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Phytochemical Study on the *Vitis thunbergii* var. *sinuata*

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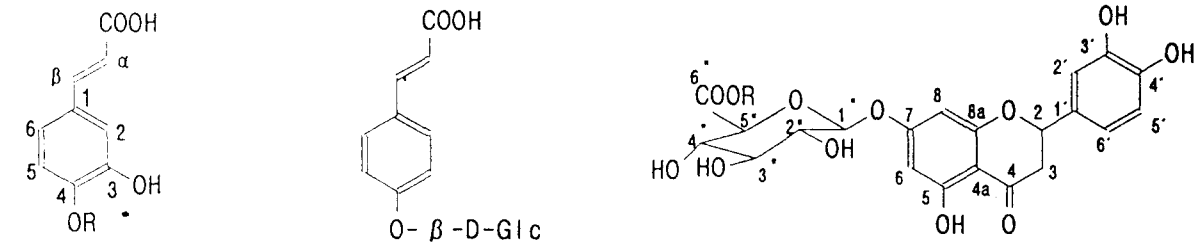
Abstract

The caffeic acid, 4-O-β-D-glucopyranosyl caffeic acid, 4-O-β-D-glucopyranosyl-ρ-coumaric acid and 7-O-β-D-glucuronide of (±)-eriodictyol have been isolated from the root of *Vitis thunbergii* var. *sinuata*. The structures of compounds were determined by chemical and spectroscopic methods.

Key words : *Vitis thunbergii* var. *sinuata*, Vitaceae, caffeic acid, 4-O-β-D-glucopyranosyl caffeic acid, 4-O-β-D-glucopyranosyl-ρ-coumaric acid, 7-O-β-D-glucuronide of (±)-eriodictyol.

The roots of *Vitis thunbergii* S. et Z. var. sinuata (Ragel) Rehder in Korea as a folk medicine " Gga Ma Gui Meo Ru " for treatment of common cold, neuralgia, and Rheumatis[1]. In the course of our chemical studies on biologically active constituents of Korean folk medicines, we investigated the constituent of the roots of Vitis thunbergii var. sinuata and isolated the caffeic acid (1), 4-O-β-D-glucopyranosyl caffeic acid (2)[2-5], 4-O-β-D-glucopyranosyl-ρ-coumaric acid (3)[6], and 7-O-β-D-glucuronide of (±)-eriodictyol (4).



1 : R = H
2 : R = β-D-Glc.

3

4a : R = H
4b : R = CH_3

Chart 1:

1. caffeic acid. 2. 4-O-β-D-glucopyranosyl caffeic acid
3. 4-O-β-D-glucopyranosyl-ρ-coumaric acid
4. 7-O-β-D-glucuronide of (±)-eriodictyol

The roots of Vitis thunbergii var. sinuata were pulverized and extracted successively with methylene chloride, 80% aqueous acetone, and ethanol at room temperature. The aqueous acetone extract was further separated as shown in Chart 2. to give fractions VA-1 to VA-3. The fraction VA-2 was subjected to column chromatography over Sephadex LH-20 and eluted with ethanol. The early fractions eluted with EtOH were further separated by polyamide column chromatography or by a combination of preparative thin-layer chromatography and Sephadex LH-20 column chromatography to give compounds 1 to 4a. Among these, compounds 1 and 3 were identified as caffeic acid (1) and 4-O-β-D-glucopyranosyl-ρ-coumaric acid (3)[2-6], respectively.

Compound 2 was obtained as colorless needles, mp 136~137 °C, $C_{15}H_{18}O_9$, $[\alpha]_D^{24}$ - 87.1 ° (MeOH). This compound was identified as 4-O-β-D-glucopyranosyl caffeic acid (2)[7,8] by detailed analysis of its proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra with the aid of ^{1}H-^{1}H shift correlation spectroscopy (COPY) and ^{1}H-detected heteronuclear multiple quantum coherence (HMQC) and ^{1}H-detected heteronuclear multiplebond multiple-quantum coherence (HMBC) spectroscopy[7-9].

