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FOUR SECOIRIDOID GLUCOSIDES FROM *FRAXINUS INSULARIS*

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Key Word Index—*Fraxinus insularis*; Oleaceae; leaves; secoiridoid glucosides; phenylethanoid glucoside; structure elucidation.

Abstract—Investigation of the leaves of *Fraxinus insularis* has led to the isolation of four new secoiridoid glucosides, insularoside-3′-*O*-*β*-D-glucoside, insularoside-3′, 6‴-di-*O*-*β*-D-glucoside, insuloside and desrhamnosyloleoacteoside, together with ligstroside. The structures of the new compounds were determined on the basis of spectroscopic methods. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

In the course of our chemical studies on the secoiridoid glucosides from the family Oleaceae, we have previously investigated the constituents of the $CHCl_3$- and *n*-BuOH-soluble portions of the MeOH extract of fresh leaves of *Fraxinus insularis* Hemsl. and isolated two new secoiridoid glucosides, insularoside (**1**) and insularoside-6‴-*O*-*β*-D-glucoside (**2**), as well as nine known compounds [1, 2]. In this preliminary study, we found that the *n*-BuOH-soluble portion contained further minor secoiridoid glucosides. This paper deals with the re-examination of the glucosidal fraction of the same plant material and the isolation and structure elucidation of four novel secoiridoid glucosides (**3**–**6**).

RESULTS AND DISCUSSION

The *n*-BuOH-soluble fraction of the methanolic extract of *F. insularis* was fractionated by column chromatography on ODS and then purified by prep. HPLC, affording four new compounds (**3**–**6**) and ligstroside [3] in addition to the compounds previously identified.

Compound **3** was recognized as an isomer of **2**, $C_{38}H_{46}O_{18}$, from its HR-SIMS. Its UV spectrum, besides the typical absorption at 231 (sh) nm of an iridoidic enol ether systems conjugated with a carbonyl group, revealed an additional absorption at 272.5 and 280 (sh) nm due to a phenolic function. It showed IR bands at 3403 (OH), 1735 (ester), 1717 and 1622 (α,*β*-unsaturated ester), and 1506 (aromatic ring) cm^{-1}. Its ^1H NMR spectrum (Table 1) exhibited the typical signals of an oleoside (**7**) unit [H-3 at δ 7.54 (*s*), an allylic acetal proton at δ 5.86 (*br s*), an anomeric proton at δ 4.82 (*d*) and an ethylidene group at δ 6.03 (1H, *qd*) and δ 1.61 (3H, *dd*)] together with an aromatic AA′BB′ spin system at δ 6.92 (2H, *d*, $J = 8.0$ Hz) and 7.20 (2H, *d*, $J = 8.0$ Hz) and an AMX spin system at δ 6.84 (1H, *d*, $J = 8.0$ Hz), 6.76 (1H, *dd*, $J = 8.0$, 2.0 Hz), and 6.52 (1H, *d*, $J = 2.0$ Hz), suggesting a structural similarity of **3** to **1**. Furthermore, the ^1H NMR spectrum of **3** showed signals ascribable to a *β*-glucopyranosyl unit [δ 4.82 (*d*, $J = 8.0$ Hz)]. Its ^{13}C NMR spectrum (Table 2) was very similar to that of **1** [1], except for the appearance of an additional set of signals assigned to a second terminal *β*-glucopyranosyl unit. Furthermore, this unit could be determined to be attached at C-3′ of the oleoside moiety since this showed a downfield shift ($\Delta\delta$ +9.6 ppm), while C-2′ and C-4′ showed smaller upfield shifts ($\Delta\delta$ −0.6 and −1.6 ppm, respectively), when compared with **1**. This was further supported by HMBC experiments with **3**, which showed cross-peaks between H-1⁗ (δ 4.58) and C-3′ (δ 87.6) as well as between H-3′ (δ 3.60) and C-1⁗ (δ 105.3). Accordingly, compound **3** was formulated as shown and designated as insularoside-3′-*O*-*β*-D-glucoside.

