Four New Lariciresinol-Based Lignan Glycosides from the Roots of *Rhus javanica* var. *roxburghiana*

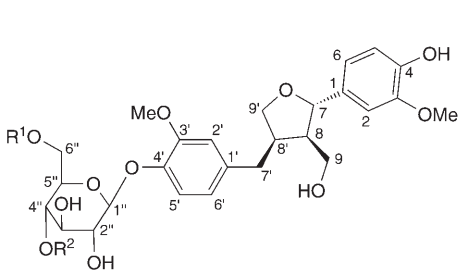
by **Ming-An Ouyang**[a]), **Yung-Shung Wein**[a]), and **Yueh-Hsiung Kuo***[a])[b])[c])[d])

[a]) Department of Chemistry, National Taiwan University, Taipei, Taiwan
(phone: +886-2-33661671; fax: +886-2-23636359; e-mail: yhkuo@ntu.edu.tw)
[b]) Agricultural Biotechnology Research Center, Academia Sinica, Taipei, Taiwan
[c]) College of Pharmacy, China Medical University, Taichung, Taiwan
[d]) Research Center of Food and Biomolecules, National Taiwan University, Taipei, Taiwan

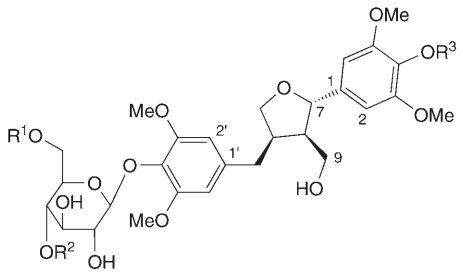
The four new lariciresinol-based lignan glycosides, (−)-lariciresinol 4′-(6″-*O*-feruloyl-β-D-glucopyranoside) (**1**), (−)-lariciresinol 4′-(4″,6″-di-*O*-feruloyl-β-D-glucopyranoside) (**2**), 5,5′-dimethoxylariciresinol 4′-(4″,6″-di-*O*-feruloyl)-β-D-glucopyranoside) (**3**), and 4-*O*-[α-(1,2-dihydroxyethyl)syringyl]-5,5′-dimethoxylariciresinol 4′-(4″,6″-di-*O*-feruloyl-β-D-glucopyranoside) (**4**), together with two known ones, lariciresinol 4′-β-D-glucopyranoside) (**5**) and tortoside B (**6**), were isolated from the BuOH extract of *Rhus javanica* var. *roxburghiana* roots, and their structures were established by means of various spectroscopic techniques.

Introduction. – The plants of Anacardiaceae are widespread in the tropical and subtropical area. Some of them are poisonous plants and lead to allergic reaction, such as *Toxicodendron radicans* and *Mangifera indica*, a tropical Asian evergreen tree cultivated for its edible fruit. Five *Rhus* plants are found in the island of Taiwan. They are *R. ambigua*, *R. hypoleuca*, *R. javanica* var. *roxburghiana* (= *R. semialata*), *R. succedanea*, and *R. sylvestris*. Previous investigations on the chemical constituents of *R. javanica* have resulted in the isolation of steroids, triterpenes, flavanoids, aromatics, and condensed tannins [1–7]. The root of this plant is used as a folk herb for the treatment of diarrhea, spermatorrhea, and malaria [8]. *Kuo et al.* have isolated 6-pentadecylsalicylic acid as an antithrombin component [3]. For the purpose of understanding the unusual secondary metabolism in *Rhus* plants and elucidating the pharmacologically active constituents of traditional Chinese medicines derived from *Rhus* plants, we initiated studies of the chemical constituents of the root of *R. javanica*. From the AcOEt-soluble fraction of the MeOH extract, we have isolated and purified 37 known compounds, two of them exhibiting significant cytotoxic activity [9]. This paper deals with the structural elucidation of the four new lariciresinol-based lignan glycosides **1**–**4** along with lariciresinol 4′-(β-D-glucoside) (**5**) [10] and tortoside B (**6**) [11], isolated from the BuOH-soluble fraction of the MeOH extract of the root of *R. javanica* ((−)-lariciresinol = (2*S*,3*R*,4*R*)-tetrahydro-2-(4-hydroxy-3-methoxyphenyl)-4-[(4-hydroxy-3-methoxyphenyl)methyl]furan-3-methanol[1]).

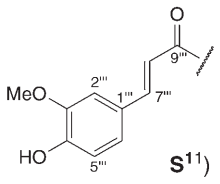
[1]) Trivial or arbitrary atom numbering; for systematic names, see the *Exper. Part*.



