Rhusemialins A—C, New Cyclolignan Esters from the Roots of *Rhus javanica* var. *roxburghiana*

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Received November 15, 2006; accepted February 10, 2007

Three new cyclolignan esters and seven known compounds including two cyclolignan isolariciresinol, lynoiresinol, and five aromatic compounds methyl ferulate, vanillin, 4-hydroxy-3,5-dimethoxybenaldehyde, 4-methoxygallic acid, gallic acid were isolated from *n*-butanol extract of *Rhus semialata* (Anacardiaceae). The structural elucidations of rhusemialins A (1), B (2), and C (3) were based on FAB-MS, 1D and 2D NMR spectra.

Key words *Rhus semialata*; Anacardiaceae; root; lignan; rhusemialin

Rhus javanica is one of five *Rhus* species (Anacardiaceae), distributing in the island of Taiwan. In the early days, the pericarp of *R. semialata* had been commonly used a substitute of salt by indigenous mountain people. The roots of it also do a folk herb for treating diarrhea, spermatorrhea and malaria.[1)] Early investigation in *Rhus* was only the plants of *R. semialata* and *R. succedanea*. Flavones, triterpenes, aromatics, tannins were isolated from them.[2—8)] This paper describes the isolation and structural elucidation of new cyclolignan esters (**1**), (**2**) and (**3**), and sever known compounds: lynoiresinol (**4**),[9—11)] isolariciresinol,[12)] methyl ferulate, vanillin, 4-hydroxy-3,5-dimethoxybenaldehyde, 4-methoxygallic acid, and gallic acid. They were isolated from the *n*-butanol extract of *R. javanica*

The *n*-butanol fraction of methanol extract was fractionated by a combination of silica gel, Sephadex LH-20, and RP-18 columns to yield ten compounds, their structures were elucidated by 1D and 2D NMR spectra and comparison with literature data.

Compound **1** was isolated a colorless powder. Its molecular formula $C_{31}H_{34}O_{11}$ was obtained from HR-FAB-MS representing fifteen unsaturations. The IR spectrum exhibited functional groups, hydroxyl (3396 cm^{-1}), α,β unsaturated conjugate ester moiety (1705 cm^{-1}) and aromatic ring (1611 cm^{-1}). Comparison of the ^{1}H- and ^{13}C-NMR data with those of compound **1** and **4** indicated the same skeleton portion (Fig. 1), which had eighteen carbon signals including two aromatic rings (twelve sp^2 carbon signals) and six aliphatic carbon signals (sp^3 carbon) in both **1** and **4**, and an α,β unsaturated conjugate ester in **1**. The ^{13}C-NMR spectrum of **1** showed the additional nine carbon signals. In the ^{1}H-NMR spectrum of **1**, the signals were at δ 7.51 (1H, d, J=16.0 Hz), 6.28 (1H, d, J=16.0 Hz), and ABX spin system of aromatic ring at δ 7.02 (1H, d, J=2.4 Hz), 6.93 (1H, dd, J=8.0, 2.4 Hz), and 6.76 (1H, d, J=8.0 Hz), while in the ^{13}C-NMR spectrum, the signals were at δ 169.3 (C-9″), 149.5 (C-4″), 148.7 (C-3″), 147.0 (C-7″), 127.6 (C-1″), 123.0 (C-6″), 116.5 (C-5″), 115.1 (C-2″), 115.0 (C-8″), these signals indicated the *trans* caffeoyl moiety.

These 18 carbon signals including two aromatic rings and six aliphatic carbons indicated that the moiety of **1** and compound **4** were lignan. The six aliphatic carbon signals of DEPT spectrum in **1** contained three methine signals (δ 45.3, 43.3, 40.9) and three methylene signals (δ 66.3, 66.6, 33.7), two of them bearing oxygen. These data and combining with degrees of unsaturation suggested that **1** was a lyoniresinol or a lingueresinol derivative.[8,9)] From the chemical shift of the four methoxy protons (δ 3.35, 3.71, 3.86), together with NOESY and HMBC correlations, the positions of four methoxy groups were established at C-3, C-5, C-3′, and C-5′. The proton signal of methoxy at δ 3.35 (upfield, at C-5 position) was shielded by the aromatic ring. The vicinal two protons (H-7′–H-8′) of **1** gave the coupling constant (J=6.0 Hz, H-7′), and the vicinal two protons (H-8′–H-8) showed the $W_{1/2}\geq$16 Hz (16 Hz of H-8′ and 23 Hz of H-8), indicating H-8′ and H-8 were axial position. So the three protons (H-7′, H-8′, and H-8) were *trans* form each. Thus, compound **1** was determined as a derivative of lyoniresinol.[8,9)]