Substance 4a was obtained as a pale brown amorphous powder, $[\alpha]_D^{30}$ -45.2° (MeOH), and showed a dark color with ferric chloride reagent and an orange color with anisaldehyde-sulfuric acid reagent. The elemental analysis

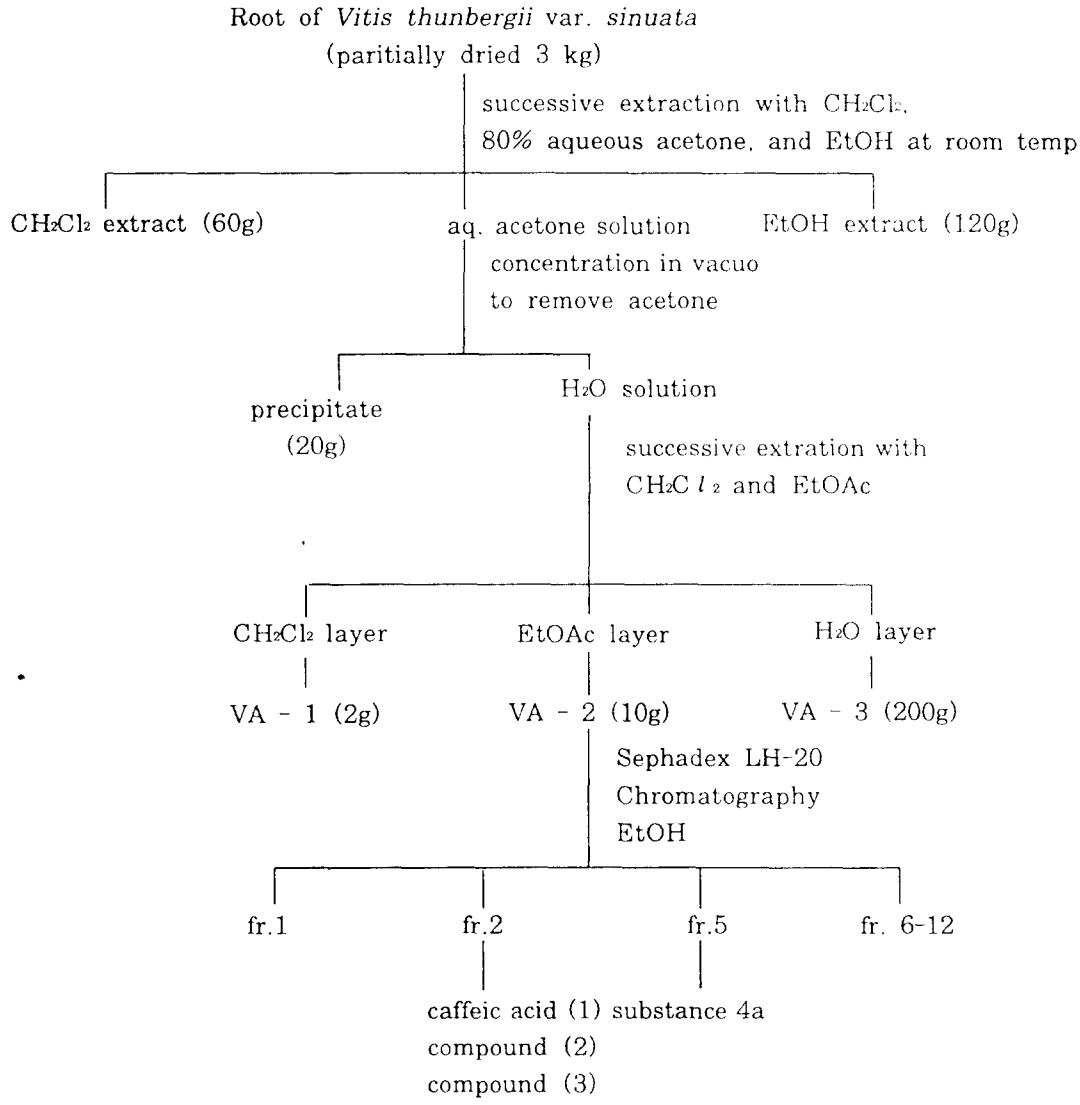


Chart 2. Isolation Scheme of the Constituents of *Vitis thunbergii* var. *sinuata*

data of 4a and the quasi-molecular ion peak in negative ion FAB-MS ($[M-H]^-$: *m/z*463) agreed well with formula $C_{21}H_{20}O_{12}$.

