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SECOIRIDOID GLUCOSIDES FROM *JASMINUM MESNYI**

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Key Word Index—*Jasminum mesnyi*; Oleaceae; secoiridoid glucosides; 9″-hydroxyjasmesoside; 9″-hydroxyjasmesosidic acid; jasminin 10″-*O*-β-D-glucoside.

Abstract—Along with the flavonoid glucoside, rutin, three new secoiridoid glucosides, 9″-hydroxyjasmesoside, 9″-hydroxyjasmesosidic acid and jasminin 10″-*O*-β-D-glucoside have been isolated from the leaves of *Jasminum mesnyi*, and their structures have been elucidated.

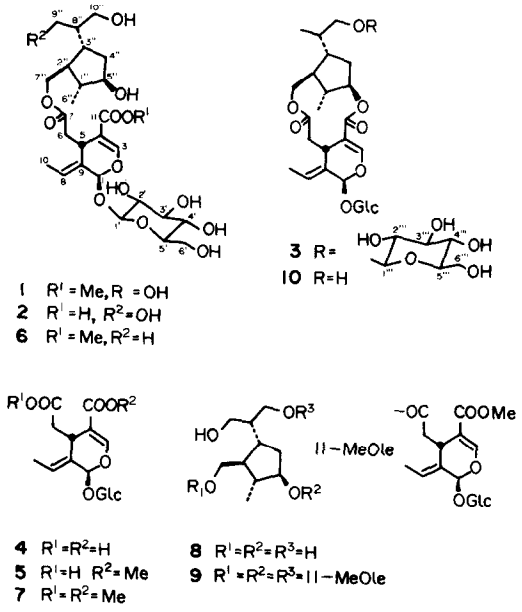
INTRODUCTION

In a previous paper [1], we reported the structure of two novel secoiridoid glucosides, jasmoside and jasmesoside which were isolated from the leaves of *Jasminum mesnyi* Hance (=*J. primulinum* Hemsley; Japanese name, Unnan-obai). In the course of further studies on the secoiridoids of the same plant, we isolated three new secoiridoid glucosides from the polar fraction of the extract. This paper deals with the structure elucidation of these glucosides.

RESULTS AND DISCUSSION

Fractionation of the methanolic extract of the leaves of *J. mesnyi* as described in the Experimental gave three new glucosides, 9″-hydroxyjasmesoside (**1**), 9″-hydroxyjasmesosidic acid (**2**) and jasminin 10″-*O*-β-D-glucoside (**3**); and the known constituent, rutin [2].

9″-Hydroxyjasmesoside (**1**) was obtained as an amorphous powder, $C_{27}H_{42}O_{14}\cdot H_2O$, $[\alpha]_D$ −164.9° (MeOH). It showed UV absorption at 237 nm (log ε 4.08) and IR bands at 3420, 1720 and 1640 cm^{-1}. Its ^1H NMR spectrum exhibited a singlet characteristic of the C-3 proton of oleoside (**4**) type secoiridoid glucosides at δ 7.53, signals for a vinyl methyl group at 1.75 (3H, *dd*, *J* = 7.1 and 1.0 Hz), an 11-carbomethoxy group at 3.72, an anomeric proton at 4.81 (1H, *d*, *J* = 7.6 Hz), an allylic acetal proton at 5.93 (1H, *br s*) and an olefinic proton at 6.12 (1H, *br q*, *J* = 7.0 Hz). These signals, together with the ^{13}C NMR spectrum (Table 1), indicated the presence of an oleoside 11-methyl ester (**5**) moiety in the molecule. Moreover, its ^1H NMR spectrum showed signals of a methyl group at δ 1.04 (*d*, *J* = 6.4 Hz) and six protons in the region δ 1.6 to 2.2 due to an iridane moiety similar to that of jasmesoside