In the HMBC experiment of **1**, the correlations were obtained between H-9′ (δ_H 4.27, 4.08) and C-9″ (δ_C 169.3), between H-9′ (δ_H 4.27, 4.08) and C-8 (δ_C 40.9), between H-9′ (δ_H 4.27, 4.08) and C-7′ (δ_C 43.3), these data indicated the

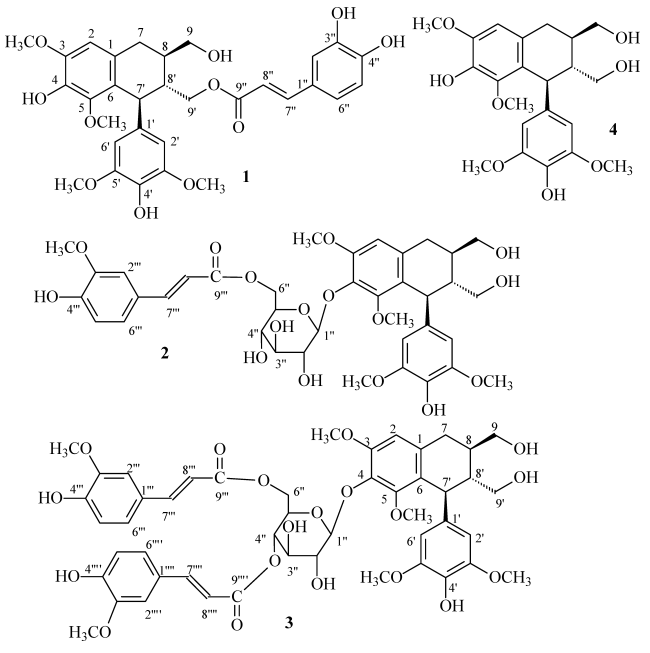

Fig. 1. The Structures of Compounds **1**—**4**

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position of the esterification at C-9′, while the carbon chemical shifts confirmed the esterifying position, such as C-8′ upfield 2.9 ppm (γ affected), C-9′ downfield 3.3 ppm (β affected), which chemical shifts were comparing with the data of compound **4** (see Table 1). Thus, the compound **1** was established as lynoiresinol-9′-*O*-(*E*)-caffeoyl ester, unambiguously, and named as rhusemialin A.

Since the NOEs were observed in an NOESY experiment, the relative configuration at C-7′, C-8′ and C-8 were decided as *rel*-(7′*S*,8′*R*,8*R*). Due to compound **4** exhibited the positive and smaller optical rotatory activity ($[\alpha]_D$+6.5°) compared with (7′*S*,8′*R*,8*R*)-lyoniresinol ($[\alpha]_D$+58°) isolated from *Cinnamomum cassia*,[13,14] it is suggested that compound **4** was a racemic mixture of (7′*S*,8′*R*,8*R*)-lyoniresinol and (7′*R*,8′*S*,8*S*)-lyoniresinol; the former enantiomer was dominant. Owing to the aglycone of compounds **1**, **4** came from the same plant, the configuration should not change. So the (7′*S*,8′*R*,8*R*)-isomer was dominant racemic lyoniresinol, this assignment was also sustained.

