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FOUR SECOIRIDOID GLUCOSIDES FROM *JASMINUM MESNYI**

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Key Word Index—*Jasminum mesnyi*; Oleaceae; secoiridoid glucosides; 2″-hydroxyjasminin; isojasminin; 4″-hydroxyisojasminin; jasmosidic acid; 2D COSY; biogenesis.

Abstract—Besides the known glucosides, jasminin, jasmesoside, jasmoside, jasminin 10″-*O*-*β*-D-glucoside and syringin, four new secoiridoid glucosides, 2″-hydroxyjasminin, isojasminin, 4″-hydroxyisojasminin and jasmosidic acid were isolated from the leaves of *Jasminum mesnyi* and their structures were established.

INTRODUCTION

We previously reported the isolation of jasmoside (**2**), jasmesoside (**3**), 9″-hydroxyjasmesoside (**4**), 9″-hydroxyjasmesosidic acid (**5**) and jasminin 10″-*O*-*β*-D-glucoside (**6**) [1, 2], as well as jasminin (**1**) [3] from the leaves of *Jasminum mesnyi* Hance (=*J.* primulinum Hemsley, Japanese name, Unnan-obai). We have now reinvestigated the constituents of the leaves of this plant and isolated four new glucosides.

RESULTS AND DISCUSSION

Fractionation of the methanolic extract of the fresh leaves of *J. mesnyi* (Experimental) gave four new secoiridoid glucosides, 2″-hydroxyjasminin (**7**), isojasminin (**8**), 4″-hydroxyisojasminin (**9**) and jasmosidic acid (**10**) along with **1**–**3**, **6** and a phenolic glucoside, syringin (**11**) [4].

The glucoside **7**,* $C_{26}H_{38}O_{13}$, was obtained as a powder $[\alpha]_D^{16}$ −160.8° (MeOH). It showed a UV maximum at 238 nm (log ε 3.95), and IR bands at 3300, 1710, 1690 and 1620 cm^{-1}. Its ^1H (Table 1) and ^{13}C NMR spectra (Table 2) were superimposable on those of jasminin (**1**) except for the signals arising from its iridane moiety, where H-2″ was lacking and two *dd* signals found in **1** for H-7″ methylene protons were replaced by an AB quartet. These features together with its molecular formula indicate the presence of a hydroxy group at C-2″ of compound **7**. This was supported by the ^{13}C NMR data, which showed a C-2″ signal resonating at δ81.00 (*s*) in **7** and 52.35 (*d*) in **1**, and was further substantiated by the fact that conventional acetylation of **7** gave the pentaacetate **7a** with a hydroxy group intact. A comparison of the FAB mass spectra (Fig. 1) of **1** and **7** provided additional evidence for this proposed structure. Both compounds also showed fragment ion peaks typical for oleoside type secoiridoid glucosides at *m/z* 211 [**f**-4] and 193 [**f**-5] and, furthermore, **7** demonstrated significant peaks at 559 $[M+H]^+$, 397 [**f**-1b], 381 [**f**-2b] and 379 [**f**-3b], which were 16 mass units higher than the corresponding peaks ($[M+H]^+$ and **f-1a**~**f-3a**) of **1**. The genesis of ion fragments at *m/z* 169, 151 and 133 due to the species, **f**-6, **f**-7 and **f**-8, could be explained in terms of the gross structure **7** for this new compound.

The stereochemistry of the iridane skeleton of **7** was deduced by comparing its NMR spectral data with those of **1**. That the cyclopentane ring in **7** adopts a nearly identical conformation to that of **1** was shown by the *W*-couplings of H-1″ with H-4″*β* in the two compounds: 1.5 Hz in **1** and 1.4 Hz in **7**. The other proton coupling constants between the corresponding positions of the cyclopentane rings of **1** and **7** showed the same relative configurations at C-1″, C-3″, and C-5″. The C-8″ in **7** resonated 8.47 ppm upfield (δ34.10) from that observed for C-8″ of **1**. This upfield shift is attributed both to the substitution of the hydroxyl oxygen at the *β*-carbon and the steric interaction between H-8″ and this group. The close proximity of the hydroxyl oxygen with H-8″ was also demonstrated by the 0.44 ppm deshielding of H-8″. Similarly, the smaller but significant upfield shift (4.55 ppm) of C-4″ and downfield shift (0.16 ppm) of H-4″α could be explained by the proximity of the same oxygen to H-4″α. These results showed that the hydroxy group at C-2″ exists on the same α face as the hydroxyisopropyl group at C-3″ and the α proton at C-4″. Thus, the structure of the new glucoside is 2″-hydroxyjasminin.

Isojasminin (**8**) was obtained as a powder, $C_{26}H_{38}O_{12}$, $[\alpha]_D^{18}$ −148.2° (MeOH). Its UV, IR, NMR and FAB mass

*Part 66 in the series 'Studies on Monoterpene Glucosides and Related Natural Products'. For Part 65 see Kuwajima, H., Hayashi, N., Takaishi, K., Inoue, K. Takeda, Y. and Inouye, H. (1990) *Yakugaku Zasshi* **110**, 484.

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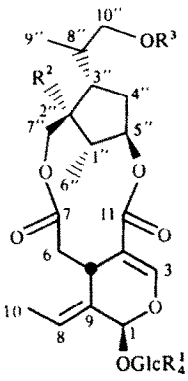
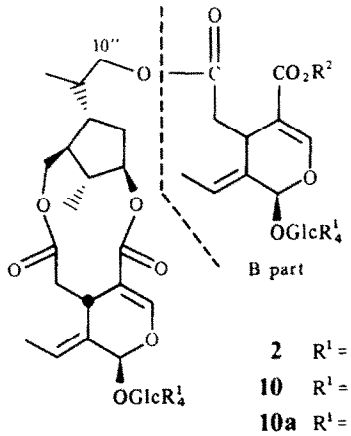
*A part of the structure elucidation of this substance was reported in a preliminary form by H. Inouye (1989) in *Iyakuhin no Kaihatsu* Vol. 2-1 (Harada, M., ed.), p. 231. Hirokawa, Tokyo.