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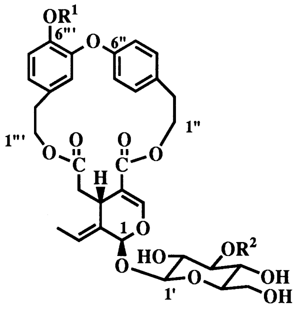

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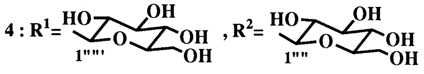
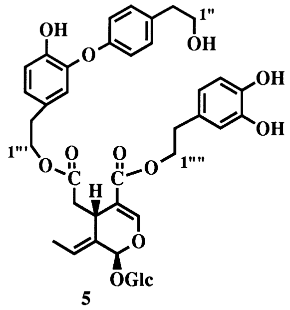
3 : R^1= H, R^2= Glc





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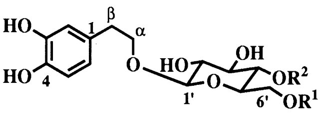

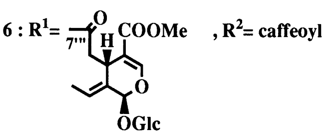

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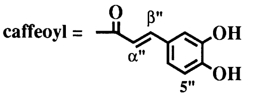
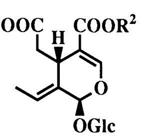
12 : R^1= caffeoyl, R^2= H
13 : R^1=R^2=H





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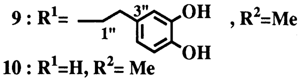

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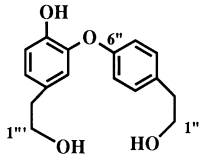

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Compound **4** was obtained as an amorphous powder. The HR-SIMS measurement revealed the molecular formula $C_{44}H_{56}O_{23}$. The ^{1}H and ^{13}C NMR (Tables 1 and 2) spectral features of **4** were similar to those of **3**, except for the presence of signals assignable to an extra β-glucopyranosyl unit and for changes in the chemical shifts of some of the signals arising from the aromatic rings. The downfield shifts of H-7‴ (Δδ+0.36 ppm) as well as C-3‴, C-5‴ and C-7‴ (Δδ +3.4, +4.0 and +1.5 ppm, respectively), when compared with the corresponding signals of **3**, suggested an attachment of a glucose unit at the hydroxyl group on C-6‴ in the aromatic ring, and this received support from the chemical shifts of an anomeric proton signal (δ 4.99) and an anomeric carbon signal (δ 103.0). The above arguments were further confirmed by comparative studies on the NMR spectra of the isolate and insularoside-6‴-*O*-β-D-glucoside (**2**). The downfield-shifted carbon signal at δ 87.6 was assigned to C-3′ of the glucose of the oleoside unit rather than to C-3′′′′′ of the glucose attached to a phenolic hydroxyl group on the basis of the HMBC experiments, which showed cross-peaks between H-2′ (δ 3.49) and C-3′ (δ 87.6), between H-2′ and C-1′ (δ 100.6), and between H-1 (δ 5.86) and C-1′. Furthermore, significant HMBC correlations were observed between H-1′′′′ (δ 4.58) and C-3′, between H-3′ (δ 3.60) and C-1′′′′ (δ 105.3), and between H-3′ and C-2′ (δ 74.2). Thus, the structure of **4** was established as insularoside-3′,6‴-di-*O*-β-D-glucoside.