Compound **2** was also isolated as a colorless powder. The molecular formula $C_{38}H_{46}O_{16}$ was established by its HR-FAB-MS and DEPT spectrum. IR spectrum of **2** afforded functional absorption for hydroxyl (3376 cm^{-1}), conjugate ester (1702 cm^{-1}), double bond (1643 cm^{-1}), and aromatic ring (1601 cm^{-1}). Acid hydrolysis of **2** yielded a sugar, which was identified as glucose, and ferulic acid by detected HPTLC. Comparison of the ^{1}H- and ^{13}C-NMR data with those of compounds **2** and **4** suggested the same lignan portion as their structures except for sugar and feruloyl moieties in **2**. The ^{1}H-NMR spectrum exhibited the typical proton signals of lyoniresinol, feruloyl [δ 7.60 (1H, d, J=16.0 Hz), 6.38 (1H, d, J=16.0 Hz) to assign *trans* double bond; 7.30 (1H, d, J=1.6 Hz, H-2‴), 7.15 (1H, dd, J=7.9, 1.6 Hz, H-6‴), 6.83 (1H, d, J=7.9 Hz, H-5‴), and 3.88 (3H, s, –OCH_3)], and glucose [δ 4.99 (1H, d, J=7.7 Hz) to assign β-form]. In the ^{1}H-NMR spectrum, the proton signals at δ_H 6.61 (H-2) and 6.47 (H-4′) were very easy distinguishing (see Table 2). So, the carbon signals C-4 and C-4′ were assigned by HMBC, unambiguously. The HMBC spectrum of **2** revealed that the correlations were between δ 6.61 (H-2) and 138.1 (C-4); between δ 6.61 (H-2) and 34.3 (C-7); between δ 4.99 (H-1″ of glucose) and 138.1 (C-4); 4.23 (H-6″ of glucose) and 166.9 (C-9‴); these cross peaks indicated a feruloyl-(9‴→6″)-glucose-(1″→4)lyoniresinol. Thus compound **2** was determined to be lyoniresinol-4-*O*-[6-*O*-(*E*)-feruloyl]-β-D-glucopyranoside, and named as rhusemialin B.

Compound **3** was isolated as a colorless powder. The molecular formula $C_{48}H_{54}O_{19}$ was established by its HR-FAB-MS and DEPT spectrum. IR spectrum of **3** showed functional absorptions for hydroxyl (3403 cm^{-1}), conjugate ester (1699 cm^{-1}), double bond (1640 cm^{-1}), and aromatic ring (1600 cm^{-1}). Acid hydrolysis of **3** afforded a sugar, which

Table 1. ^{13}C- and ^{1}H-NMR Data of Compounds **1** and **4**

No.		**1**[a]		HMBC	**4**[b]	
1	C	130.0			129.1	
2	CH	107.8	6.61, s	C_1, C_6, C_7, C_4	106.4	6.55, s
3	C	147.4			146.9	
	3-OMe	56.8	3.86, s	C_3	55.8	3.82, s
4	C	138.7			137.8	
5	C	146.7			146.3	
	5-OMe	60.3	3.35, s	C_5	58.9	3.24, s
6	C	125.8			125.8	
7	CH_2	33.7	2.63, dd, 15.0, 11.2,[c] H_{ax} 2.79, dd, 15.0, 4.8, H_{eq}	C_2, C_6, $C_{8'}$, C_9	33.4	2.59, dd, 15.2, 11.5, H_{ax} 2.66, dd, 15.2, 5.6, H_{eq}
8	CH	40.9	1.75, m, $W_{1/2}$=23	C_1, $C_{7'}$, $C_{9'}$	40.7	1.67, m, $W_{1/2}$=26
9	CH_2	66.3	3.52, dd, 10.8, 6.4, Ha 3.64, dd, 10.8, 6.4, Hb	C_7, $C_{8'}$	66.0	3.55, d, 11.0
1′	C	138.9			138.6	
2′	CH	106.6	6.34, s	$C_{7'}$, $C_{1'}$, $C_{3'}$, $C_{4'}$	106.6	6.41, s
3′	C	149.0			147.6	
4′	C	134.6			134.2	
5′	C	149.0			147.6	
6′	CH	106.6	6.34, s	$C_{7'}$, $C_{1'}$, $C_{3'}$, $C_{4'}$	106.6	6.41, s
7′	CH	43.3	4.28, d, 6.0	$C_{1'}$, C_5, C_8, $C_{9'}$ $C_{2',6'}$	42.1	4.24, d, 6.0
8′	CH	45.9	2.24, m, $W_{1/2}$=16	C_6, $C_{1'}$	48.8	1.96, m, $W_{1/2}$=18
9′	CH_2	66.6	4.08, dd, 10.8, 5.6, Ha 4.27, dd, 10.8, 5.6, Hb	$C_{9''}$, $C_{7'}$, C_8	63.3	3.51,d, 11.3
	3′,5′-OMe	56.9	3.71, s	$C_{3'}$, $C_{5'}$	56.2	3.71, s
		Caffeoyl				
1″	C	127.6				
2″	CH	115.1	7.02, d, 2.4	$C_{7''}$, $C_{6''}$, $C_{4''}$		
3″	C	148.7				
4″	C	149.5				
5″	CH	116.5	6.76, d, 8.0	$C_{1''}$, $C_{3''}$		
6″	CH	123.0	6.93, dd, 8.0, 2.4	$C_{7''}$, $C_{4''}$		
7″	CH	147.0	7.51, d, 16.0	$C_{2''}$, $C_{6''}$, $C_{9''}$		
8″	CH	115.0	6.28, d, 16.0	$C_{1''}$, $C_{9''}$		
9″	C	169.3				