It showed UV absorptions at 284(log ϵ 4.30) and 329nm (log ϵ 3.65) and IR absorptions at 3400(OH, very strong), 1643(conjugated C=0), 1578, and 1520cm^{-1} (aromatic ring). In the ^{1}H-and ^{13}C-NMR spectra, it showed signals assignable to and anomeric proton and an anomeric carbon at around δ H 5.2 and δ C 99, respectively, suggesting the presence of a suger group.

In addition, the IR spectrum of 4a showed characteristic absorptions at 3200-2400 (br) and 1733cm^{-1}, which could be ascribed to a carboxyl group. Methylation of 4a with deazomethane afforded a methyle ester (4b), V_{max} 1740cm^{-1} (ester CO), which showed the quasi-molecular ion peak at *m/z* 477 $[M-H]^-$ in the negative ion FAS-MS. In the ^{1}H-^{13}C long-range COSY of 4b, the ester carbonyl carbon (δ 170.1) showed long-range correlations with the methoxy protons (around δ 3.70) and with two protons at round δ 3.70(4″-H) and 4.23 (5″-H) which may be ascribed to methine protons in the sugar moiety.

Extensive analysis of the ^{1}H-and ^{13}C-NMR spectra of 4a and 4b with the aid of ^{1}H-^{1}H, ^{1}H-^{13}C, and long-range ^{1}H-^{13}C COSY and ^{1}H J-resolved two-dimensional nuclear magnetic resonance(2D NMR) led to a suggestion that 4a may be a flavonoid β-glucuronide. However, it was found that some of the proton and carbon signals appeared. As pairs of closely asjacent double lines(Table Ⅰ and Ⅱ). Therefore, 4a was considered to be mixture of two isomers. Treatment of 4a with 3% aqueous hydrochloric acid according to Hori et al.[10] gave a crystalline compound, mp 264-266° C, $[\alpha]_D^{32}$ 0° (MeOH), which was identifid as (±)-eriodictyol by comparisons of its spectral data with those published for the (-)-enantiomer[10]. Thus 4a was believed to be a diastereomeric mixture of eriodictyol β-glucuronides. However, attempts at the separation of these diastereomers were unsuccessful.

Next, in order to clarify the position of the glucuronide lingkage, we measured the long-range C-H J-resolved 2D NMR (LRCJR) spectrum[11-12] under selective irradiation at 1″-H (Fig.1). The signals due to C-7 (δ 165.0 and 164.9) were split into doublets (J = 2.1Hz). Thus, the glucuroide group should be located at the C-7 position of eriodictyol. Since only D-glucuronic acid is known in nature, 4a was determined to be the 7-0-β-D-glucuronide of (±)-eriodictyol.

Experimental

Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected.

Opical rotations were measured in MeOH solutions on a JASCO DIP-4 automatic polarimeter or a JASCO DIP-140 digital polarimeter at 24-32 ° C. UV spectra were taken with a Shimadzu 202 UV spectrophotometer in MeOH and IR spectra were recorded on a JASCO IR-2 spectrometer or a Nicolet 5DX FT-IR spectrometer in KBr discs. Electron impact mass spectrum (EI-MS) (ionization voltage, 70eV ; accelerating voltage, 3kV) and negative ion FAB-MS were obtained with a JEOL D-300 spectrometer using a direct inlet system and triethanolamine was used as a matrix in negative ion FAB-MS measurements. ^{1}H and ^{13}C-NMR spectra were taken on a JEOL JNM-GX400 spectrometer with tetrame thylsilane as an internal standard and chemical shifts are recorded in δ values. Multiplicities of ^{13}C-NMR signals were determined by means of the distortionless enhancement by polarization transfer (DEPT) method and are indicated as s (singlet), d (doublet), t (triplet), and q (quartet).