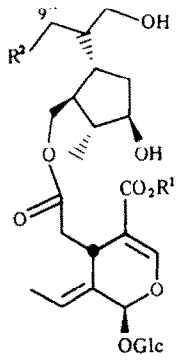


1 $R^1 = R^2 = R^3 = H$
6 $R^1 = R^2 = H, R^3 = Glc$
7 $R^1 = R^2 = H, R^2 = OH$
7a $R^1 = R^2 = Ac, R^2 = OH$

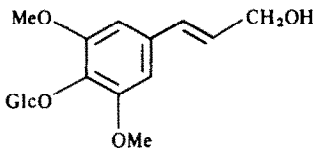


A part B part

2 $R^1 = H, R^2 = Me$
10 $R^1 = R^2 = H$
10a $R^1 = Ac, R^2 = H$



3 $R^1 = Me, R^2 = H$
4 $R^1 = Me, R^2 = OH$
5 $R^1 = H, R^2 = OH$



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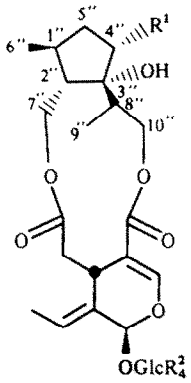
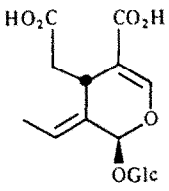
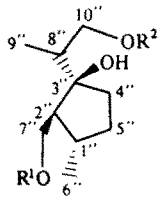


8 $R^1 = R^2 = H$
8a $R^1 = H, R^2 = Ac$
9 $R^1 = OH, R^2 = H$



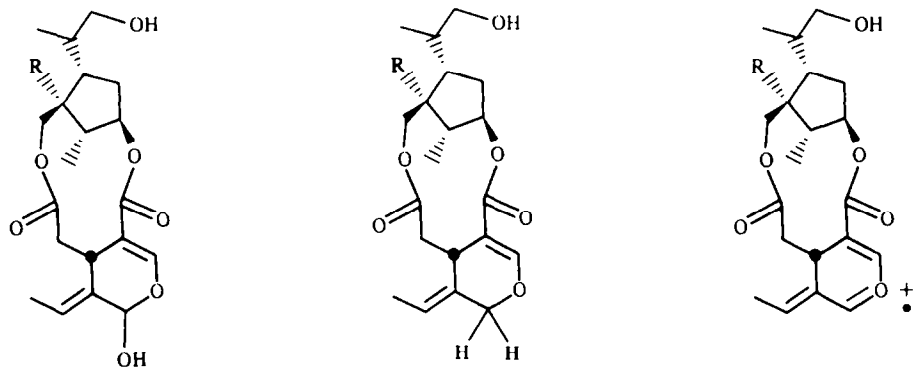
12



13 $R^1 = R^2 = H$
13a $R^1 = R^2 = Ac$

spectra were typical of those of oleoside (**12**) type glucosides. Its ^1H-^1H COSY spectrum revealed two partial structures, designated **p**-1 and **p**-2, in addition to an oleoside (**12**) moiety. Its ^{13}C NMR spectrum limited to 10 the carbon signals assignable to these two structures, i.e. two methyls, two methylene carbons, three methine carbons, two acyloxy methylene groups and one tertiary carbinol carbon. This information allowed the depiction of **p**-1 and **p**-2 as the single structure **p**-3 with a cyclopentane ring. The partial structure **p**-3 was also supported by the FAB mass spectrum of **8**, where ion species were observed at *m/z* 153 (**f**-9) and 135 (**f**-10). Hydrolysis of **8** afforded **12** and the triol **13**. A detailed ^1H NMR analysis of **13** allowed us to fit all of the signals to the proposed structure **p**-3.

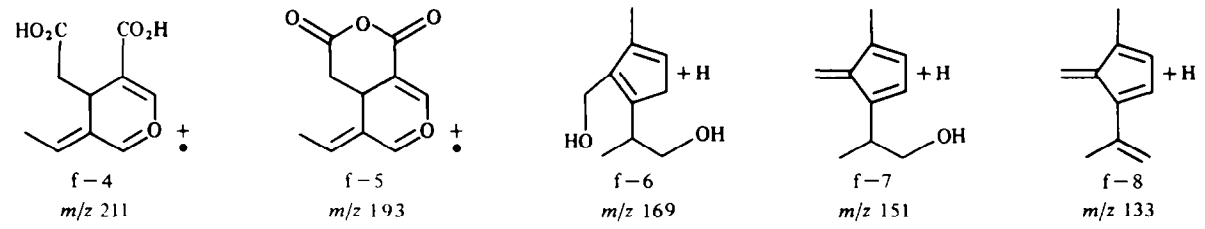
The stereochemistry of the cyclopentane ring in **13** was established by NOE experiments. NOEs were observed between H-2″, H_3-6″ (8.2%) and H_3-9″ (8.9%) and between H-1″ and H-5″α (15.5%), but not between H-1″, H-2″ and H-5″β. These findings indicated that the relative configurations of the methyl group at the C-1″, hydroxymethyl group at the C-2″ and hydroxyisopropyl group at the C-3″ positions of **13** are the same as those of jasminin (**1**), and confirmed the β disposition of the hydroxyl at C-3″. This was further supported by the NOESY spectrum of **13** as well as ^1H and ^{13}C NMR studies of its acetate **13a**. A comparison of the ^{13}C NMR spectra of **8** and **13** determined the sites of attachment of oleoside (**12**) to the triol **13**. The downfield shifts of C-7″ and C-10″ as well as upfield shifts of C-2″ and C-8″ in **8** relative to those in **13** are ascribed to the acylation effect [5], and suggest that the C-7 and C-11 carboxy groups of the oleoside **12** moiety are attached to the C-7″ and C-10″ hydroxy groups of triol **13**. This conclusion received further support from the downfield acylation shifts of H_2-7″ and H_2-10″ in the ^1H NMR spectrum of **8**. Furthermore, ester linkage of C-11 to C-10″ was corroborated by long-range selective proton decoupling (LSPD) experiments, where irradiation of H-10″ at δ3.64 caused sharpening of the carbonyl carbon signal of C-11 at δ168.48. The remaining