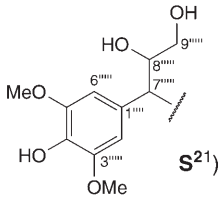
1[1]) R^1 = **S**[1], R^2 = H
2[1]) R^1 = R^2 = **S**[1]
5[1]) R^1 = R^2 = H



3[1]) R^1 = R^2 = **S**[1], R^3 = H
4[1]) R^1 = R^2 = **S**[1], R^3 = **S**[2]
6[1]) R^1 = R^2 = R^3 = H



S[11])



S[21])

Results and Discussion. – Compound **1** revealed an $[M+1]^+$ peak at *m*/*z* 699 in the FAB-MS. The HR-FAB-MS spectrum suggested the molecular formula $C_{36}H_{42}O_{14}$. The IR spectrum showed absorptions of a conjugated-ester carbonyl group (1699 cm^{-1}) and aromatic rings (1600 cm^{-1}). Basic hydrolysis of **1** afforded two products, ferulic acid (=(2*E*)-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoic acid; **S**[1]-OH) and a glucoside which was identified as lariciresinol 4′-(*β*-D-glucoside) (**5**) [10]. The ^{1}H- and ^{13}C-NMR (*Table 1*), COSY, HMQC, HMBC, and NOESY data allowed to identify **1** as (−)-lariciresinol 4′-(6″-*O*-feruloyl-*β*-D-glucopyranoside).

The DEPT experiment established the presence of 3 MeO, 4 CH_2, and 19 CH groups and of 10 quaternary C-atoms in **1**. The ^{1}H-NMR and ^{1}H,^{1}H-COSY data showed the presence of three *ABX* patterns in the aromatic region, *trans* double-bond protons at *δ* 7.61 (*d*, *J* = 16.0 Hz, 1 H) and 6.32 (*d*, *J* = 16.0 Hz, 1 H), and a sugar anomeric proton at *δ* 4.90 (*d*, *J* = 7.2 Hz). The ^{1}H-NMR data of **1** and its aglycone disclosed a diarylepoxylignan skeleton characterized by the presence of one downfield-shifted benzylic CH signal at *δ* 4.75 (*d*, *J* = 6.0 Hz, H−C(7)), benzylic CH_2 signals at *δ* 2.88 (*dd*, *J* = 13.4, 4.5 Hz, H_a−C(7′)) and 2.46 (*dd*, *J* = 13.4, 4.8 Hz, H_b−C(7′)), and CH_2OH signals (*δ* 3.81 and 3.64, each 1 H, overlapping with other singals). Such an NMR pattern along with two sets of *ABX* system signals of aromatic protons and two MeO signals suggested that the aglycone should be lariciresinol [10]. The NOESY experiment confirmed that H−C(8) and H−C(8′) are in *cis*-configuration. Only one phenolic proton at *δ* 8.50 was observed, the other phenolic position of the lariciresinol part was considered to be linked to a glucose moiety. The HMQC and HMBC exhibited the following key correlations: H−C(7) (*δ* 4.75)/C(1), C(2), C(6), C(8), C(9), C(8′), and C(9′), H−C(7′) (*δ* 2.88)/C(1′), C(2′), C(6′), C(8′), and C(9′), H−C(1″) (*δ* 4.90)/C(4′) and C(2″). The more deshielded proton of CH_2(6″) (*δ*(H) 4.35 and 4.51)

Table 1. *^{13}C- and ^{1}H-NMR Data* (400 and 100 MHz) *of Compounds* **1** *and* **2**[1]). δ in ppm, J in Hz.