Compound **5**, named insuloside, on HR-SIMS exhibited a peak at *m*/*z* 781.2697 ($[M-H]^-$) consistent with a molecular formula of $C_{40}H_{46}O_{16}$. Its ^{1}H NMR (Table 1) spectrum, excluding the presence of the signals attributable to a 3,4-dihydroxyphenethyl moiety, showed a close similarity to that of **1**. The ^{13}C NMR (Table 2) spectrum of **5** also revealed signals corresponding to an oleoside (**7**), a diphenyl ether (**8**) moiety and a 3,4-dihydroxyphenethyl alcohol moiety. Inspection of the ^{13}C NMR data of **5**, **8** and oleuropein (**9**) indicated that the C-1‴ hydroxyl group of **8** and an aliphatic hydroxyl group of 3,4-dihydroxyphenethyl alcohol were esterified with the C-7 and C-11 carboxyl groups of the oleoside unit in **5**. The HMBC experiments with **5** revealed cross-peaks between H-3 and C-11 (δ 168.1), between H_2-6 and C-7 (δ 173.2), between H-1‴ (δ 4.26), H-7‴ (δ 6.87) and C-3‴ (δ 131.0), and between H-1′′′′ (δ 4.07), H-4′′′′ (δ 6.665), H-7′′′′ (δ 6.667) and C-3′′′′ (δ 131.5), confirming the assignments of both carbonyl carbons and the methylene protons at C-1‴ and C-1′′′′. Furthermore, significant HMBC connectivities between H-1‴ (δ 4.26) and C-7 and between H-1′′′′ (δ 4.07) and C-11 established the ester linkages. Thus, the structure of insuloside was represented by **5**.

Compound **6**, $[\alpha]_D -94°$ (MeOH), was analyzed for $C_{40}H_{48}O_{21}$ from its HR-SIMS measurement. Its ^{1}H NMR spectrum displayed, besides the signals of an oleoside 11-methyl ester (**10**) unit, signals assigned to β-glucose [H-1′, δ 4.39 (*d*, *J* = 8.0 Hz)], *trans*-caffeoyl [an aromatic AMX spin system at δ 6.78, 6.96, 7.05, a pair of *trans*-olefinic protons at δ 6.28 and 7.59 (each, *d*, *J* = 16.0 Hz)], and 3,4-dihydroxyphenethyl [an aromatic AMX spin system at δ 6.56, 6.67, and