f−1a R=H, *m/z* 381
f−1b R=OH, *m/z* 397

f−2a R=H, *m/z* 365
f−2b R=OH, *m/z* 381

f−3a R=H, *m/z* 363
f−3b R=OH, *m/z* 379



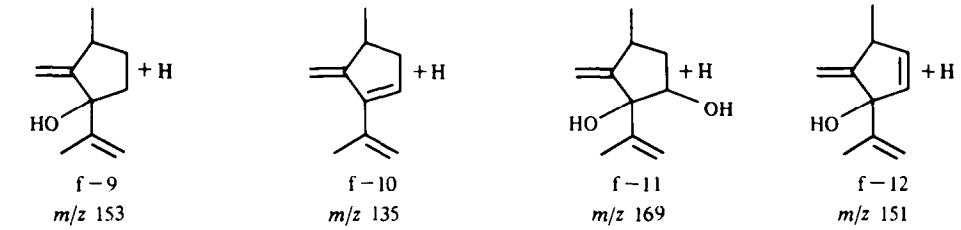
f−4 *m/z* 211

f−5 *m/z* 193

f−6 *m/z* 169

f−7 *m/z* 151

f−8 *m/z* 133



f−9 *m/z* 153

f−10 *m/z* 135

f−11 *m/z* 169

f−12 *m/z* 151

Fig. 1. FAB mass spectral fragments of glucosides **1**, **7**–**9**.

C-7 should therefore be linked to C-7″. Thus, the structure of isojasminin is represented by **8**.

The third glucoside, 4″-hydroxyisojasminin (**9**) was isolated as a powder, $C_{26}H_{38}O_{13}$, $[\alpha]_D^{14}$ −172.0° (MeOH). All spectral features of this compound were analogous to those of **8**. The differences in their spectra could be accounted for by the simple addition of a single oxygen atom to form a hydroxy group. ^1H–^1H COSY experiments allowed us to assign all ^1H resonances. Starting from H_3-6″ at δ1.11, signals for H-1″, H_2-5″ and H-4″ were assigned; the deshielding of H-4″ thereby indicated the position of the hydroxy group at C-4″. This assumption was also supported by the ^{13}C NMR of **9** which showed a downfield shift of C-4″ from δ34.69 to 73.97 as well as a downfield shift of C-5″ by 10.19 ppm and upfield shifts of C-1″, C-2″ and C-3″ by 1.83, 1.86 and 2.09 ppm, respectively, when compared with those of **8**. Moreover, the FAB mass spectrum ion peaks at *m/z* 169 (**f**-11), 151 (**f**-12) and 133 (**f**-8) also agreed with this proposed structure. The stereochemistry of the iridane moiety of **9** was deduced from NOESY experiments, where cross peaks between H-2″, H_3-6″ and H_3-9″, between H-5″β, H-5″α, H_3-6″ and H-8″, and between H-8″ and H-9″ indicated that the relative configuration of its cyclopentane ring was the same as in triol **13** apart from the stereochemistry of C-4″. The ^1H NMR spectrum of **9** displayed H-5″α at lower field than in those of **8** and **13** owing to the anisotropic effect of the hydroxy group in **9**. This observation suggested a *cis* relationship between the hydroxy group at C-4″ and H-5″α and hence an α orientation for this group. The linkages of the iridane and oleoside (**12**) moieties of **9** were determined to be the same as in **8** by ^{13}C–^1H COLOC experiments, which showed cross peaks between H-7″ and C-7, and between H_2-10″ and C-11. Thus, the glucoside **9** is characterized as 4″-hydroxyisojasminin. The co-occurrence of **7**–**9** with jasminin (**1**) in this plant allowed us to assume the absolute stereochemistry of these new glucosides is as shown.

Table 1. ^{1}H NMR data of glucosides **1**, **7**, **7a**, **8**, **8a**, **9**, **10**, **10a**, **13** and **13a**