	1 ((D$_6$)acetone)		**2** (CD$_3$OD)	
	δ(C)	δ(H)	δ(C)	δ(H)
C(1)	139.7		139.2	
H–C(2)	112.9	6.79 (*d*, *J* = 2.4)	112.9	6.86 (*d*, *J* = 2.1)
C(3)	146.5		150.7	
C(4)	149.9		146.3	
H–C(5)	117.5	7.12 (*d*, *J* = 8.0)	117.9	6.77 (*d*, *J* = 8.4)
H–C(6)	118.7	6.76 (*dd*, *J* = 8.0, 2.4)	119.2	7.04 (*dd*, *J* = 8.4, 2.1)
H–C(7)	82.9	4.75 (*d*, *J* = 6.0)	83.3	4.70 (*d*, *J* = 6.8)
H–C(8)	53.8	2.22–2.29 (*m*)	53.6	2.22–2.28 (*m*)
CH$_2$(9)	60.3	3.81[a]), 3.64[a])	60.3	3.87[a]), 3.59[a])
*Me*O–C(3)	56.2	3.79 (*s*)	56.8	3.77 (*s*)
C(1′)	133.1		133.0	
H–C(2′)	111.1	6.96 (*d*, *J* = 2.0)	110.9	6.89 (*d*, *J* = 2.0)
C(3′)	148.0		148.4	
C(4′)	145.4		145.1	
H–C(5′)	115.6	6.72 (*d*, *J* = 8.0)	115.8	6.78 (*d*, *J* = 8.0)
H–C(6′)	121.6	6.32 (*dd*, *J* = 8.0, 2.0)	121.8	6.58 (*dd*, *J* = 8.0, 2.0)
CH$_2$(7′)	33.5	2.88 (*dd*, *J* = 13.4, 4.5), 2.46 (*dd*, *J* = 13.4, 4.8)	33.5	2.82 (*dd*, *J* = 13.6, 4.4), 2.40 (*dd*, *J* = 13.6, 4.9)
H–C(8′)	43.3	2.61 (*m*)	43.4	2.61 (*m*)
CH$_2$(9′)	73.1	3.85[a]), 3.81[a])	73.5	3.92[a]), 3.57[a])
*Me*O–C(3′)	56.3	3.79 (*s*)	56.7	3.79 (*s*)
H–C(1″)	102.5	4.90 (*d*, *J* = 7.2)	102.6	4.90 (*d*, *J* = 7.8)
H–C(2″)	74.6	3.53[a])	74.2	3.55[a])
H–C(3″)	77.7	3.59[a])	75.1	3.70[a])
H–C(4″)	71.2	3.48[a])	72.5	5.06 (*t*, *J* = 9.6)
H–C(5″)	75.0	3.73[a])	72.9	3.82[a])
CH$_2$(6″)	64.1	4.51 (*dd*, *J* = 12.4, 2.0), 4.35 (*dd*, *J* = 12.4, 6.8)	64.1	4.33 (*dd*, *J* = 12.0, 6.0), 4.24 (*dd*, *J* = 12.0, 5.0)
C(1‴)	127.2		126.8	
H–C(2‴)	111.0	7.33 (*d*, *J* = 2.4)	111.2	7.09 (*d*, *J* = 2.0)
C(3‴)	148.6		148.9	
C(4‴)	149.9		150.3	
H–C(5‴)	116.0	6.87 (*d*, *J* = 7.6)	116.3	6.78 (*d*, *J* = 8.0)
H–C(6‴)	124.0	7.13 (*dd*, *J* = 7.6, 2.4)	124.0	7.00 (*dd*, *J* = 8.0, 2.0)
H–C(7‴)	145.8	7.61 (*d*, *J* = 16.0)	147.5	7.56 (*d*, *J* = 16.0)
H–C(8‴)	115.4	6.32 (*d*, *J* = 16.0)	115.8	6.33 (*d*, *J* = 16.0)
C(9‴)	167.2		168.2	
*Me*O–C(3‴)	56.4	3.90 (*s*)	56.4	3.84 (*s*)
C(1⁗)			126.7	
H–C(2⁗)			111.1	7.07 (*d*, *J* = 2.0)
C(3⁗)			148.9	
C(4⁗)			150.3	
H–C(5⁗)			116.3	6.78 (*d*, *J* = 8.0)
H–C(6⁗)			124.0	7.00 (*dd*, *J* = 8.0, 2.0)
H–C(7⁗)			146.9	7.62 (*d*, *J* = 16.0)
H–C(8⁗)			115.7	6.22 (*d*, *J* = 16.0)
C(9⁗)			168.0	
*Me*O–C(3⁗)			56.3	3.84 (*s*)

[a]) Overlapping with other signals.

showed a HMBC correlation with C(9‴), the carbonyl group of the ester, that confirmed that the feruloyl moiety is linked to C(6″).

Compound **2** had the molecular formula $C_{46}H_{50}O_{17}$ according to the exact molecular ion in the HR-FAB-MS and the ^{13}C-NMR spectra (*Table 1*). The IR absorptions were assignable to conjugated ester carbonyl groups (1699 cm^{-1}), C=C bonds (1633 cm^{-1}), and aromatic rings (1597 and 1522 cm^{-1}). Comparison of the NMR data (*Table 1*) of compounds **1** and **2** revealed a closely similar aglycone and sugar moiety, the only difference being the presence of an additional feruloyl moiety in **2**. The structure of **2** was determined to be (−)-lariciresinol 4′-(4″,6″-di-*O*-feruloyl-*β*-D-glucopyranoside).