Table 1. ^{1}H NMR spectral data of compounds **3**, **4** and **5** in CD_3OD

H	**3**		**4**			**5**
1	5.86 *br s*		5.86 *br s*			5.85 *br s*
3	7.54 *s*		7.54 *s*			7.45 *s*
5	3.79 *dd* (10.5, 3.5)		3.79 *dd* (10.5, 3.5)			3.87 *dd* (9.0, 4.5)
6	2.16 *dd* (15.0, 10.5)		2.15 *dd* (15.0, 10.5)			2.30 *dd* (14.0, 9.0)
	2.31 *dd* (15.0, 3.5)		2.32 *dd* (15.0, 3.5)			2.59 *dd* (14.0, 4.5)
8	6.03 *qd* (7.0, 1.0)		6.03 *qd* (7.0, 1.0)			6.05 *qd* (7.5, 1.0)
10	1.61 *dd* (7.0, 1.5)		1.62 *dd* (7.0, 1.5)			1.58 *dd* (7.5, 1.5)
1′,1⁗,1⁗′	4.82 *d* (8.0)	4.58 *d* (8.0)	4.84 *d* (7.5)	4.58 *d* (7.5)	4.99 *d* (7.5)	4.77 *d* (7.5)
2′,2⁗,2⁗′	3.49 *dd* (8.5, 8.0)	3.27 *dd* (9.0, 8.0)	3.49 *dd* (9.0, 7.5)	3.27 *dd* (9.0, 7.5)	3.50 *dd* (9.0, 7.5)	3.29 *dd* (9.0, 7.5)
3′,3⁗,3⁗′	3.60 *t* (8.5)	3.38 *t* (9.0)	3.60 *t* (9.0)			
4′,4⁗,4⁗′	3.42 *dd* (9.5, 8.5)	3.28 *t* (9.0)	3.42 *t* (9.0)			
5′,5⁗,5⁗′	3.30–3.38 *m*	3.30–3.38 *m*	3.28–3.42 *m*	3.28–3.42 *m*	3.28–3.42 *m*	3.30–3.40 *m*
6′,6⁗,6⁗′	3.63^{a} *dd* (12.0, 5.5)	3.66^{a} *dd* (12.0, 5.5)	3.64^{c} *dd* (12.0, 6.0)	3.66^{c} *dd* (12.0, 6.0)	3.69^{c} *dd* (12.0, 5.5)	3.64 *dd* (12.0, 6.0)
	3.88^{b} *dd* (12.0, 2.5)	3.87^{b} *dd* (12.0, 2.5)	3.89^{d} *dd* (12.0, 2.0)	3.87^{d} *dd* (12.0, 2.0)	3.87^{d} *dd* (12.0, 2.0)	3.86 *dd* (12.0, 1.5)
1″	4.47 *ddd* (10.5, 9.0, 3.5)		4.46 *ddd* (12.0, 9.0, 3.0)			3.71 *t* (7.5)
	4.52 *ddd* (10.5, 5.0, 4.0)		4.54 *ddd* (12.0, 5.5, 4.0)			2.75 *br t* (7.0)
2″	2.91 *ddd* (15.0, 5.0, 3.5)		2.92 *ddd* (14.0, 5.5, 3.0)			
	3.01 *ddd* (15.0, 9.0, 4.0)		3.02 *ddd* (14.0, 9.0, 4.0)			
4″,8″	7.20 *d* (8.0)		7.21 *d* (8.0)			7.12 *d* (8.5)
5″,7″	6.92 *d* (8.0)		6.96 *d* (8.0)			6.83 *d* (8.5)
1‴	4.01 *ddd* (11.0, 6.0, 5.0)		4.03 *dt* (11.0, 5.5)			4.20^{e} *dt* (10.5, 6.5)
	4.27 *ddd* (11.0, 6.0, 4.5)		4.27 *dt* (11.0, 5.5)			4.26 *dt* (10.5, 6.5)
2‴	2.75 *br t* (5.5)		2.79 *br t* (4.5)			2.79 *br t* (6.5)
4″	6.52 *d* (2.0)		6.56 *d* (2.5)			6.79 *d* (2.0)
7‴	6.84 *d* (8.0)		7.20 *d* (8.5)			6.87 *d* (8.0)
8‴	6.76 *dd* (8.0, 2.0)		6.88 *dd* (8.5, 2.5)			6.89 *dd* (8.0, 2.0)
1⁗						4.07 *dt* (10.5, 6.5)
						4.19^{e} *dt* (10.5, 6.5)
2⁗						2.77 *br t* (6.5)
4⁗						6.665 *d* (2.0)
7⁗						6.667 *d* (8.0)
8⁗						6.53 *dd* (8.0, 2.0)

Coupling constants (in Hz) in parentheses.

$^{a–e}$ Values with the same superscript are interchangeable.

Table 2. ^{13}C NMR spectral data of compounds **3**–**5**, **8** and **9** in CD_3OD