(**6**), although only one doublet for the methyl groups in this moiety could not be observed. The FABMS spectrum of **1** showed a quasimolecular ion peak $[M+H]^+$ at *m/z* 591 indicating an increase of sixteen mass units in comparison with that of **6**. These facts strongly suggested that **1** had a structure similar to that of **6**, but with a hydroxymethyl group at C-6″ or C-9″ instead of a methyl group as in **6**. A comparison of the ^{13}C NMR spectra of **6** and **1** gave evidence that the position of this hydroxymethyl group was C-9″ since the carbon signals for C-1″, 2″, 4″, 5″, 6″ and 7″ of both glucosides appeared at nearly identical frequencies in the two spectra while the C-8″, C-3″ and C-10″ signals of **1** showed a 7.8 ppm downfield shift and 3.6 and 4.5 ppm upfield shifts, respectively. Thus, the glucoside **1** was assumed to be 9″-hydroxyjasmesoside.

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Table 1. ^{13}C NMR data of compounds **1**, **2**, **3**, **6** and **10** in CD_3OD

C	1	2	3	6	10
1	95.1 *d*	94.9 *d*	95.0 *d*	95.0 *d*	95.0 *d*
3	155.2 *d*	155.1 *d*	154.8 *d*	155.2 *d*	154.8 *d*
4	109.4 *s*	109.6 *s*	109.8 *s*	109.4 *s*	109.7 *s*
5	32.0 *d*	31.9 *d*	31.7 *d*	32.0 *d*	31.5 *d*
6	41.3 *t*	41.3 *t*	44.0 *t*	41.3 *t*	44.0 *t*
7	173.3 *s*	173.4 *s*	173.4 *s*	173.3 *s*	173.2 *s*
8	124.9 *d*	124.7 *d*	123.7 *d*	124.8 *d*	123.6 *d*
9	130.7 *s*	130.8 *s*	131.4 *s*	130.7 *s*	131.3 *s*
10	13.7 *q*	13.7 *q*	13.3 *q*	13.7 *q*	13.2 *q*
11	168.7 *s*	170.0 *s*	167.8 *s*	168.6 *s*	167.7 *s*
OMe	52.0 *q*	—	—	52.0 *q*	—
1′	100.8 *d*	100.7 *d*	100.8 *d**	100.8 *d*	100.8 *d*
2′	74.8 *d*	74.7 *d*	74.8 *d*	74.7 *d*	74.7 *d*
3′	78.0 *d*	77.9 *d*	78.0 *d*	77.9 *d*	77.9 *d*
4′	71.5 *d*	71.4 *d*	71.6 *d*	71.5 *d*	71.5 *d*
5′	78.5 *d*	78.4 *d*	78.5 *d*	78.4 *d*	78.4 *d*
6′	62.8 *t*	62.7 *t*	62.8 *t*	62.7 *t*	62.7 *t*
1″	46.7 *d*	46.6 *d*	44.9 *d*	46.8 *d*	44.7 *d*
2″	47.8 *d*	47.8 *d*	52.1 *d*	48.1 *d*	52.4 *d*
3″	38.6 *d*	38.6 *d*	42.5 *d*	42.2 *d*	42.6 *d*[a]
4″	36.9 *t*	36.8 *t*	36.0 *t*	37.8 *t*	36.1 *t*
5″	79.7 *d*	79.6 *d*	82.7 *d*	79.7 *d*	82.6 *d*
6″	18.4 *q*	18.4 *q*	20.7 *q*	18.4 *q*	20.7 *q*
7″	68.7 *t*	68.6 *t*	67.6 *t*	69.1 *t*	67.6 *t*[b]
8″	48.9 *d*	48.8 *d*	40.1 *d*	41.1 *d*	42.1 *d*[a]
9″	63.3 *t*	63.3 *t*	16.2 *q*	15.9 *q*	16.0 *q*
10″	62.0 *t*	62.0 *t*	75.2 *t*	66.5 *t*	67.1 *t*[b]

*Glucoside **3** shows additional signals due to C-1‴–C-6‴ of the glucosyl moiety at 104.4 *d*, 74.8 *d*, 78.0 *d*, 71.8 *d*, 78.2 *d* and 62.9 *t*, respectively.