H	**1**	**7**	**7a**	**8**	**8a**	**9**
1	5.95 *t* like *s*	5.95 *t* like *s*	5.66 *t* like *s*	5.87 *t* like *s*	5.71 *t* like *s*	5.93 *t* like *s*
3	7.46 *s*	7.45 *s*	7.46 *s*	7.51 *s*	7.49 *s*	7.51 *s*
5	4.08 *dd*	4.08 *dd*	4.01 *dd*	3.95 *dd*	3.90–3.96 *m*	4.01 *dd*
	(12.0 and 4.0)	(11.5, 3.5)	(13.0, 4.0)	(10.0, 2.5)		(10.0, 3.5)
6a	2.34 *t*	2.40 *dd*	2.28 *t*	2.37 *dd*	2.36–2.42 *m*	2.40 *dd*
	(12.0)	(13.0, 11.5)	(13.0)	(13.0, 2.5)		(12.0, 10.0)
6b	2.50 *dd*	2.50 *dd*	2.51 *dd*	2.47 *dd*	2.36–2.42 *m*	2.45 *dd*
	(2.0, 4.0)	(13.0, 3.5)	(13.0, 4.0)	(13.0, 10.0)		(12.0, 3.5)
8	6.07 *br qd*	6.06 *br qd*	5.98 *br qd*	6.05 *qd*	5.94 *br qd*	6.05 *qd*
	(7.0, 1.5)	(6.8, 1.5)	(7.0, 1.0)	(7.0, 1.0)	(7.0, 1.0)	(7.0, 1.5)
10	1.80 *dd*	1.80 *dd*	1.80 *dd*	1.84 *dd*	1.83 *dd*	1.81 *dd*
	(7.0, 1.5)	(6.8, 1.5)	(7.0, 1.5)	(7.0, 1.5)	(7.0, 1.5)	(7.0, 1.5)
1′	4.81 *d*	4.81 *d*	5.03 *d*	4.79 *d*	5.17 *d*	4.80 *d*
	(8.0)	(8.0)	(8.0)	(8.0)	(8.1)	(8.0)
2′		3.28 *dd*	5.11 *dd*	3.28 *dd*	5.00 *dd*	3.27 *dd*
		(9.0, 8.0)	(9.0, 8.0)	(9.0, 8.0)	(9.9, 8.1)	(9.0, 8.0)
3′	3.43 *t*	3.41 *t*	5.27 *t*	3.41 *t*	5.08 *dd*	3.40 *dd*
	(9.5)	(9.0)	(10.0)	(9.0)	(9.9, 9.5)	(9.0, 8.7)
4′			5.15 *t* like		5.32 *t*	
			(~10.0)		(9.5)	
5′	3.34 *ddd*	3.34 *ddd*	3.76 *ddd*			3.34 *ddd*
	(9.5, 6.0, 2.0)	(10.0, 6.0, 2.0)	(10.0, 5.0, 2.5)			(10.0, 5.5, 2.0)
6′a	3.64 *dd*	3.64 *dd*	4.30 *dd*	3.64 *dd*	4.31 *dd*	3.64 *dd*
	(11.5, 6.0)	(12.0, 6.0)	(13.0, 5.0)	(12.0, 6.0)	(12.0, 4.4)	(11.5, 5.5)
6′b	3.88 *dd*	3.89 *dd*	4.12 *dd*	3.88 *dd*	4.13 *dd*	3.90 *dd*
	(11.5, 2.0)	(12.0, 2.0)	(13.0, 2.5)	(12.0, 2.0)	(12.0, 2.2)	(11.5, 2.0)

1″	2.27 *qt*	2.37 *br qd*	2.48 *qd*	1.88–1.91 *m*		1.88–1.99 *m*
	(7.5, 1.5)	(7.7, 1.4)	(7.5, 1.0)	1.88–1.91 *m*		
2″	1.71–1.79 *m*	—	—			1.79–1.85 *m*
3″	2.46–2.53 *m*	2.67 *ddd*	2.56 *dt*	—	—	—
		(13.5, 6.5, 5.0)	(14.0, 7.0)			
4″α	1.75 *dt*	1.91 *td*	1.74 *td*	1.79 *ddd*	1.80 *ddd*	4.06 *dd*
	(13.5 and 3.5)	(13.5, 3.5)	(14.0, 3.0)	(14.5, 11.0, 6.0)	(14.3, 11.0, 5.9)	(8.4, 5.2)
4″β	1.93 *br ddd*	1.79 *m*	1.83 *ddt*	1.58 *ddd*	1.58 *ddd*	—
	(13.5, 7.5, 1.0)		(14.0, 7.0, 1.0)	(14.5, 9.0, 5.5)	(14.3, 8.5, 5.5)	
5″α	4.88 *br d*	4.93 *br d*	4.98 *d*	1.20 *m*		1.55 *dt*
	(3.5)	(3.5)	(3.0)			(13.4, 8.4)
5″β	—	—	—	1.92–1.96 *m*		1.80 *dt*
						(13.4, 5.2)
6″	1.00 *d*	0.97 *d*	1.00 *d*	1.17 *d*	1.17 *d*	1.11 *d*
	(7.5)	(7.7)	(7.5)	(6.0)	(6.9)	(6.3)
7″a	3.83 *dd*	3.71 *d*	3.74 *d*	4.03 *br d*	4.02 *br d*	3.78 *br d*
	(11.5, 3.0)	(11.0)	(11.0)	(11.5)	(11.5)	(11.0)
7″b	4.94 *dd*	4.57 *d*	4.65 *d*	covered with 10″b	4.51	4.73 *dd*
	(11.5 and 1.5)	(11.0)	(11.0)		(covered with 10″b)	(11.0, 5.5)
8″	1.61 *br quint. dt*	2.05 *m*		1.99 *quint.*		2.06 *br quint.*
	(7.0, 6.5, 3.5, 1.5)			(7.0)		(6.9)
9″	1.07 d	1.08 d	1.18 d	1.10 d	1.10 d	1.09 (*d*)
	(7.0)	(7.7)	(7.0)	(7.0)	(7.3)	(7.0)
10″a	3.43 *dd*	3.49 *dd*	3.94 *dd*	covered with 6′a	3.90–3.96 *m*	3.86 *dd*
	(10.5, 7.0)	(11.0, 7.5)	(11.0, 7.0)			(11.5, 6.0)
10″b	3.60 *dd*	3.52 *dd*	4.16 *dd*	4.53 *d*	4.53 *d*	4.55 *br d*
	(10.5, 3.5)	(11.0, 6.0)	(11.0, 5.0)	(12.0)	(11.8)	(11.5)
OAc	—	—	2.02, 2.03, 2.04	—	1.98, 2.01, 2.05	—
			2.07, 2.09 (each s)		(each s)	