C	**3**		**4**			C	**5**			**8**		**9**
1	95.1		95.2			1	95.2					95.2
3	155.3		155.3			3	155.1					155.1
4	109.8		109.8			4	109.6					109.4
5	31.4		31.4			5	31.9					31.8
6	40.9		40.9			6	41.4					41.2
7	172.6		172.5			7	173.2					173.2
8	125.1		125.2			8	124.9					124.9
9	130.0		130.0			9	130.5					130.5
10	13.7		13.7			10	13.6					13.5
11	167.9		167.9			11	168.1					168.7
1′,1′′′′,1′′′′′	100.5	105.3	100.6	105.3	103.0	1′	100.9					100.9
2′,2′′′′,2′′′′′	74.2	75.6	74.2	75.6	74.9	2′	74.8					74.7
3′,3′′′′,3′′′′′	87.6	78.2^{a}	87.6	78.2^{c}	78.3^{c}	3′	78.0					77.9
4′,4′′′′,4′′′′′	69.9	71.6	70.0	71.6^{d}	71.4^{d}	4′	71.5					71.4
5′,5′′′′,5′′′′′	77.9^{a}	78.1^{a}	77.9^{c}	78.1^{c}	78.0^{c}	5′	78.5					78.4
6′,6′′′′,6′′′′′	62.6^{b}	62.7^{b}	62.5^{e}	62.6^{e}	62.6^{e}	6′	62.8					62.7
1″,1‴	66.0	66.4	66.0	66.1		1″,1‴,1′′′′	64.4	66.4	66.7	64.4	64.4	66.9
2″,2‴	35.9	34.8	35.9	34.9		2″,2‴,2′′′′	39.5	35.2	35.6	39.5	39.4	35.4
3″,3‴	135.5	132.2	136.0	135.6		3″,3‴,3′′′′	134.5	131.0	131.5	134.5	132.4	130.7
4″,4‴	131.6	120.1	131.7	120.3		4″,4‴,4′′′′	131.1	122.6	117.0^{f}	131.1	122.3	117.1
5″,5‴	120.9	147.0	121.4	151.0		5″,5‴,5′′′′	118.2	145.1	146.3	118.3	145.1	146.2
6″,6‴	157.5	147.7	157.0	147.9		6″,6‴,6′′′′	157.9	148.8	145.0	158.0	148.5	144.9
7″,7‴	120.9	117.7	121.4	119.2		7″,7‴,7′′′′	118.2	118.2	116.4^{f}	118.3	118.0	116.4
8″,8‴	131.6	125.0	131.7	124.8		8″,8‴,8′′′′	131.1	126.4	121.3	131.1	126.3	121.3
						OMe	—					51.9

[a–f] Values with the same superscript are interchangeable.

6.68, and an ABX_2 system of a OCH_2CH_2Ar moiety at δ 3.72, 3.97, and 2.80] groups. These findings, together with UV maxima at 221, 232, 291.5, 302 (sh), and 332.5 nm and IR absorptions at 3419, 1732, 1699, 1630, 1609 and 1522 cm^{-1}, implied that compound **6** was an ester of oleoside 11-methyl ester (**10**) with desrhamnosylacteoside (**11**) or 2-(3,4-dihydroxyphenyl)ethyl-(6-*O*-caffeoyl)-*β*-D-glucopyranoside (**12**), both of which had previously been isolated from this plant material [2]. Comparison of the ^{13}C NMR (Table 3) data of **6** with those of **11**, **12** and 2-(3,4-dihydroxyphenyl)ethyl-*β*-D-glucopyranoside (**13**) [4] demonstrated that the hydroxyl groups at C-4′ and C-6′ in the central glucose were acylated in the structure of **6**. The HMBC spectrum of **6** revealed a correlation of C-7‴ (δ 172.8) with H-6′ (δ 4.18), suggesting that the C-7‴ carboxyl group of the oleoside 11-methyl ester unit was esterified with the 6′-hydroxyl group of the desrhamnosylacteoside unit. Based on these data, compound **6** was characterized as a desrhamnosyl derivative of oleoacteoside [5] and designated as desrhamnosyloleoacteoside.

EXPERIMENTAL

^1H (500 MHz) and ^{13}C (125 MHz) NMR: TMS as int. standard. SIMS: glycerol or 3-nitrobenzyl alcohol as matrix.

Plant material

The plant material used was published previously [2].

Isolation of glucosides

Solvent extraction was carried out as reported previously [2]. The rest (48 g) of the *n*-BuOH extract was chromatographed on a Wakogel LP-40C_{18} (Wako Pure Chemical Industries, Ltd., Osaka, Japan) column with MeOH-H_2O of increasing MeOH content. The following fractions were further purified by chromatography on a Wakogel LP-40C_{18} column or by prep HPLC (μBondasphere 5μ C18-100 Å, MeOH-H_2O, 2 : 3, 9 : 11 or 13 : 12). The 30% MeOH fr. yielded quercitrin (9.3 mg) and insularoside-6‴-*O*-*β*-D-glucoside (**2**) (11.0 mg); the 38% MeOH fr. yielded quercitrin (99.8 mg), kaempferol 3-*O*-α-L-rhamnopyranoside (12.4 mg), **2** (339 mg), ligstroside (2.5 mg), insularoside -3′, 6‴-di-*O*-*β*-D-glucoside (**4**) (8.8 mg), and desrhamnosyloleoacteoside (**6**) (6.7 mg); the 50% MeOH fr.: insularoside (**1**) (370 mg), insularoside-3′-*O*-*β*-D-glucoside (**3**) (16.0 mg), and insuloside (**5**) (7.5 mg).