2D NMR spectra (^{1}H-^{1}H COSY, ^{1}H J-resolved 2D NMR, ^{1}H-^{13}C COSY, long-range ^{1}H-^{13}C COSY HMQC, HMBC,

Table I. 400 MHz ^{1}H-NMR Data (δ ppm, J Values in Parenthesis in Hz) for 4a and 4b[a]

Proton	4a[b]		4a[c]		4b[d]	
2-H	5.46 br dd	5.43 br dd	5.28 dd	5.27 dd	5.44 dd	5.33 dd
	(12.5, 2.5)	(12.5, 2.5)	(12.8, 3.1)	(12.8, 3.1)	(12.8, 3.1)	(12.8, 3.1)
3-Ha	3.27 dd		3.10 dd	3.09 dd	3.21 dd	3.20 dd
	..(16.9, 12.5)		(17.0, 12.8)	(17.0, 12.8)	(17.1,12.8)	(17.1, 12.8)
3-He	2.75 dd	2.74 dd	2.72 dd	2.71 dd	2.77 dd	2.76 dd
	(16.9, 2.5)	(16.9, 2.5)	(17.0, 3.1)	(17.0, 3.1)	(17.1, 3.1)	(17.1, 3.1)
6-H	6.17 d	6.16 d	6.16 d		6.14 d	6.13 d
	(2.3)	(2.3)	(2.1)		(1.8)	(1.8)
8-H	6.21 d	6.20 d	6.17 d		6.17 d	
	(2.3)	(2.3)	(2.1)		(1.8)	
2'-H	6.92 s	6.91 s	6.92 br s		7.04 br s	
5'-H	6.77 s		6.78 br s		6.87 br s	
6'-H	6.77 s		6.78 br s		6.87 br s	
1"-H	5.19 d	5.17 d	5.07 d	5.06 d	5.27 d	5.25 d
	(7.5)	(7.5)	(7.5)	(7.5)	(7.6)	(7.6)
2"-H	3.28 dd		3.51 dd		3.54 dd	
	(8.5, 7.5)		(8.0, 7.5)		(8.5, 7.6)	
3"-H	3.34 dd		3.53 t		3.61 dd	
	(9.4, 8.5)		8.0)		(9.2, 8.5)	
4"-H	3.41 t		3.62 dd		3.69 t	3.70 t
	(9.4)		(9.5, 8.0)		(9.2)	(9.2)
5"-H	4.02 d	4.01 d	4.05 d	4.03 d	4.24 d	4.23 d
	(9.4)	(9.4)	(9.5)	(9.5)	(9.2)	(9.2)
$CO_2\underline{CH_3}$	—		—		3.71 s	3.70 s
3'-O<u>H</u>	9.09 br s				8.18 br s	
4'-O<u>H</u>	9.09 br s				8.23 br s	
5'-O<u>H</u>	12.06 s				12.07 s	12.06 s
2"-O<u>H</u>					4.93 br s	
3"-O<u>H</u>					4.65 br s	
4"-O<u>H</u>					4.68 br s	

a) Signal assignments are based on the results of ^{1}H-^{1}H COSY, ^{1}H homonuclear J-resolved 2D NMR, ^{1}H-^{13}C COSY, and long-range ^{1}H-^{13}C COSY experiments.

b, c, and d) Values in DMSO-d_6, methanol-d_4 and acetone-d_6, respectively.