The ^{1}H NMR spectrum of **2** exhibited two sets of *trans* double-bond protons at δ 7.56 (*d*, *J* = 16.0 Hz, 1 H) and 6.33 (*d*, *J* = 16.0 Hz, 1 H), and 7.62 (*d*, *J* = 16.0 Hz, 1 H) and 6.22 (*d*, *J* = 16.0 Hz, 1 H), four *ABX* systems of aromatic protons, an anomeric sugar proton at δ 4.90 (*d*, *J* = 7.8 Hz), a benzylic CH signal at δ 4.70 (*d*, *J* = 6.8 Hz), and benzylic CH_2 signals at δ 2.82 (*dd*, *J* = 13.6, 4.4 Hz, H_a−C(7′)) and 2.40 (*dd*, *J* = 13.6, 4.9 Hz, H_b−C(7′)). The following key HMBC correlations were observed: CH_2(6″) (δ 4.33 and 4.24)/C(9‴), H−C(4″) (δ 5.06)/C(9‴), H−C(7)/C(1), C(2), C(6), C(9), C(8′), and C(9′), H−C(7′) (δ 2.82 and 2.40)/C(8), C(1′), C(2′), C(6′), C(8′), and C(9′), and H−C(1″)/C(4′) (*Fig. 1*). The signal at δ 5.08 (*t*, *J* = 9.6 Hz) was assigned as H−C(4″) since it had a NOESY correlation with H−C(6″). The above evidence revealed that the sugar moiety is a glucose and the secondary feruloyl group is linked at C(4″).

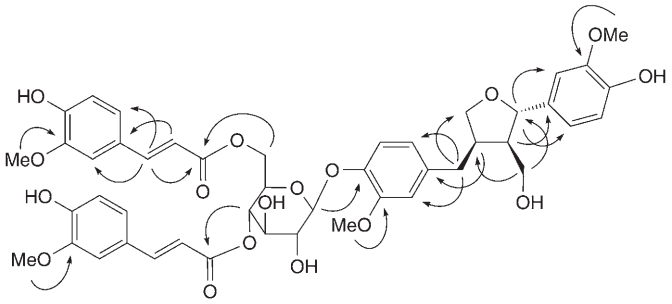


Fig. 1. *HMBC Correlations in Compound* **2**

Compound **3** was obtained as colorless powder. Based on the HR-FAB-MS and ^{13}C-NMR data (*Table 2*), compound **3** has the molecular formula $C_{48}H_{54}O_{19}$. The IR spectrum indicated the presence of OH (3422 cm^{-1}) and conjugated ester carbonyl groups (1708 cm^{-1}), of C=C bonds (1633 cm^{-1}), and of aromatic rings (1596 and 1501 cm^{-1}). On basic hydrolysis, **3** gave ferulic acid and tortoside B (**6**) [11]. The structure of **3** was elucidated as 5,5′-dimethoxylariciresinol 4′-(4″,6″-di-*O*-feruloyl-*β*-D-glucopyranoside).

The ^{1}H- and ^{13}C-NMR spectra (*Table 2*) showed the presence of a *β*-D-glucopyranosyl moiety (δ(C) 105.4; δ 4.87 (*d*, *J* = 7.6 Hz)), two tetrasubstituted symmetrical benzene rings, two feruloyl ester moieties, three CH_2 groups (δ(C) 34.3, 60.4, 73.0, the later two being oxygenated), and three CH groups (δ(C) 54.0, 83.3, and 43.2) along with four MeO signals (δ 3.82 (*s*, 6 H) and 3.79 (*s*, 6 H)). Comparison of the ^{1}H- and ^{13}C-NMR spectra of **3** and tortoside B (**6**) [11] showed that they have a similar structure, except for two additional feruloyl moieties in **3**. The signal at δ 5.09 (*t*, *J* = 9.0 Hz) was assigned as H−C(4″) which exhibited a NOESY correlation with CH_2(6″) (δ 4.21 and 4.18). This evidence confirmed that the two feruloyl moieties were connected to C(6″) and C(4″).