Insularoside-3′-O-*β*-D-*glucoside* (**3**)

Colourless amorphous powder, $[\alpha]_D^{23} -84°$ (*c* 0.18, MeOH); UV λ_{max}^{MeOH} nm (log ε): 231 sh (4.33), 272.5

Table 3. ^{13}C NMR spectral data of compounds **6**, **11**, **12** and **13** in CD_3OD

C	**6**	**11**	**12**	**13***
1	131.5	131.6	131.5	131.6
2	116.4[a]	116.6[c]	116.6[f]	116.4
3	146.2	146.2[d]	146.2[g]	146.1
4	144.7	144.8	144.7	144.6
5	117.2	117.2	117.1	117.2
6	121.3	121.3	121.3	121.3
α	72.4	72.3	72.4	72.1
β	36.7	36.6	36.7	36.6
1′	104.5	104.5	104.6	104.4
2′	73.2[b]	73.3[e]	75.1[h]	75.2
3′	75.2[b]	75.9[e]	78.0	78.0
4′	72.6	72.6	71.8	71.7
5′	75.7[b]	76.2[e]	75.5[h]	78.1
6′	64.6	62.6	64.7	62.8
1″	127.8	127.8	127.7	
2″	114.8	114.8	114.9	
3″	149.8	149.8	149.7	
4″	146.9	146.9[d]	146.8[g]	
5″	116.6[a]	116.4[c]	116.4[f]	
6″	123.1	123.1	123.2	
α″	115.3	115.3	115.1	
β″	147.8	147.7	147.3	
CO	168.4	168.7	169.2	
1‴	95.4			
3‴	155.1			
4‴	109.4			
5‴	31.5			
6‴	41.3			
7‴	172.8			
8‴	125.0			
9‴	130.7			
10‴	13.7			
11‴	168.7			
OMe	52.0			
1⁗	101.0			
2⁗	74.8			
3⁗	78.0			
4⁗	71.5			
5⁗	78.4			
6⁗	62.8			

[a–h] Values with the same superscript are interchangeable.

* Data taken from Ref. [4].

(3.64), 280 sh (3.58); IR ν_{max}^{KBr} cm^{-1}: 3403, 1731, 1709, 1622, 1506, 1076; ^{1}H and ^{13}C NMR (CD_3OD): Tables 1 and 2; SIMS *m*/*z*: 789 $[M-H]^-$, 627. HR-SIMS Found: 789.2585 $[M-H]^-$; $C_{38}H_{45}O_{18}$ requires 789.2607.

Insularoside-3′,6‴-di-O-*β*-D-*glucoside* (**4**)

Colourless amorphous powder, $[\alpha]_D^{23}-72°$ (*c* 0.12, MeOH); UV λ_{max}^{MeOH} nm (log *ε*): 230 (4.29), 273 sh (3.39), 278 sh (3.31); IR ν_{max}^{KBr} cm^{-1}: 3413, 1716, 1646, 1508, 1074; ^{1}H and ^{13}C NMR (CD_3OD): Tables 1 and 2; SIMS *m*/*z*: 975 $[M+Na]^+$. HR-SIMS Found: 975.3103 $[M+Na]^+$; $C_{44}H_{56}O_{23}Na$ requires 975.3112.

Insuloside (**5**)

Colourless amorphous powder, $[\alpha]_D^{26}-111°$ (*c* 0.13, MeOH); UV λ_{max}^{MeOH} nm (log *ε*): 222 (4.42), 278 sh (3.80), 282 (3.81); IR ν_{max}^{KBr} cm^{-1}: 3409, 1705, 1628, 1506, 1076; ^{1}H and ^{13}C NMR (CD_3OD): Tables 1 and 2; SIMS *m*/*z*: 781 $[M-H]^-$, 421. HR-SIMS Found: 781.2697 $[M-H]^-$; $C_{40}H_{45}O_{16}$ requires 781.2709.