a) Spectra recorded at 400 MHz for proton and 100 MHz for carbon in CD_3OD. *b*) Spectra recorded at 400 MHz in CD_3COCD_3. *c*) The *J* values in Hz.

was identified as glucose, and ferulic acid by detected HPTLC. The ^{1}H-NMR spectrum (Table 2) exhibited the typical proton signals of lyoniresinol, such as 6.64 (1H, s, H-2), 6.43 (2H, s, H-2′, H-6′), 1.98 (1H, m, $W_{1/2}$=16.2), and 1.61 (1H, m, $W_{1/2}$=21.0), and two ABX spin systems of aromatic ring signals [7.31 (d, J=1.6 Hz, H-2‴), 7.11 (dd, J=8.0, 1.6 Hz, H-6‴), 6.84 (d, J=8.0 Hz, H-5‴) and 7.25 (d, J=1.6 Hz, H-2⁗), 7.04 (dd, J=8.1, 1.6 Hz, H-6⁗), 6.82 (d, J=8.1 Hz, H-5⁗)], six methoxy signals [3.87 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H), 3.70 (s, 6H), and 3.32 (s, 3H)], including four methoxy signals in lynoiresinol and two methoxy signals in the ABX-spin aryls, two *trans* double bond signals [7.62 (d, J=15.6 Hz, H-7‴), 6.40 (d, J=15.6 Hz, H-8‴) and 7.52 (d, J=16.0 Hz, H-7⁗), 6.28 (d, J=16.0 Hz, H-8⁗)]. The chemical shifts of two ABX spin systems of aromatic ring signals, two *trans* double bond signals, and two methoxy signals disclosed two feruloyl moieties. The ^{1}H-NMR spectrum also showed a sugar signals of an anomeric proton at δ 4.98 (d, J=7.6 Hz) and δ_H 3.60—5.10. In the HMBC spectrum, the key correlations were revealed that it was the cross peaks of the proton signal at δ 6.61 (H-2) and 138.1 (C-4); at δ 4.98 (d, J=7.6 Hz, H-1″ of glucose) and 138.1 (C-4); at δ 4.19 (2H, br d, J=5.0 Hz, H-6″ of glucose) and 166.7 (C-9‴); at δ 5.06 (t, J=10.0 Hz, H-4″ of glucose) and 166.8 (C-9⁗); these cross peaks manifested a glucose linking at the C-4 position of lynoiresinol and one feruloyl linking at the C-6 po-

Table 2. ^{13}C- and ^{1}H-NMR Data of Compounds **2** and **3**[a)]