The HR-FAB-MS of compound **4** had a pseudomolecular-ion peak $[M+H]^+$ at *m/z* 1161.4170 consistent with the molecular formula $C_{59}H_{68}O_{24}$. The IR spectrum indicated the presence of OH (3337 cm^{-1}) and conjugated ester carbonyl groups (1706 cm^{-1}), of C=C bonds (1632 cm^{-1}), and of aromatic rings (1600 and 1514 cm^{-1}), while the UV absorptions were similar to those of **3**. Comparison with the NMR data of **3** and **4** revealed a close resemblance of **3** and **4**; except for an additional syringylglyceryl-derived moiety in compound **4**. Compound **4** was elucidated as 4-*O*-[α-(1,2-dihydroxyethyl)syringyl]-5,5′-dimethoxylariciresinol 4′-(4″,6″-di-*O*-feruloyl-β-D-glucopyranoside).

The ^{1}H- and ^{13}C-NMR spectra of **4** showed the presence of a β-D-glucopyranosyl moiety, two feruloyl ester moieties, a 5,5′-dimethoxylariciresinol part, and a syringylglyceryl-derived unit with the signals δ(H) 6.69 (*s*, H–C(2‴″), H–C(6‴″)), δ(C) 141.2 (C(1‴″)), 104.7 (C(2‴″), C(6‴″)), 153.7 (C(3‴″), C(5‴″)), and 132.6 (C(4‴″)), two CH signals at δ(H) 4.98 (*d*, J = 6.2 Hz, 1 H) and δ(C) 87.8 C(7‴″)), and δ(H) 4.16–4.21 (*m*, 1 H) and δ(C) 73.0 (C(8‴″)), CH_2 signals at δ(H) 3.83 and 3.44 and δ(C) 61.0 (C(9‴″), and two MeO signals at δ(H) 3.84 (*s*, 6 H). The COSY experiment with **4** indicated the contiguous protons shown by bold lines in *Fig. 2*. The chemical shifts of H–C(7‴″) and C(7‴″) appeared downfied in **4** as compared to 'syringylglycerol' [12–14], establishing that H–C(7‴″) was linked to a phenol OH group rather than to an alcohol OH group. The HMQC and HMBC experiments (*Fig. 2*) of **4** revealed the following correlations: CH_2(6″) (δ 4.23, 4.21)/C(9‴) (δ 166.8), H–C(4″) (δ 5.08)/C(9‴″) (δ 166.7), H–C(1″) (δ 4.84)/C(4′) (δ 134.3), and H–C(7‴″) (δ 4.98)/C(4) (δ 135.6).

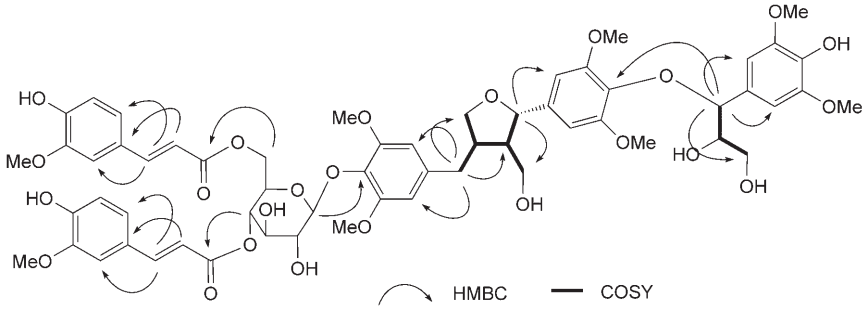


Fig. 2. *HMBC and COSY Correlations in Compound* **4**

Experimental Part

General. CC = Column chromatography. TLC: *Merck* TLC plates (silica gel *60 F_{254}*), visualization by spraying with 5% (*v/v*) H_2SO_4 in EtOH. Optical rotations: *Jasco DIP-180* digital polarimeter. UV Spectra: *Hitachi S-3200*; λ_{max} (log ε) in nm. IR Spectra: *Perkin-Elmer 983G*; in cm^{-1}. ^{1}H- and ^{13}C-NMR, DEPT, ^{1}H,^{1}H-COSY, NOESY, TOCSY, HMQC, and HMBC: *Varian Unity-Plus-400* instrument. FAB-MS: *Jeol JMS-HX-110* instrument; in *m/z* (rel. %).

Plant Material. The roots of *R. javanica* var. *roxburghiana* were collected from the suburb of Penton, Taiwan, in 1998. A voucher specimen (No. 191230) was deposited in the Department of Botany, National Taiwan University.