Desrhamnosyloleoacteoside (**6**)

Amorphous powder, $[\alpha]_D^{22}-94°$ (*c* 0.26, MeOH); UV λ_{max}^{MeOH} nm (log *ε*): 221 (4.34), 232 (4.29), 291.5 (4.04), 302 sh (4.03), 332.5 (4.16); IR ν_{max}^{KBr} cm^{-1}: 3419, 1732, 1699, 1630, 1609, 1522, 1076; ^{1}H NMR (CD_3OD): *δ* 1.69 (3H, *dd*, *J* = 7.0, 1.5 Hz, H_3-10‴), 2.45 (1H, *dd*, *J* = 14.5, 9.0 Hz, H-6‴), 2.71 (1H, *dd*, *J* = 14.5, 4.5 Hz, H-6‴), 2.80 (2H, *m*, H_2-*β*), 3.32 (1H, *dd*, *J* = 9.0, 8.0 Hz, H-2′), 3.65 (1H, *dd*, *J* = 12.0, 6.0 Hz, H-6⁗), 3.66 (3H, *s*, OMe), 3.72 (1H, *dt*, *J* = 11.0, 8.0 Hz, H-*α*), 3.73 (1H, *dd*, *J* = 9.0, 4.5 Hz, H-5‴), 3.87 (1H, *dd*, *J* = 12.0, 2.0 Hz, H-6⁗), 3.97 (1H, *dt*, *J* = 11.0, 7.0 Hz, H-*α*), 4.07 (1H, *dd*, *J* = 12.0, 3.0 Hz, H-6′), 4.18 (1H, *dd*, *J* = 12.0, 5.0 Hz, H-6′), 4.39 (1H, *d*, *J* = 8.0 Hz, H-1′), 4.80 (1H, *d*, *J* = 8.0 Hz, H-1⁗), 5.89 (1H, *br s*, H-1‴), 6.05 (1H, *qd*, *J* = 7.0, 1.0 Hz, H-8‴), 6.28 (1H, *d*, *J* = 16.0 Hz, H-*α*″), 6.56 (1H, *dd*, *J* = 8.0, 2.0 Hz, H-6), 6.67 (1H, *d*, *J* = 8.0 Hz, H-5), 6.68 (1H, *d*, *J* = 2.0 Hz, H-2), 6.78 (1H, *d*, *J* = 8.0 Hz, H-5″), 6.96 (1H, *dd*, *J* = 8.0, 2.0 Hz, H-6″), 7.05 (1H, *d*, *J* = 2.0 Hz, H-2″), 7.48 (1H, *s*, H-3‴), 7.59 (1H, *d*, *J* = 16.0 Hz, H-*β*″); ^{13}C NMR (CD_3OD): Table 3; SIMS *m*/*z*: 863 $[M-H]^-$, 701, 403. HR-SIMS Found: 863.2613 $[M-H]^-$; $C_{40}H_{47}O_{21}$ requires 863.2611.

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REFERENCES

1. Tanahashi, T., Shimada, A., Nagakura, N., Inoue, K., Kuwajima, H., Takaishi, K. and Chen, C.-C., *Phytochemistry*, 1993, **33**, 397.
2. Tanahashi, T., Shimada, A., Nagakura, N., Inoue, K., Kuwajima, H., Takaishi, K., Chen, C.-C., He, Z.-D. and Yang, C.-R., *Chemical and Pharmaceutical Bulletin*, 1993, **41**, 1649.
3. Tanahashi, T., Takenaka, Y. and Nagakura, N., *Phytochemistry*, 1996, **41**, 1341.
4. Shimomura, H., Sashida, Y. and Adachi, T., *Phytochemistry*, 1987, **26**, 249.
5. Kikuchi, M., Yamauchi, Y., Takahashi, Y. and Sugiyama, M., *Yakugaku Zasshi*, 1989, **109**, 366.