Table 1. *Continued*

	10		**10a**			
H	A†	B	A	B	**13**	**13a**
1	5.95 *t* like *s*	5.83 *br s*	5.76 *t* like *s*	5.66 *t* like *s*		
3	7.47 *s*	7.33 *br s*	7.46 *s*	7.58 *s*		
5	covered with 7″a		4.14 *dd* (12.0, 4.0)	4.00 *dd* (9.0, 4.0)		
6a	2.35 *t* (12.0)	2.91 *br d* (13.0)	2.24 *t* (12.0)	2.46 *dd* (14.5, 9.0)		
6b	2.50 *dd* (12.0, 4.0)		2.51 *dd* (12.0, 4.0)	2.76 *dd* (14.5, 4.0)		
8	6.01–6.09 *m*	6.01–6.09 *m*	5.96 *br qd* (7.0, 1.0)	6.03 *br qd* (7.0, 1.0)		
10	1.80 *br dd* (7.0, 1.0)	1.74 *br d* (7.0)	1.80 *dd* (7.0, 1.5)	1.76 *dd* (7.0, 1.5)		
1′	4.80 or 4.81 *d* (8.0)	4.80 or 4.81 *d* (8.0)	5.03 or 5.05 *d* (8.5)	5.03 or 5.05 *d* (8.5)		
2′						
3′			5.27 or 5.28*t* (9.5)	5.27 or 5.28 *t* (9.5)		
4′						
5′						
6′a						
6′b						
1″	2.27 *br q* (~7.5)		2.32 *br qd* (~7.5)		2.09 *t quint* (9.7, 6.7)	
2″					1.43 *ddd* (9.4, 5.6, 2.9)	1.66 *dt* (7.0, 6.0

3″				—	—
4″α				1.99 *ddd* (13.5, 7.6, 3.6)	
4″β				1.66 *ddd* (13.4, 10.2, 7.5)	
5″α	4.88 *dr d* (3.0)	4.93 *br d* (4.0)		1.03 *dt d* (12.3, 10.0, 7.2)	
5″β				1.85 *dtd* (12.2, 7.2, 3.6)	
6″	1.01 d (7.5)	1.00 *d* (7.0)		1.01 *d* (6.6)	1.04 *d* (7.0)
7″a	4.06 *dd* (11.0, 4.0)	4.93 *br dd* (Aa or b) or (Ba or b)		3.76 *dd* (11.2, 5.7)	4.07 *dd* (11.5, 6.0)
7″b	4.92 *br d* (11.0)	(11.0, 1.0)	3.87 *dd*	3.87 *dd* (11.2, 2.9)	4.27 *dd* (11.5, 7.0)
8″				1.89 *quint. d* (7.1, 3.9)	2.07 *quint. d* (7.0, 4.5)
9″	1.09 *d* (7.0)	1.05 *d* (6.5)		0.95 *d* (7.1)	1.04 *d* (6.2)
10″a	4.15 *dd* (11.0, 4.5)			3.64 *dd* (11.0, 7.2)	3.91 *dd* (11.0, 8.0)
10″b				3.77 *dd* (11.1, 3.9)	4.24 *dd* (11.0, 4.5)
OAc	—	2.02, 2.03, 2.04 2.09 (each *s*)			2.02, 2.04 (each *s*)

The spectra of **7**–**10** were measured in methanol-d_4; **7a**, **8a**, **10a** and **13a** were measured in chloroform-*d*; **13** was measured in chloroform-*d* + D_2O.
The spectra of **8**, **9** and **13** were taken on 400 MHz; **7**, **7a**, **8a**, **10**, **10a** and **13a** were taken on 500 MHz.
Assignments of the signals of **8**, **9** and **13** were made by 2D COSY and decoupling experiments.
†A, jasminin part; B, oleosyl or methyl oleosyl part: see the formula **10**.

Table 2. ^{13}C NMR data of glucosides **1**, **7**, **8**, **9**, **13** and **13a** (in CD_3OD)

C	1	7	8	9	13	13a
1	94.96 *d*	95.11	95.31	95.40		
3	154.80 *d*	154.78	155.05	155.41		
4	109.71 *s*	110.07	110.55	110.17		
5	31.53 *d*	31.50	31.71	31.84		
6	44.00 *t*	44.20	44.73	44.32		
7	173.22 *s*	172.44	173.79	173.53		
8	123.62 *d*	123.57	123.10	123.40		
9	131.31 *s*	131.52	132.80	132.33		
10	13.16 *q*	13.09	13.08	13.04		
11	167.67 *s*	167.72	168.48	168.77		
1′	100.78 *d*	100.83	100.74	100.92		
2′	74.70 *d*	74.77	74.63	74.85		
3′	77.86 *d*	78.13	77.79	78.06		
4′	71.49 *d*	71.56	71.42	71.64		
5′	78.35 *d*	78.47	78.25	78.55		
6′	62.71 *t*	62.76	62.60	62.81		
1″	44.68 *d*	47.24[c]	37.73	35.90	36.56	38.02
2″	52.35 *d*	81.00 *s*	53.84 *d*	51.98 *d*	54.88 *d*	52.90 *d*
3″	42.11 *d*[a]	47.75[c]*	84.33 *s*	82.24 *s*	86.67 *d*	84.71 *s*
4″	36.05 *t*	31.50 *t*	34.69 *t*	73.97 *d*	37.61 *t*	36.47 *t*
5″	82.61 *d*	81.44 *d*	31.24 *t*	41.43 *t*	32.23 *t*	32.12 *t*
6″	20.72 *q*	18.15	19.45	19.48	20.23	20.47
7″	67.06 *t*[b]	65.92	63.95	64.49	62.25	65.69
8″	42.57*d*[a]	34.10	42.81	40.77	44.89	41.81
9″	15.96 *q*	14.06 *q*	14.77 *q*	13.31 *q*	13.09 *q*	13.18 *d*
10″	67.55 *t*[b]	69.16	67.22	66.49	65.52	67.81

The spectrum of glucoside **1** was measured at 125.65 MHz; the others were measured at 100.61 MHz.

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

Assignments of the signals of glucosides **1**, **7**, **13** and **13a** were made by gated decoupling mode and selective decoupling mode, and the signals of **8** and **9** were assigned on the basis of ^{13}C–^{1}H COSY spectra.

*Splitting is not clear because of the overlapping of the solvent signals.

Multiplicities are not repeated if identical for all compounds.

The fourth glucoside (**10**) was obtained as a powder. The ^{1}H and ^{13}C NMR spectra (Table 3) of this compound were similar to those of jasmoside (**2**) except for the lack of a methoxy signal, which indicated that **10** is a demethylated derivative of **2**. This was substantiated by methylation of **10** with diazomethane to **2**. Thus, the new glucoside is unequivocally assigned to jasmosidic acid (**10**).