Table Ⅱ. 100 MHz ^{13}C NMR Data 4a and 4b[a]

Compd.	4a[b]			4a[c]			4a[d]		
^{13}C	δ	^1H Long-range coupled ($^3J_{CH}$	$^2J_{CH}$)[e]	δ	^1H Long-range coupled ($^3J_{CH}$	$^2J_{CH}$)[e]	δ	^1H Long-range coupled ($^3J_{CH}$	$^2J_{CH}$)[e]
2	79.00d 78.95d			81.4d 81.3d	2'	$3_{ax.}$	87.7d 80.6d		
3	42.4t			44.9t 44.8t			44.02t 43.99t		
4	197.4 s 197.3s		$3_{ax.}$, $3_{eq.}$	199.3s	2	$3_{ax.}$, 3_{eq}	198.5s 198.4s		$3_{ax.}$, 3_{eq}
4a	103.6s	6,8,5-OH	$3_{ax.}$, 3_{eq}[f]	105.1s	6,8,5-OH		105.1s	6,8,5-OH	
5	163.1s		6,5-OH	165.5s 165.5s		6	165.10s 165.07s	6	5-OH
6	96.5d	5-OH		98.61d 98.60d			97.9d	8,5-OH	
7	165.0s 164.9s	1"[f]	6,8	167.23s 167.18s		6,8	166.6s	1"	6,8
8	95.5d 95.4 d	6		97.71d 97.66d	6		96.7d	6	
8a	163.0s 162.9s	2[f]	8	165.2s		8	165.5s 164.5s		8
1'	129.4s	$3_{ax.}$,$3_{eq.}$[f],5'	2',6'	132.18s 132.15s	5'	2',6'	131.7s	$3_{ax.}$,5'	6'
2'	114.6d	2		115.5d	2',6'		115.2d	2,3'-OH	
3'	145.4s	5'	2'	147.1s	5'		146.5s	5'	6'
4'	146.0s	2',6'	5'	157.6s	2',6'	5'	147.0s	2',6'	5'
5'	115.6d			117.0d			116.5d	4'-OH	
6'	118.3d	2,2'		120.1d	2,2'		119.8d	2,2'	
1"	99.1d 99.0d			101.64d 101.61d	5"		101.1d 100.9d	4",5"	
2"	72.9d			75.0d			74.5d		
3"	75.7d			77.8d			77.3d		
4"	71.4d			73.6d			73.0d		
5"	75.5d			77.2d			76.8d		
6"	170.2s	4"	5"	172.80s 172.79s		5"	170.1s	4",OCH_3	5"
$-COCH_3$	—			—			52.9q		

a) Signal assignments are based on the results of ^1H-^{13}C COSY and long-range ^1H-^{13}C COSY.

b, c, and d) Values in DMSO-d_6, methanol-d_4, and acetone-d_6, respectively. e) $^3J_{CH}$ and $^2J_{CH}$ indicate the protons coupled with carbon through two and three bonds, respectively, which were observed in the long-range ^1H-^{13}C COSY and long-range C-H J-resolved 2D NMR spectra. f) Long-range coupling was confirmed by LRCJR experiments under selective irradiation at the respective proton signals.

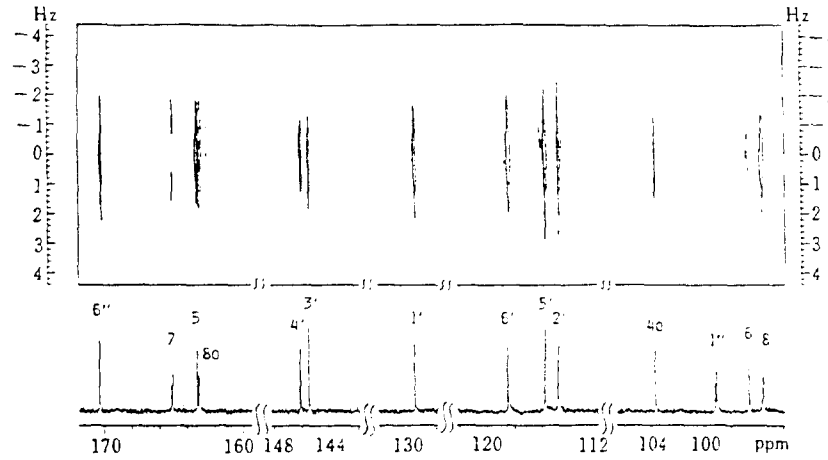


Fig. 1. Long-range C-H J-Resolved 2D NMR Spectrum of the 7-O-β-D-Glucuronide of (±)-Eriodictyol (4a) in DMSO-d_6 under Selective Irradiation of 1''-H at around δ 5.18.

and LRCJR) were measured by the use of JEOL standard pulse sequences and collected data were treated by JEOL standard software. Difference NOE spectra were obtained by the use of a JEOL standard pulse sequence with irradiation for 5s.