No.		**2**		HMBC	**3**		HMBC
1	C	135.7			135.7		
2	CH	108.9	6.61, s	C_1, C_6, C_7, C_4	108.6	6.64, s	
3	C	152.1			152.4		
4	C	138.1			138.1		
5	C	152.2			152.4		
6	C	126.8			126.8		
7	CH_2	34.3	2.62, br d, 8.4 [b)]	C_2, C_6, $C_{8'}$, C_9	34.1	2.63, br d, 8.4	C_2, C_6, $C_{8'}$, C_9
			4.29, d, 6.4			4.27, d, 6.4	
8	CH	40.7	1.63, m		40.7	1.61, m	
9	CH_2	66.3	3.54, overlap		66.2	3.54, overlap	
	3-OMe	56.6	3.80, s	C_3	56.6	3.82, s	C_3
	5-OMe	60.9	3.34, s	C_5	60.9	3.32, s	C_5
1′	C	134.2			134.7		
2′	CH	107.4	6.47, s	$C_{7'}$, $C_{1'}$, $C_{3'}$, $C_{4'}$	107.0	6.43, s	$C_{7'}$, $C_{1'}$, $C_{3'}$, $C_{4'}$
3′	C	148.2			148.2		
4′	C	138.8			138.8		
5′	C	148.2			148.2		
6′	CH	107.4	6.47, s	$C_{7'}$, $C_{1'}$, $C_{3'}$, $C_{4'}$	107.0	6.43, s	$C_{7'}$, $C_{1'}$, $C_{3'}$, $C_{4'}$
7′	CH	42.5	4.25, d, 6.2	$C_{1'}$, C_5, C_8, $C_{9'}$ $C_{2',6'}$	42.6	4.27, d, 6.4	$C_{1'}$, C_5, C_8, $C_{9'}$ $C_{2',6'}$
8′	CH	48.9	1.98, m	C_6, $C_{1'}$	48.9	1.98, m	C_6, $C_{1'}$
9′	CH_2	63.5	3.57, overlap	$C_{7'}$, C_8	63.5	3.59, overlap	$C_{7'}$, C_8
	3′,5′-OMe	56.9	3.71, s	$C_{3'}$, $C_{5'}$	56.8	3.70, s	$C_{3'}$, $C_{5'}$
	Glucose						
1″	CH	104.7	4.99, d, 7.7	C_4, $C_{3''}$, $C_{5''}$	104.5	4.98, d, 7.6	C_4, $C_{3''}$, $C_{5''}$
2″	CH	73.9	3.03, overlap		75.8	3.63, overlap	
3″	CH	77.4	3.37, overlap		75.1	3.77, overlap	
4″	CH	71.2	3.26, t, 9.0		72.2	5.06, t, 10.0	$C_{9'''}$, $C_{2'''}$
5″	CH	76.3	3.40, overlap		73.0	3.80, overlap	
6″	CH_2	63.9	4.23, m	$C_{9''}$, $C_{4'''}$	63.7	4.19, m	$C_{9''}$, $C_{4''}$
	Feruloyl						
1‴	C	127.2			127.1		
2‴	CH	111.3	7.30, d, 1.6	$C_{7'''}$, $C_{6'''}$, $C_{4'''}$	111.1	7.31, d, 1.6	$C_{7'''}$, $C_{6'''}$, $C_{4'''}$
3‴	C	148.5			148.5		
4‴	C	149.9			150.0		
5‴	CH	115.7	6.83, d, 7.9	$C_{1'''}$, $C_{3''}$	115.9	6.84, d, 8.0	$C_{1'''}$, $C_{3'''}$
6‴	CH	124.2	7.15, dd, 7.9, 1.6	$C_{7'''}$, $C_{4'''}$	124.0	7.11, dd, 8.0, 1.6	$C_{7'''}$, $C_{4'''}$
7‴	CH	146.5	7.60, d, 16.0	$C_{9'''}$, $C_{2'''}$, $C_{6'''}$	146.3	7.62, d, 15.6	$C_{9'''}$, $C_{2'''}$, $C_{6'''}$
8‴	CH	115.2	6.38, d, 16.0	$C_{9'''}$, $C_{1'''}$	115.2	6.40, d, 15.6	$C_{9'''}$, $C_{1'''}$
9‴	C	166.9			166.7		
	3‴-OMe	56.5	3.88, s	$C_{3'''}$	56.3	3.87, s	$C_{3'''}$
1⁗	C				127.1		
2⁗	CH				111.0	7.25, d, 1.6	$C_{7''''}$, $C_{6''''}$, $C_{4''''}$
3⁗	C				148.5		
4⁗	C				149.9		
5⁗	CH				115.9	6.82, d, 8.1	$C_{1''''}$, $C_{3'''}$
6⁗	CH				123.9	7.04, dd, 8.1, 1.6	$C_{7''''}$, $C_{4''''}$
7⁗	CH				145.8	7.52, d, 16.0	$C_{9''''}$, $C_{2''''}$, $C_{6''''}$
8⁗	CH				115.2	6.28, d, 16.0	$C_{9''''}$, $C_{1''''}$
9⁗	C				166.8		
	3⁗-OMe				56.3	3.85, s	$C_{3''''}$