[a,b] Values with the same superscript are interchangeable.

The second glucoside, 9″-hydroxyjasmesosidic acid (**2**), appeared as a colourless amorphous powder, $C_{26}H_{40}O_{14}\cdot 5/2H_2O$, $[\alpha]_D$ −161.0° (MeOH). Compound **2** showed UV absorption at 234 nm (log ε 4.01) and IR bands at 3400, 1710 and 1640 cm^{-1}. The ^1H and ^{13}C NMR spectra of this glucoside were very similar to those of **1** except for the absence of a signal due to a methoxy group. On methylation with diazomethane it gave glucoside **1**, while on alkaline hydrolysis followed by methylation, it afforded oleoside dimethyl ester (**7**) [3, 4], and tetraol which was identical with **8**, a compound which was derived from sambacoside A (**9**), a constituent recently isolated from the leaves of *Jasminum sambac* (L.) Ait. [3]. Thus, the stereostructures of glucosides **1** and **2** were established as shown.

The third glucoside (**3**) was obtained as colourless needles, mp 153–154°, $C_{32}H_{48}O_{17}\cdot 5/2H_2O$, $[\alpha]_D$ −236.7° (pyridine). This glucoside exhibited UV absorption at 238 nm (log ε 4.05) and IR bands at 3420, 1735, 1710 and 1635 cm^{-1}. The ^1H NMR spectrum of **3** showed a signal due to an anomeric proton at δ 4.27 (1H, *d*, *J* = 7.6 Hz) in addition to signals attributable to jasminin (**10**) [5] while the ^{13}C NMR spectrum showed, besides these signals, resonances relevant to a glucose moiety. The glucoside linkage on C-10″ of the jasminin (**10**) moiety was verified by glycosidation shift (+8.1) observed for the signal of this carbon (Table 1). Finally, enzymatic hydrolysis of **3** by β-D-glucosidase have jasminin (**10**). Thus, compound **3** was characterized as jasminin 10″-*O*-β-D-glucoside.

EXPERIMENTAL

Mps: uncorr. NMR: ^1H, 200 MHz, ^{13}C, 50.10 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 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-20 (Mitsubishi Kasei). DCCC: Pyrex glass tubes (120 cm × 2.4 mm) connected by Teflon tubing (140 cm × 1.35 mm), carried out by the ascending method with *n*-BuOH–EtOH–H_2O (4:1:1).

Plant material. Leaves of *J. mesnyi* Hance grown in the Botanical Garden of Osaka City University, Kisaichi, Osaka were collected in September and October 1984. A voucher specimen (H. Inouye No. 4) is deposited in the Herbarium of the Institute of Botany, Faculty of Science, Kyoto University, Kitashirakawaoiwake-cho, Sakyo-ku, Kyoto 606, Japan.