Column chromatography was done with Sephadex LH-20 (Pharmacia) or Polyamide C-100 (40-100 mesh. Wako Pure Chemical Industries, Ltd.).

TLC and preparative TLC were carried out on precoated Merck Kieselgel F_{254} plates(0.25 or 0.5mm) or precoated Merck RP-18F_{254} reversed-phase plates (0.25mm) with EtOAc-EtOH-H_2O (20:2:1 or 10:2:1) or MeOH-H_2O (2:3) as the developing solvent, and spots were detected under UV light, or by using $FeCl_3$ reagent, anisaldehyde-H_2SO_4 reagent, or $Ce(SO_4)_2$-10% H_2SO_4 (1:99) reagent.

Extraction and Fractionation

Partially air-dried root (3kg) of Vitis thunbergii var. sinuata collected at Mt. Ji Ri, South Korea, in August, 1988, were pulverized and extracted successively with CH_2Cl_2, 80% aqueous acetone, and EtOH at room temperature to afford a CH_2Cl_2 extract (60g), an aqueous acetone solution, and an EtOH extract(120g), respectively.

The aqueous acetone solution was concentrated under reduced pressure to remove acetone and the precipitate formed (20g) was collected by filteration. The filtrate (1.5 *l*) was extracted successively with CH_2Cl_2 and EtOAc. Each extract and the remaining water layer were evaporated to dryness in vacuo to give fractions VA-1 (2g), VA-2 (10g) and VA-3 (200g), respectively.

Isolation of 1 to 4a from Fraction DA-2

Fraction VA-2 (10g) was subjected to column chromatography on Sephadex LH-20 (bed, 5 × 54cm) and eluted

successively with EtOH (6 *l*). Fractions were collected in 5ml portions and they were monitored by TLC and finally divided into 12 fractions. A portion (310mg) of fr. 2 (total 600mg) was rechromatographed on a polyamide column (0.4g ; bed, 1.2 × 17cm). Elution with H_2O gave a crystalline substance (50mg), which was recrystallized from MeOH to give caffeic acid (1) (15mg) as pale brown needles.

Another portion (150mg) of fr. 2 was separated by preparative TLC with EtOAc-EtOH-H_2O(20:2:1). The least polar fraction gave caffeic acid (1) (4mg) and the most polar fraction (20mg) was further purified by reversed-phase preparative TLC with MeOH-H_2O(2:3) to give a crystalline substance, which was subjected again to chromatography on a Sephadex LH-20 column and eluted with H_2O to give compound 3 (7mg) and compound 2 (5mg).

Fraction 5 gave substance 4a (400mg) as a pale brown amorphorus powder.

Caffeic Acid (1) Pale brown needles (from MeOH), mp 196-197 ° C. ^{1}H-NMR(methanol-d_4) δ : 6.23 (1H, d, J = 15.9 Hz, α-H), 6.78 (1H, d, J = 8.2 Hz, 5-H), 6.93 (1H, dd, J = 8.2, 2.0 Hz, 6-H), 7.04 (1H, d, J = 2.0 Hz, 2-H), 7.53 (1H, d, J = 15.9 Hz β-H). ^{13}C-NMR (methanol-d_4) δ 115.9 (d, C-5), 116.4 (d, C-2), 117.3 (d, C-α), 171.9 (s, COOH), 123.6 (d, C-6), 128.6 (s, C-1), 147.5 (s, C-3), 147.8 (d, C-β), 150.2 (s, C-4). The ^{1}H- and ^{13}C-NMR data were identical with those of an authentic sample.

