl_3$/MeOH (from 3:1 to 1:10) to afford 13 mg of pure material. *Fr.* A_{17} (9.0 g) was further purified over a SiO_2 column (100 g; 200–300 mesh) eluting stepwise with $CHCl_3$/MeOH (from 5:1 to 1:8), and then over *Sephadex LH-20* eluting with MeOH to obtain β-sitosterol (16 mg) and daucosterol (15 mg), resp.

*3-(Hydroxymethyl)-5-[(*E*)-2-(4-hydroxyphenyl)ethenyl]phenyl 6-*O*-[(2*R*,3*R*,4*R*)-3,4-Dihydroxy-4-(hydroxymethyl)tetrahydrofuran-2-yl]-2-*O*-[(4-hydroxy-3-methoxyphenyl)carbonyl]-β-*D*-glucopyranoside* (**1**). Pale yellow amorphous powder. $[\alpha]_D^{25} = -72.4$ ($c = 0.12$, MeOH). UV (MeOH): 258 (4.65), 308 (4.38), 326 (4.47). IR (KBr): 3429, 1715, 1600, 1508, 1456, 1280, 1140, 1054. ^{1}H- and ^{13}C-NMR: *Table 1*. FAB-MS: 687 ($[M+H]^+$), 555 ($[M+H-132]^+$), 537 ($[M+H-150]^+$), 405 ($[M+H-150-132]^+$), 243 ($[M+H-162-150-132]^+$), 151 ([vanilloyl]$^+$). HR-FAB-MS: 687.2296 ($[M+H]^+$, $C_{34}H_{39}O_{15}^+$; calc. 687.2289).

*3-(Hydroxymethyl)-5-[(*E*)-2-(4-hydroxyphenyl)ethenyl]phenyl 6-*O*-(6-Deoxy-α-L-mannopyranosyl)-2-*O*-[(2*E*)-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoyl]-β-*D*-glucopyranoside* (**2**). Pale yellow amorphous powder. $[\alpha]_D^{25} = -78.7$ ($c = 0.25$, MeOH). UV (MeOH): 218 (4.46), 306 (3.98), 324 (4.18). IR (KBr): 3431, 1701, 1632, 1600, 1512, 1455, 1276, 1141, 1055, 972. ^{1}H- and ^{13}C-NMR: *Table 2*. FAB-MS: 727 ($[M+H]^+$), 581 ($[M+H-146]^+$), 551 ($[M+H-176]^+$), 405 ($[M+H-176-146]^+$), 243 ($[M+H-162-176-146]^+$), 177 ([feruloyl]$^+$). HR-FAB-MS: 727.2610 ($[M+H]^+$, $C_{37}H_{43}O_{15}^+$; calc. 727.2602).

2-Methoxyphenyl β-D-Glucopyranoside. Colorless needles. FAB-MS: 287 ($[M+H]^+$), 125 ($[M+H-162]^+$).

Acantrifoside A. White powder. FAB-MS: 943 ($[M+H]^+$), 797 ($[M+H-146]^+$), 635 ($[M+H-146-162]^+$), 473 ($[M+H-146-162\times2]^+$).

Acid Hydrolysis of Compounds **1** *and* **2** *and Determination of the Absolute Configuration of the Monosaccharides:* Compounds **1** and **2** (each 10 mg) were dissolved in MeOH (10 ml) and 2N HCl (5 ml), resp. The mixtures were refluxed with magnetic stirring in a H_2O bath at 90° for 2 h. After cooling, the mixture was diluted with H_2O (5 ml) and extracted with AcOEt (2 ml × 3). The AcOEt phases were evaporated, and vanillic acid and (*E*)-ferulic acid were identified by TLC through comparison with authentic samples. The aq. layer was neutralized by passing through an ion-exchange resin (*Amberlite MB-3*) column eluted with H_2O, then concentrated and dried to furnish a monosaccharide residue. The residue was dissolved in pyridine (0.2 ml), to which 0.10M D-cysteine methyl ester hydrochloride in pyridine (0.2 ml) was added. The mixture was kept at 60° for 1.5 h. After the mixture was dried *in vacuo*, the residue was trimethylsilylated with 1-trimethylsilylimidazols (0.15 ml) for 2 h. The mixture was partitioned between hexane and H_2O (0.3 ml each), and the hexane extract was analyzed by GC/MS under the following conditions: *HP-5* MS fused silica capillary column (30 m × 0.25 mm, film thinkness 0.25 μm), column temp. at 230°, injection temp. at 250°, N_2 as carrier gas. In the acid hydrolysate of **1** and **2**, D-glucose, D-apiose, and L-rhamnose were confirmed by comparison of the retention times of their derivatives with those of D-glucose (26.1 min), L-glucose (22.8 min), D-apiose (13.5 min), L-apiose (11.1 min), D-rhamnose (12.7 min), L-rhamnose (13.2 min) [25], resp.

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