Extraction and Isolation. The dry roots of *R. javanica* (8 kg) were extracted with MeOH for 2 weeks. The extract was concentrated, the residue (300 g) dissolved and suspended in H_2O (2.5 l) and partitioned with AcOEt (3 × 3 l), and then the aq. phase extracted with BuOH (3 × 3 l). The BuOH extract was concentrated and the residue (70 g) subjected to dry CC (silica gel (1.0 kg), $CHCl_3$/MeOH/H_2O

Table 2. *^{13}C- and ^{1}H-NMR Data* (CD_3COCD_3, 400 and 100 MHz) *of Compounds* **3** *and* **4**[a])

	3		**4**	
	δ(C)	δ(H)	δ(C)	δ(H)
C(1)	135.3		135.2	
H–C(2,6)	104.1	6.64 (*s*)	103.7	6.72 (*s*)
C(3)	148.5		148.2	
C(4)	135.6		135.6	
H–C(7)	83.3	4.77 (*d*, *J* = 6.0)	83.3	4.83 (*d*, *J* = 6.0)
H–C(8)	54.0	2.35 (br. *sept.*, *J* = 6.4)	53.8	2.34 (br. *sept.*, *J* = 6.4)
CH_2(9)	60.4	3.69[a]), 3.85[a])	60.5	3.46[a]), 3.88[a])
*Me*O–C(3,5)	56.6	3.79 (*s*)	56.6	3.80 (*s*)
C(1′)	138.7		138.6	
H–C(2′,6′)	107.3	6.58 (*s*)	107.3	6.58 (*s*)
C(3′,5′)	153.7		153.7	
C(4′)	134.4		134.3	
CH_2(7′)	34.3	2.95 (*dd*, *J* = 13.2, 4.8, H_a), 2.52 (*dd*, *J* = 13.2, 11.2, H_b)	34.2	2.95[a]), 2.52 (*dd*, *J* = 13.2, 11.2, H_b)
H–C(8′)	43.2	2.72 (*m*)	43.2	2.72 (*m*)
CH_2(9′)	73.0	3.96 (*dd*, *J* = 8.4, 6.8), 3.67[a])	73.2	3.96 (*dd*, *J* = 8.4, 6.8), 3.67[a])
*Me*O–C(3′,5′)	56.9	3.82 (*s*)	56.9	3.83 (*s*)
H–C(1″)	105.4	4.87 (*d*, *J* = 7.6)	105.3	4.84 (*d*, *J* = 7.6)
H–C(2″)	75.9	3.62 (*t*, *J* = 9.0)	75.9	3.62 (*t*, *J* = 9.0)
H–C(3″)	75.2	3.78[a])	75.1	3.78[a])
H–C(4″)	73.0	5.09 (*t*, *J* = 9.0)	72.3	5.08 (*t*, *J* = 9.0)
H–C(5″)	72.3	3.80[a])	73.5	3.80[a])
CH_2(6″)	63.9	4.18 (*dd*, *J* = 12.0, 4.0), 4.21 (*dd*, *J* = 12.0, 6.6)	63.9	4.21 (*dd*, *J* = 12.0, 4.0), 4.23 (*dd*, *J* = 12.0, 6.4)
C(1‴)	127.2		127.1	
H–C(2‴)	111.1	7.32 (*d*, *J* = 1.6)	111.1	7.32 (*d*, *J* = 1.6)
C(3‴)	148.5		148.5	
C(4‴)	150.0		150.0	
H–C(5‴)	115.9	6.85 (*d*, *J* = 8.0)	115.9	6.85 (*d*, *J* = 8.0)
H–C(6‴)	124.0	7.12 (*dd*, *J* = 8.0, 1.6)	124.0	7.12 (*dd*, *J* = 8.0, 1.6)
H–C(7‴)	146.2	7.63 (*d*, *J* = 15.6)	146.3	7.63 (*d*, *J* = 15.6)
H–C(8‴)	115.3	6.42 (*d*, *J* = 15.6)	115.3	6.42 (*d*, *J* = 15.6)
C(9‴)	166.8		166.8	
*Me*O–C(3‴)	56.3	3.85 (*s*)	56.3	3.89 (*s*)
C(1⁗)	127.2		127.1	
H–C(2⁗)	111.1	7.26 (*d*, *J* = 2.0)	111.1	7.26 (*d*, *J* = 2.0)
C(3⁗)	148.5		148.5	
C(4⁗)	149.9		149.9	
H–C(5⁗)	115.9	7.05 (*dd*, *J* = 8.4, 2.0)	115.9	7.05 (*dd*, *J* = 8.4, 2.0)
H–C(6⁗)	123.9	6.82 (*d*, *J* = 8.4)	123.9	6.82 (*d*, *J* = 8.4)
H–C(7⁗)	145.8	7.55 (*d*, *J* = 15.6)	145.8	7.55 (*d*, *J* = 15.6)
H–C(8⁗)	115.2	6.32 (*d*, *J* = 15.6)	115.2	6.32 (*d*, *J* = 15.6)
C(9⁗)	166.7		166.7	
*Me*O–C(3⁗)	56.3	3.86 (*s*)	56.3	3.87 (*s*)
C(1⁗)			141.2	
H–C(2⁗,6⁗)			104.7	6.69 (*s*)
C(3⁗,5⁗)			153.7	