a) Spectra recorded at 400 MHz for proton and 100 MHz for carbon in CD_3COCD_3. *b*) The *J* values in Hz.

sition of the glucose and another feruloyl linking at the C-4 position of the same glucose. Thus compound **3** was determined as lynoiresinol-4-*O*-[4,6-*O*-(*E*)-diferuloyl]-*β*-D-glucopyranoside, and named as rhusemialin C.

Experimental

General Experimental Procedures Melting points were determined on a Yanaco MP-S3 apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer 983G. Optical rotations were measured with a Jasco DIP-180 digital polarimeter and UV was on a UV/VIS spectrophotometer. ^{1}H, ^{13}C, DEPT, ^{1}H–^{1}H COSY, NOESY, TOCSY, HMQC and HMBC NMR spectra were obtained on a Varian Unity Plus 400 instrument. FAB mass spectra were recorded on a Jeol JMS-HX 110 instrument. Thin-layer chromatography was performed on Merck TLC plates (Kieselgel 60 F_{254}), with compounds visualized by spraying with 5% (v/v) H_2SO_4 in alcohol solution.

Plant Material The roots of *Rhus Javanica* var. *roxburghii* were collected from the suburb of Taipei, 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 *Rhus semialata* (8 kg) were extracted with methanol for 2 weeks. The extract was concentrated to dryness under reduced pressure, the residue (300 g) was dissolved and suspended in water (2.5 l) and partitioned with ethyl acetate (3×3 l) and then water layer was extracted with *n*-butanol (3×3 l). The *n*-butanol extract was evaporated *in vacuo* to give a residue of 80 g. The residue was subjected to dry column chromatography (DCC) on silica gel (1.0 kg), eluted with $CHCl_3$–MeOH–H_2O (10 : 2 : 0.2) to get thirteen fractions. Each fraction was subjected to Sephadex LH-20, and RP-18 columns eluted with methanol–water (10—90%) and finally, purified by a silica gel column with CH_2Cl_2–EtOAc–MeOH (10 : 10 : 1) to yield **1** (18 mg), **2** (21 mg), **3** (39 mg), **4** (8 mg), **5** (25 mg), **6** (14 mg), **7** (8 mg), **8** (20 mg), **9** (133 mg), **10** (6 mg).

Acid Hydrolysis A solution of compound **2** or **3** (5 mg) was heated at 100 °C in 2 M aqueous H_2SO_4 and dioxane (1 ml each) refluxed on a water bath for 3 h. After this period, the reaction mixture was diluted with H_2O (10 ml) and extracts with CH_2Cl_2 (3×5 ml). The combined CH_2Cl_2 extract was washed with H_2O and then evaporated to dryness *in vacuo*. After evaporation to dryness of the aqueous layer, the sugars were analyzed by silica gel HPTLC by comparison with standard sugars [solvent system $CHCl_3$–MeOH–H_2O (7 : 3 : 1) lower-layer 9 ml+1 ml HOAc for sugars] on silica gel HPTLC. The extract was derivated with thiazolidine as described.[15] Monosaccharide was detected by GC and conditions: column, SupelcoSPB-1 0.25 mm×27 m; column temperature, 230 °C; carrier gas, N_2; t_R, L-glucose (13.3 min), D-glucose (13.8 min); D-glucose was detected in **2** and **3**.