The biosynthetic pathway of the secoiridoid glucosides in *Jasminum mesnyi* can be reasonably explained by postulating the formation of a key intermediate (**16**) from 11-methyloleoside (**14**) [6] and dihydroxyiridane **15** as shown in Fig. 2.

EXPERIMENTAL

General. Mps: uncorr. NMR: ^{1}H, 500, 400 MHz, ^{13}C, 125.65, 100.61 MHz, TMS as int. standard. TLC: silica gel GF_{254}, spots visualized by irradiation under UV light (254 nm), by exposure to I_2 vapour or by spraying with anisaldehyde–H_2SO_4 reagent followed by heating; prep. TLC: silica gel PF_{254}, bands detected under UV light or by exposure to I_2 vapour; CC: silica gel (Merck) and highly porous polymer Diaion HP-21 (Mitsubishi Kasei Co. Ltd.); medium pressure CC: silica gel PF_{254}; prep. HPLC: column dimension, 22 × 300 mm, packing, ODS YMC S-30 (Yamamura Chemical Laboratories Co. Ltd.), detect., UV 254 nm, flow rate, 7.0 ml min^{-1}.

Plant material. Leaves of *Jasminum mesnyi* were collected in October 1986 in the Herbal Garden, Faculty of Pharmaceutical Sciences, Kinki University. A voucher specimen (K. Inoue OL No. 2) was deposited in the Herbarium of the Institute of Botany, Faculty of Science, Kyoto University, Kitashirakawaoiwake-cho, Sakyo-ku, Kyoto 606, Japan.

Isolation of glucosides The fresh leaves (6.0 kg) of *J. mesnyi* were extracted with hot MeOH (30 l × 4) and the residue obtained by the removal of the solvent *in vacuo* was triturated with H_2O (5.0 l). The insoluble material was filtered off through a Celite layer, which was washed with H_2O (1.7 l). The combined filtrate and washings were concd *in vacuo* to *ca* 800 ml. The aq. soln was successively extracted with $CHCl_3$ (800 ml × 3) and *n*-BuOH (800 ml × 4). The *n*-BuOH layer was concd *in vacuo* to give a residue (494.5 g), which was chromatographed on silica gel (3.0 kg) with $CHCl_3$–MeOH. The frs were eluted with $CHCl_3$–MeOH (9:1) and (7:3) concd *in vacuo* to give residues R-1 (259.9 g) and R-2 (56.9 g), respectively. R-1 was further submitted to medium pressure CC on silica gel (3.6 kg) with $CHCl_3$–MeOH and the combined frs were eluted with $CHCl_3$–MeOH (37:3) and (9:1) to give R-1/1 (16.5 g) and R-1/2 (31.1 g). Recrystallization of R-1/1 from EtOH gave jasminin (**1**) (13.4 g). The mother liquor was submitted to prep. TLC