4-O-β-D-Glucopyranosylcaffeic Acid (2) Colorless needles (from MeOH), mp 136-137 ° c, $[\alpha]_D^{24}$ -87.1 ° (c = 0.7, MeOH). UV λmax nm (logε): 217 (4.13), 236 (4.04), 287 (4.17), 315 (4.08). IR ν_{max}cm^{-1} : 3250 (OH), 3200-2400 (br, COOH), 1660 (COOH), 1605, 1500 (aromatic ring), 1280, 1070, 860, 800. Negative ion FAB-MS m/z : 341 [M-H]$^-$. ^{1}H-NMR (methanol-d_4) δ : 7.56 (1H, d, J = 15.9Hz, β-H), 7.16 (1H, d, J = 8.3 Hz, 5-H), 7.10 (1H, d, J = 2.1 Hz, 2-H), 7.03(1H, dd, J = 8.3, 2.1 Hz, 6-H), 6.31 (1H, d, J = 15.9 Hz, α-H), 4.85 (1H, d, J = 7.3 Hz, 1' -H), 3.91 (1H, dd, J = 11.2, 1.8 Hz, 6' -H), 3.72 (1H, dd, J = 11.2, 5.1 Hz, 6' -H), 3.53 (1H, t, J = 7.3 Hz, 3' -H), 3.51 (1H, t, J = 7.3 Hz, 2' -H), 3.42 (1H, dd, J = 9.0, 7.3 Hz, 4' -H), 3.45 (1H, m, 5' -H). ^{13}C-NMR (methanol-d_4) δ : 171.4 (s, COOH), 149.5 (s, C-4; long-range-correlated with 1' -H, 2' -H, and 6-H in the HMBC spectrum), 149.3 (s, C-3; long-range-correlated with 5-H in the HMBC spectrum), 146.9 (d, C-β), 131.9 (s, C-1), 122.9 (d, C-6), 118.9 (d,C-α), 118.5 (d, C-5), 116.7 (d, C-2), 104.3 (d, C-1'), 79.1 (d, C-5'), 78.3 (d, C-2'), 75.5(d, C-3'), 72.0 (d, C-4'), 63.2 (t, C-6').

4-0-β-D-Glucopyranosyl-ρ-coumaric acid (3) Colorless needles (from Me-OH), mp 191-192.5 ° c, $[\alpha]_D^{24}$ -72.6 ° (c = 0.7, MeOH). UV λmax nm (logε): 223 (3.96), 288.5 (4.15), 297 sh (4.14). IR ν_{max}cm^{-1} : 3350 (OH), 3200-2400 (br,COOH), 1675 (COOH) 1600, 1500 (aromatic ring), 1245, 1080, 825. Negative ion FAB-MS m/z ; 325 [M-H]$^-$. ^{1}H-NMR (methanol-d_4) δ : 7.62 (1H, d, J = 16.0 Hz, β-H), 7.55 (2H, d, J = 8.5 Hz, 2,6-H), 7.12 (2H, d, J = 8.5 Hz, 3,5-H), 6.36(1H, d, J = 16.0 Hz, α-H), 4.96 (1H, d, J = 7.5 Hz, 1' -H), 3.90 (1H, dd, J = 12.1, 2.1 Hz, 6' -H), 3.70 (1H, dd, J = 7.5, 7.0 Hz, 2' -H), 3.46 (1H, ddd, J = 9.0, 5.5, 2.1 Hz, 5' -H), 3.40 (1H, dd, J = 9.0, 7.0 Hz, 4' -H). ^{13}C-NMR (methanol-d_4) δ : 171.4 (s, COOH), 161.6 (s, C-4), 146.7 (d, C-β), 131.5 (2×C, d, C-2,6), 130.8 (s, C-1), 118.8 (2×C, d, C-3,5), 118.2 (d, C-α), 102.6 (d, C-1'), 79.0 (d, C-5'), 78.7(d, C-2'), 75.6 (d, C-3'), 72.1 (d, C-4'), 63.3 (t, C-6').