Alkaline Hydrolysis The sample (5 mg) was refluxed with 5% KOH (1 ml) for 1 h. The reaction mixture was adjusted to pH 6 with dilute HCl and then extracted with H_2O-saturated *n*-BuOH (3×10 ml). The combined *n*-BuOH extracts were washed by H_2O. Evaporation of the *n*-BuOH gave the progenin. The acidic hydrolysis of progenin in 2 N HCl and dioxane (1 ml each) for 2 h at 100 °C furnished glucose (HPTLC with authentic sample).

Rhusemialin A (**1**), Lyoniresinol-9′-*O*-(*E*)-caffeoyl Ester: A colorless powder, $C_{31}H_{34}O_{11}$, $[\alpha]_D^{27}$ −1.57° (*c*=3.05, acetone); Positive FAB-MS *m*/*z* 583 $[M+H]^+$, 537, 507, 460, 402, 371, 329, 307, 289; HR-FAB-MS *m*/*z* 583.21790 (Calcd for $C_{31}H_{35}O_{11}$); UV λ_{max} (MeOH) (log ε): 216 (4.30), 243 (sh), 287 (sh), 302 (sh), 330 (4.19) nm; IR (KBr) ν_{max}: 3396, 2944, 2846, 1705, 1611, 1518, 1462, 1366, 1234, 1116 cm^{-1} (see Table 1).

Rhusemialin B (**2**), Lynoiresinol-4-*O*-*β*-D-glucopyranosyl-6″-*O*-(*E*)-feruloyl Ester: A colorless powder, $[\alpha]_D^{27}$ −9.4° (*c*=1.1, acetone); Positive FAB-MS *m*/*z* 759 $[M+H]^+$, 515, 460, 420, 307, 289; HR-FAB-MS *m*/*z* 759.28637 (Calcd for $C_{38}H_{47}O_{16}$) $[M+H]^+$; UV λ_{max} (MeOH) (log ε): 219 (4.33), 233 (sh), 282 (4.03), 301 (4.00), 331 (4.13) nm; IR (KBr) ν_{max}: 3376, 2942, 2843, 1702, 1643, 1601, 1514, 1460, 1270, 1151, 1143, 1026 cm^{-1} (see Table 2).

Rhusemialin C (**3**), Lynoiresinol-4-*O*-*β*-D-glucopyranosyl-4″,6″-*O*-(*E*)-diferuloyl Ester: A colorless powder, $[\alpha]_D^{27}$ −3.1° (*c*=1.9, acetone); Positive FAB-MS *m*/*z* 935 $[M+H]^+$, 613, 515, 460, 420, 391, 307, 289; HR-FAB-MS *m*/*z* 935.33371 (Calcd for $C_{48}H_{55}O_{19}$) $[M+H]^+$; UV λ_{max} (MeOH) (log ε): 220 (4.14), 288 (4.08), 303 (sh), 330 (4.19) nm; IR (KBr) ν_{max}: 3403, 2940, 2840, 1699, 1640, 1600, 1514, 1461, 1269, 1156, 1129, 1036 cm^{-1} (see Table 2).

Lyoniresinol (**4**): A colorless powder, $C_{22}H_{28}O_8$, $[\alpha]_D^{27}$ +6.50° (*c*=1.5, acetone); Positive FAB-MS *m*/*z* 421 $[M+H]^+$, 391, 369, 329, 307, 289; HR-FAB-MS *m*/*z* 421.18597 (Calcd for $C_{22}H_{29}O_8$) $[M+H]^+$; UV λ_{max} (MeOH) (log ε): 230 (4.02), 276 (3.47) nm; IR (KBr) ν_{max}: 3393, 1695, 1605, 1517, 1504, 1368, 1464, 1221, 1116 cm^{-1} (see Table 1).

Acknowledgements Project supported by the Natural Science Council of R.O.C.

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