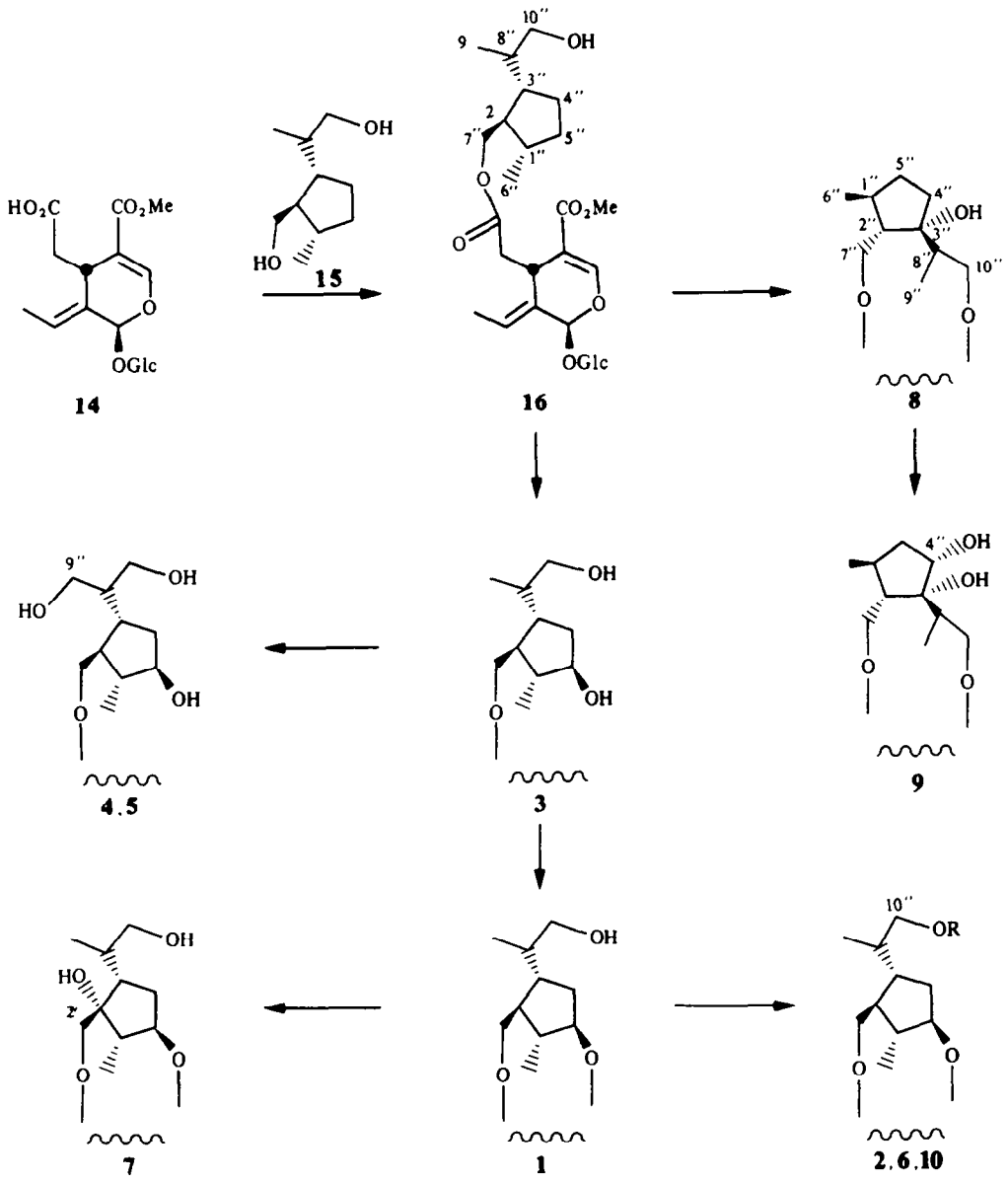


Fig. 2. Biogenesis of secoiridoid glucosides in *Jasminum mesnyi*.

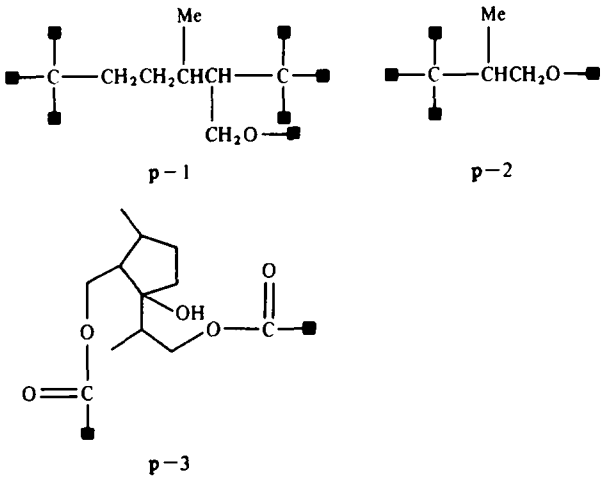


Table 3. ^{13}C NMR data of glucosides **2** and **10** (in CD_3OD)

	2		10	
C	A	B	A	B
1	94.99 *d*	95.16	94.87	95.01
3	154.85 *d*	155.14	154.85	154.85
4	109.68 *s*	109.41	109.75	109.75
5	31.62 *d*	31.97	30.77	31.65
6	44.00 *t*	41.28	44.05	41.38
7	173.24 *s*	173.24	173.29	173.68
8	123.67 *d*	124.74	123.77	124.13
9	131.31 *s*	130.77	131.52	131.28
10	13.31 *q*	13.77	13.33	13.84
11	167.67 *s*	168.57	167.72	167.72
OMe	--	52.96 *q*	—	--
1′	100.83 *d*	100.83	100.85	100.85
2′	74.75 *d*	74.75	74.80	74.80
3′	77.91 *d*	77.91	77.96	77.96
4′	71.52 *d*	71.52	71.56	71.56
5′	78.45 *d*	78.45	78.50[b]	78.42[b]
6′	62.81 *t*[a]	62.73[a]	62.83[c]	62.76[c]
1″	44.80 *d*		44.86 *d*	
2″	52.49 *d*		52.44 *d*	
3″	42.42 d		42.52 d	
4″	36.12 *t*		36.07 *t*	
5″	82.51 *d*		82.56 *d*	
6″	20.80 *q*		20.80 *q*	
7″	67.43 *t*		67.43 *t*	
8″	39.60 *d*		39.50 *d*	
9″	16.35 *q*		16.39 *q*	
10″	69.76 *t*		69.74 *t*	

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

Assignments of the signals were made by gated decoupling mode and selective decoupling mode.

A: jasminin part; B: oleosyl or methyl oleosyl part.

Multiplicities are not repeated if identical for all compounds.

(C_6H_6–EtOAc–EtOH, 2:8:1, 3 developments) to give isojasminin (**8**) (422.5 mg). An aliquot of R-1/2 (14.2 g) was chromatographed on medium pressure CC with C_6H_6–EtOAc–EtOH (2:8:1) as eluant to afford residues R-1/2/1 (4.12 g) and R-1/2/2 (5.46 g). Further purification of R-1/2/1 yielded syringin (**11**) (11.1 mg) and jasmoside (**2**) (27.1 mg). CC of R-1/2/2 followed by HPLC gave 2″-hydroxyjasmin (**7**) (20.0 mg), jasmesoside (**3**) (19.0 mg) and 4″-hydroxyisojasminin (**9**) (20.3 mg), respectively. [**7**: R_f 18 min; **3**: R_f 26 min, MeOH–H_2O (1:1) and **9**: R_f 47 min, MeOH–H_2O (9:11)]. R-2 was subjected to CC on Diaion HP-21 (1.12 l), eluting with MeOH–H_2O. Elution with 40% MeOH–H_2O gave R-2/1 (4.32 g), and 50–60% MeOH–H_2O R-2/2 (5.01 g). On further purification by a combination of CC and prep. TLC using $CHCl_3$–MeOH, the residues R-2/1 and R-2/2 gave jasminin 10″-*O*-β-D-glucoside (**6**) (102.1 mg) and jasmosidic acid (**10**) (261.6 mg), respectively.

2″-Hydroxyjasminin (**7**). $[\alpha]_D^{16}$ −160.8° (MeOH; *c* 0.77); UV λ_{max}^{MeOH} nm (log ε): 238 (3.95); IR ν_{max}^{KBr} cm^{-1}: 3300, 1710, 1690, 1620; FABMS *m/z* 559 $[M+H]^+$, 541 $[M+H-H_2O]^+$, 397, 381, 379, 211, 193, 169, 151, 133. (Found: C, 56.02; H, 6.75. $C_{26}H_{38}O_{13}$ requires: C, 55.91; H, 6.86%).