Table 2 (cont.)

	3		**4**	
	δ(C)	δ(H)	δ(C)	δ(H)
C(4‴″)			132.6	
H–C(7‴″)			87.8	4.98 (*d*, *J* = 6.2)
H–C(8‴″)			73.0	4.16–4.24 (*m*)
CH_2(9‴″)			61.0	3.83[a]), 3.44[a])
*Me*O–C(3‴″,5‴″)			56.5	3.84 (*s*)

[a]) Overlapping with other signals.

10 : 2 : 0.2): 13 fractions. Each fraction was subjected to *Sephadex LH-20* and *PR-18* (10 → 90% MeOH/H_2O) and finally, purified by CC (silica gel, CH_2Cl_2/AcOEt/MeOH 10 : 10 : 1 and $CHCl_3$/MeOH/H_2O 10 : 2 : 0.2): **1** (18 mg), **2** (30 mg), **3** (58 mg), **4** (21 mg), **5** (17 mg), and **6** (34 mg).

*(−)-Lariciresinol 4′-(6″-*O*-Feruloyl-β-*D*-glucopyranoside)* (*=2-Methoxy-4-{[(3*R*,4*R*,5*S*)-tetrahydro-5-(4-hydroxy-3-methoxyphenyl)-4-(hydroxymethyl)furan-3-yl]methyl}phenyl β-*D*-Glucopyranoside 6-[(2*E*)-3-(4-Hydroxy-3-methoxyphenyl)prop-2-enoate]*; **1**): White powder. $[\alpha]_D^{27} = -30.8$ (*c* = 0.21, acetone). UV (MeOH): 227 (4.16), 232 (4.01), 276 (4.00), 301 (sh), 330 (4.08). IR (KBr): 3370, 1699, 1600, 1514, 1461. ^{1}H- and ^{13}C-NMR: see *Table 1*. FAB-MS: 699 (0.5, $[M+1]^+$), 613 (1.5), 515 (3.7), 460 (4.0), 391 (42.5), 307 (100), 289 (56). HR-FAB-MS: 699.2659 ($[M+1]^+$, $C_{36}H_{43}O_{14}^+$; calc. 699.2652).

*(−)-Lariciresinol 4′-(4″,6″-Di-*O*-feruloyl-β-*D*-glucopyranoside)* (*=2-Methoxy-4-{[(3*R*,4*R*,5*S*)-tetrahydro-5-(4-hydroxy-3-methoxyphenyl)-4-(hydroxymethyl)furan-3-yl]methyl}phenyl β-*D*-Glucopyranoside 4,6-Bis[(2*E*)-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoate]*; **2**): White powder. $[\alpha]_D^{27} = -21.4$ (*c* = 0.20, acetone). UV (MeOH): 227 (4.34), 233 (4.07), 278 (sh), 300 (4.01), 331 (4.11). IR (KBr): 3383, 1699, 1633, 1597, 1520. ^{1}H- and ^{13}C-NMR: see *Table 1*. FAB-MS: 875 (0.3, $[M+1]^+$), 615 (1.0), 515 (2.7), 460 (5.0), 391 (2.5), 307 (100), 289 (60). HR-FAB-MS: 875.3131 ($[M+1]^+$, $C_{64}H_{51}O_{17}^+$; calc. 857.3125).