Isolation of glucosides. Fresh leaves (2.78 kg) of the plant were extracted with hot MeOH (7 l × 4). After concn of the combined extracts *in vacuo*, H_2O (1 l) was added and the insoluble material was filtered off through a Celite layer, which was washed with H_2O (0.3 l × 3). The combined filtrate and washings were successively extracted with AcOEt (1 l × 3) and *n*-BuOH (1 l × 3). The residue obtained through concn *in vacuo* of the EtOAc layer was crystallized from EtOH to afford crude jasminin (**10**) (4.92 g). The mother liquor and the *n*-BuOH layer were combined and concd to give a viscous residue (93.4 g), which was chromatographed on a silica gel column (1.8 kg), eluting with $CHCl_3$–MeOH of increasing MeOH content. Combined fractions eluted with $CHCl_3$–MeOH (4:1) and MeOH were concd *in vacuo* to afford residues R-1 (2.12 g) and R-2 (24.01 g), respectively. R-1 was purified by silica gel CC (EtOAc–C_6H_6–EtOH, 16:4:5) and prep. TLC (1st Me_2CO–$CHCl_3$ H_2O, 16:4:1; 2nd $CHCl_3$–MeOH, 7:3) giving 9″-hydroxyjasmesoside (**1**) (81.0 mg). R-2 was chromatographed on a Diaion HP-20 (155 g) column, eluting with H_2O–MeOH of increasing MeOH content (Chrom. 1). Eluate with H_2O yielded pale yellow crystals (3.29 g) of rutin. The residue (6.89 g) obtained through the evaporation of the mother liquor was subjected to DCCC followed by CC on silica gel (EtOAc–C_6H_6–EtOH, 4:1:1) to give 9″-hydroxyjasmesosidic acid (**2**) (856.2 mg) as a white powder. Eluates of Chrom. 1 with 5%, 10%, 20%, 30% and 40% MeOH–H_2O were combined and concd *in vacuo*. On successive purification of the residue (7.55 g) through DCCC, silica gel CC (EtOAc–EtOH, 17:3) and recrystallization from EtOH jasminin 10″-*O*-β-D-glucoside (**3**) (349.9 mg) was obtained as colourless needles.

9″-Hydroxyjasmesoside (**1**). $[\alpha]_D^{22}$ −164.9° (MeOH; *c* 0.49). UV λ_{max}^{MeOH} nm (log ε): 237 (4.08). IR ν_{max}^{KBr} cm^{-1}: 3420, 1720, 1640. ^1H NMR (CD_3OD): δ 1.04 (3H, *d*, *J* = 6.4 Hz, 6″-H_3), 1.75 (3H, *dd*, *J* = 7.1 and 1.0 Hz, 10-H_3), 2.48 (1H, *dd*, *J* = 14.2 and 9.0 Hz, 6-Ha), 2.74 (1H, *dd*, *J* = 14.2 and 4.4 Hz, 6-Hb), 3.72 (3H, *s*, COOMe), 3.58 (1H, *dd*, *J* = 11.0 and 6.4 Hz, 7″-Ha), 4.01 (1H, *dd*, *J* = 9.0 and 4.2 Hz, 5-H), 4.20 (1H, *dd*, *J* = 10.7 and 4.6 Hz, 7″-Hb), 4.81 (1H, *d*, *J* = 7.6 Hz, 1′-H), 5.93 (1H, *br s*, 1-H), 6.12 (1H, *brq*, *J* = 7.0 Hz, 8-H), 7.53 (1H, *s*, 3-H). FABMS *m/z*: 591 $[M+H]^+$. (Found: C, 53.29; H, 7.12. $C_{27}H_{42}O_{14}\cdot H_2O$ requires: C, 53.28; H, 7.29%).

9″-Hydroxyjasmesosidic acid (**2**). $[\alpha]_D^{21}$ −161.0° (MeOH; *c* 0.65). UV λ_{max}^{MeOH} nm (log ε): 234 (4.01). IR ν_{max}^{KBr} cm^{-1}: 3400, 1710,

1640. ^{1}H NMR (CD_3OD): δ 1.03 (3H, *d*, J = 5.9 Hz, 6″-H_3), 1.76 (3H, *br d*, J = 7.1 Hz, 10-H_3), 2.48 (1H, *dd*, J = 14.2 and 9.3 Hz, 6-Ha), 2.78 (1H, *dd*, J = 13.9 and 4.4 Hz, 6-Hb), 3.58 (1H, *dd*, J = 11.1 and 3.0 Hz, 7″-Ha), 4.00 (1H, *dd*, J = 9.3 and 4.4 Hz, 5-H), 4.19 (1H, *dd*, J = 10.5 and 4.6 Hz, 7″-Hb), 4.83 (1H, *d*, J = 7.6 Hz, 1′-H), 5.93 (1H, *br s*, 1-H), 6.11 (1H, *br q*, J = 7.0 Hz, 8-H), 7.54 (1H, *s*, 3-H). FABMS *m/z*: 577 $[M+H]^+$. (Found: C, 50.21; H, 6.98. $C_{26}H_{40}O_{14}\cdot 5/2H_2O$ requires: C, 50.24; H, 7.29%).