Isojasminin (**8**). $[\alpha]_D^{18}$ −148.2° (MeOH; *c* 0.99); UV λ_{max}^{MeOH} nm (log ε): 240 (4.11); IR ν_{max}^{KBr} cm^{-1}: 3350, 1710, 1690, 1620; FABMS *m/z* 543 $[M+H]^+$, 525 $[M+H-H_2O]^+$, 381, 365, 363, 345, 211, 193, 153, 135. (Found: C, 57.42; H, 7.03. $C_{26}H_{38}O_{12}$ requires: C, 57.56; H, 7.06%).

4″-Hydroxyisojasminin (**9**) $[\alpha]_D^{14}$ −172.0 (MeOH; *c* 0.50); UV λ_{max}^{MeOH} nm (log ε): 238 (3.97); IR ν_{max}^{KBr} cm^{-1}: 3500, 1720, 1700sh, 1620; FABMS *m/z* 559 $[M+H]^+$, 541 $[M+H-H_2O]^+$, 397, 381, 379, 211, 193, 169, 151, 133. (Found: C, 54.93; H, 6.80. $C_{26}H_{38}O_{13}$ requires: C, 55.02; H, 6.75%).

Jasmosidic acid (**10**). $[\alpha]_D^{16}$ −144.0° (MeOH; *c* 0.50); UV λ_{max}^{MeOH} nm (log ε): 237 (4.28); IR ν_{max}^{KBr} cm^{-1}: 3400, 1735sh, 1710, 1630; FABMS *m/z* 915 $[M+H]^+$, 897 $[M+H-H_2O]^+$, 775, 757, 735. Compound **10** (22.4 mg) was acetylated with pyridine–Ac_2O (each 0.2 ml) in the usual way and the product (23.6 mg) was purified by prep. TLC ($CHCl_3$–MeOH, 9 1, R_f 0.6) to give jasmosidic acid octaacetate (**10a**) (20.1 mg) as a powder. $[\alpha]_D^{14}$ −142.9 ($CHCl_3$; *c* 0.52). UV λ_{max}^{EtOH} (log ε): 233 (4.25); IR ν_{max}^{KBr} cm^{-1}: 3450, 1760, 1640; FABMS *m/z* 1251 $[M+H]^+$. (Found: C, 55.52; H, 5.82. $C_{58}H_{74}O_{30}$ requires: C, 55.68; H, 5.96%).

Acetylation of 2″-hydroxyjasminin (**7**). Compound **7** (16.9 mg) was acetylated with pyridine–Ac_2O (each 0.3 ml) in the usual way. The product (21.0 mg) was purified by prep. TLC (Et_2O, R_f 0.4) to give on recrystallization from EtOH–H_2O needles (11.8 mg) of 2″-hydroxyjasminin pentaacetate (**7a**). Mp 145–146°; $[\alpha]_D^{12}$ −128.6° ($CHCl_3$; *c* 0.70). UV λ_{max}^{EtOH} (log ε): 237 (4.01); IR ν_{max}^{KBr} cm^{-1}: 3450, 1740, 1700sh, 1630; FABMS *m/z* 769 $[M+H]^+$. (Found: C, 56.00; H, 6.41. $C_{36}H_{48}O_{18}$ requires: C, 56.25; H, 6.29%).

Acetylation of isojasminin (**8**). Compound **8** (51.0 mg) was acetylated with pyridine–Ac_2O (each 0.5 ml) in the usual way. The product (60.0 mg) was purified by prep. TLC ($CHCl_3$–MeOH, 97:3) to afford isojasminin tetraacetate (**8a**) as needles (54.0 mg) (from EtOH), mp 182°, $[\alpha]_D^{14}$ −116.8° ($CHCl_3$; *c* 1.01); UV λ_{max}^{MeOH} nm (log ε): 238 (4.07); IR ν_{max}^{KBr} cm^{-1}: 3450, 1750, 1730, 1710, 1620; FABMS *m/z* 711 $[M+H]^+$. (Found: C, 57.21; H, 6.49. $C_{34}H_{46}O_{16}$ requires: C, 57.46; H, 6.52%).

Alkaline hydrolysis of isojasminin (**8**). A soln of **8** (100 mg) in 0.5 M NaOH (2.5 ml) was stirred for 16 hr at room temp. and neutralized with Amberlite IR-120 B (H^+ form). The resulting residue (109.9 mg), after concn *in vacuo*, was subjected to prep. TLC ($CHCl_3$–MeOH, 6:1) to give triol (**13**) (27.7 mg) and oleoside (**12**) (30.5 mg). The latter was identified after methylation as dimethyl ester [6] (^1H NMR, IR, $[\alpha]_D$).

Triol **13**. Syrup. $[\alpha]_D^{16}$ +21.1° (MeOH; *c* 0.95); IR ν_{max}^{KBr} cm^{-1}: 3350. (HREIMS, Found: 170.1306. Calcd. for $C_{10}H_{18}O_2$ $[M-H_2O]^+$: 170.1307).

Acetylation of triol **13**. Compound **13** (17.7 mg) was acetylated with pyridine–Ac_2O (each 0.2 ml) in the usual way and the product (22.9 mg) was purified by prep. TLC ($CHCl_3$–MeOH, 97:3) to give diacetate **13a** as a syrup. $[\alpha]_D^{14}$ −2.38° ($CHCl_3$; *c* 0.88); IR ν_{max}^{KBr} cm^{-1}: 3450, 1740. (HREIMS, Found: 212.1410. Calcd for $C_{12}H_{20}O_3$ $[M-MeCO_2]^+$: 212.1412).

Methylation of jasmosidic acid (**10**). A soln of **10** (13.5 mg) in MeOH (2.0 ml) was treated with excess ethereal CH_2N_2 in the usual way. Prep. TLC (Me_2CO–$CHCl_3$–H_2O, 16:4:1, 2 developments) of the product gave a powder (6.7 mg). The substance was identical with jasmoside (**2**). (^1H NMR, IR, $[\alpha]_D$).

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