*5,5′-Dimethoxylariciresinol 4′-(4″,6″-Di-*O*-feruloyl-β-*D*-glucopyranoside)* (*=2,6-Dimethoxy-4-{[(3*R*,4*R*,5*S*)-tetrahydro-5-(4-hydroxy-3,5-dimethoxyphenyl)-4-(hydroxymethyl)furan-3-yl]methyl}-phenyl β-*D*-Glucopyranoside 4,6-Bis[(2*E*)-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoate]*; **3**): Colorless powder. $[\alpha]_D^{27} = -11.6$ (*c* = 2.1, acetone). UV (MeOH): 224 (4.40), 232 (sh), 288 (4.10), 301 (4.03), 330 (4.10). IR (KBr): 3422, 2945, 1708, 1633, 1596, 1501, 1465. ^{1}H- and ^{13}C-NMR: see *Table 2*. FAB-MS: 935 (0.5, $[M+1]^+$), 766 (0.3), 679 (0.4), 662 (0.3), 613 (3), 515 (5), 460 (11), 420 (4), 391 (7), 307 (100), 289 (49). HR-FAB-MS: 935.3332 ($[M+1]^+$, $C_{48}H_{55}O_{19}^+$; calc. 935.3337).

*4-*O*-[α-(1,2-Dihydroxyethyl)syringyl]-5,5′-dimethoxylariciresinol 4′-(4″,6″-Di-*O*-feruloyl-β-*D*-glucopyranoside)* (*=4-{{(3*R*,4*R*,5*S*)-5-{4-[2,3-Dihydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)propoxy]-3,5-dimethoxyphenyl}tetrahydro-4-(hydroxymethyl)furan-3-yl}methyl}-2,6-dimethoxyphenyl β-*D*-Glucopyranoside 4,6-Bis[(2*E*)-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoate]*; **4**): Colorless powder. $[\alpha]_D^{27} = +5.9$ (*c* = 0.9, acetone). UV (MeOH): 227 (4.44), 232 (4.01), 278 (4.12), 302 (4.05), 331 (4.11). IR (KBr): 3337, 2946, 1706, 1632, 1600, 1514, 1461. ^{1}H- and ^{13}C-NMR: see *Table 2*. FAB-MS: 1161 (0.2, $[M+1]^+$), 933 (6), 725 (0.5), 682 (0.2), 515 (10), 507 (7), 446 (9), 420 (15), 391 (20), 339 (5), 307 (100), 289 (60). HR-FAB-MS: 1161.4170 ($[M+1]^+$, $C_{59}H_{69}O_{24}^+$; calc. 1161.4178).

REFERENCES

[1] N. Parveen, N. U. D. Khan, *J. Indian Chem. Soc.* **1988**, *65*, 737.

[2] S. Taniguchi, K. Yazaki, Y. U. Ryoko, K. Y. Kawakami, H. Ito, T. Hatano, T. Yoshida, *Phytochemistry* **2000**, *53*, 357.

[3] S. C. Kuo, C. M. Teng, L. G. Chiu, T. S. Wu, S. C. Huang, J. B. Wu, T. Y. Shieh, R. J. Chang, T. C. Chou, *Planta Med.* **1991**, *57*, 247.

[4] N. Parveen, M. P. Singh, N. U. Khan, Y. B. Achari, M. K. Logani, *Phytochemistry* **1991**, *30*, 2415.

[5] C. K. Sung, T. Akiyama, U. Sankawa, Y. Iitaka, D. S. Han, *J. Chem. Soc., Chem. Commun.* **1980**, *19*, 909.
[6] S. El, A. El, *Planta Med.* **1996**, *14*, 171.
[7] M. Takechi, Y. Tanaka, M. Takehara, G. I. Nonaka, I. Nishioka, *Phytochemistry* **1985**, *24*, 2245.
[8] P. G. Xiao, 'Chinese Medicinal Herb Iconograph', Taiwan Business & Affairs Publishing House, Taipei, 1989, Vol. 1, p. 105.
[9] T. H. Lee, J. L. Chiou, C. K. Lee, Y. H. Kuo, *J. Chin. Chem. Soc.* **2005**, *52*, 833.
[10] M. Sugiyama, M. Kikuchi, *Heterocycles* **1993**, *36*, 117.
[11] C. Wang, Z. Jia, *Phytochemistry* **1997**, *45*, 159.
[12] H. Otsuka, M. Takeuchi, Y. Inoshiri, T. Sato, K. Yamasaki, *Phytochemistry* **1989**, *28*, 883.
[13] M. Sugiyama, M. Kikuchi, *Chem. Pharm. Bull.* **1992**, *40*, 325.
[14] S. Hara, H. Okabe, K. Mihashi, *Chem. Pharm. Bull.* **1986**, *34*, 1843.

Received November 24, 2006