Substance 4a (7-O-β-O-D-Glucuronide of (±)-Eriodictyol) Pale brown powder, $[\alpha]_D^{30}$ -45.2 ° (c = 1.0, MeOH). UV λmax nm (logε) : 284 (4.30), 329 (3.65). IR ν_{max}cm^{-1} : 3400 (OH), 3200-2400 br (COOH), 1730 (CO) 1640 (COOH), 1615, 1580, 1520 (aromatic ring), 1450, 1200, 1180. EI-MS m/z : 288 [genin]$^+$176. Negative ion FAB-MS m/z : 463 [M-H]$^-$. Anal. Calcd for $C_{21}H_{20}O_{12}$: C, 54.31 ; H, 4.34. Found : C, 54.13 ; H, 4.25. ^{1}H- and ^{13}C-NMR : see Table Ⅱ and Ⅲ.

Methylation of 4a 4a (25mg) was methylated with excess CH_2N_2 in ether and the crude product (26mg) was purified by preparative TLC [MeOH-CH_2Cl_2 (2:8)] to afford a methyl ester **(4b)** (19.4mg), amorphous powder,

$[\alpha]_D^{32}$ - 89.1 ° (c = 1.2, MeOH). UV λ_{max}nm (logϵ): 283 (4.20), 330 (3.64). IR $\nu_{max}cm^{-1}$; 3350(OH), 1740, 1630 (CO), 1580, 1510 (aromatic ring), 1445, 1380, 1280, 1200, 1170. Negative ion FAS-MS m/z : 477 [M-H]. ^{1}H and ^{13}C-NMR (acetone-d_6) : see Table Ⅰ. and Ⅱ.

Acid Hydrolysis of 4a 4a (100mg) was refluxed with 3% aqueous HCl solution (8ml) for 1h.[10] The reaction mixture was extracted with EtOAc, and the extract was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to give a syrup. The residue was separated by preparative TLC with EtOAc-EtOH-H_2O(10:2:1) to give (±)-eriodictyol (14mg), yellow needles (from MeOH), mp 264-266 ° C (dec.), $[\alpha]_D^{32}$ 0 ° (c = 1.0, MeOH). UV λmax nm (logϵ) : 215 (4.35), 224 sh (4.31), 288 (4.28), 329 sh (3.78). IR $\nu_{max}cm^{-1}$: 3350 (OH), 1635 (CO), 1605, 1480 (aromatic ring), 1450, 1210, 1160. EI-MS m/z : 288 (M^+, base peak), 153, 136, 123. ^{1}H-NMR (methanol-d_4) δ : 2.69 (1H, dd, J = 17.1, 3.1 Hz,3-H_e), 3.06 (1H, dd, J = 17.1, 12.8 Hz, 3-Ha), 5.27 (1H, dd, J = 12.8, 3.1 Hz, 2-H), 5.88 (1H, d, J = 2.1 Hz, 6-H), 5.90 (1H, d, J = 2.1 Hz, 8-H), 6.78 (1H, ABtype, 5' -H), 6.79 (1H, AB type, 6' -H), 6.91 (1H, br s, 2' -H). ^{13}C-NMR (methanol-d_4) δ : 81.3 (d, C-2), 44.9 (t, C-3), 198.5 (s, C-4), 104.1 (s, C-4a), 166.2 (s, C-5), 97.8 (d, C-6), 169.2 (s, C-7), 97.0 (d, C-8), 165.6 (s, C-8a), 132.5 (s, C-1'), 115.5 (d, C-2'), 147.3 (s, C-3' ; long-range-correlated with 2' -H and 5' -H in the long-range ^{1}H-^{13}C COSY), 147.6 (C-4' ; long-range-correlated with 2' -H, 5' -H, and 6' -H in the long-range ^{1}H-^{13}C COSY), 117.1 (d, C-5'), 120.0 (d, C-6').

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