Jasminin 10″-*O*-β-D-*glucoside* (**3**). Mp 153–154°. $[\alpha]_D^{21}$ −236.7° (pyridine; *c* 0.49). UV λ_{max}^{MeOH} nm (log ε): 238 (4.05). IR ν_{max}^{KBr} cm^{-1}: 3420, 1735, 1710, 1635. ^{1}H NMR (CD_3OD): δ 1.00 (3H, *d*, J = 7.6 Hz, 6″-H_3), 1.10 (3H, *d*, J = 6.6 Hz, 9″-H_3), 1.83 (3H, *dd*, J = 7.1 and 1.5 Hz, 10-H_3), 2.29 (1H, *t*, J = 12.2 Hz, 6-Ha), 2.50 (1H, *dd*, J = 12.2 and 4.2 Hz, 6-Hb), 4.08 (1H, *dd*, J = 11.5 and 4.2 Hz, 5-H), 4.27 (1H, *dd*, J = 7.6 Hz, 1‴-H), 4.81 (1H, *d*, J = 7.8 Hz, 1′-H), 4.91 (1H, *dd*, J = 13.2 and 1.2 Hz, 5″-H), 5.95 (1H, *br s*, 1-H), 6.06 (1H, *brqd*, J = 7.1 and 1.0 Hz, 8-H), 7.47 (1H, *s*, 3-H). FABMS *m/z*: 705 $[M+H]^+$. (Found: C, 51.30; H, 6.90. $C_{32}H_{48}O_{17}\cdot 5/2H_2O$ requires: C, 51.26; H, 7.13%).

Methylation of 9″-*hydroxyjasmesosidic acid* (**2**). 9″-Hydroxyjasmesosidic acid (**2**) (124.9 mg) was dissolved in MeOH and methylated with ethereal CH_2N_2 in the usual way. On purification through prep. TLC ($CHCl_3$–MeOH, 7:3) the product gave a white powder (98.3 mg). This substance was identical with 9″-hydroxyjasmesoside (**1**) [^{1}H NMR, IR, $[\alpha]_D^{22}$ −172.1° (MeOH; *c* 0.96)].

Alkaline hydrolysis of 9″-*hydroxyjasmesosidic acid* (**2**). A soln of **2** (100.5 mg) in 0.5 M NaOH (3 ml) was stirred for 20 hr at room temp, neutralized with Amberlite IR-120 (H^+ form) and concd *in vacuo*. The resulting residue (108.3 mg) was methylated with CH_2N_2–Et_2O in the usual way and the product (120.0 mg) was subjected to prep. TLC ($CHCl_3$–MeOH, 7:3) to give oleoside dimethyl ester (**7**) (39.0 mg) and tetraol (**8**) (24.5 mg). The former was identified after acetylation as oleoside dimethyl ester tetraacetate [3,4] (^{1}H NMR, IR and $[\alpha]_D$). The latter was identified as compound **8** obtained from sambacoside A (**9**) [3] (^{1}H NMR, IR and $[\alpha]_D$).

Enzymatic hydrolysis of jasminin 10″-*O*-β-D-*glucoside* (**3**). β-D-Glucosidase (Sigma) (0.6 mg) was added to an acetate buffer soln (0.1 M, pH 5.0) (12 ml) of **3** (30.0 mg) and the mixture was incubated for 6 hr at 37°. The soln was chromatographed on Diaion HP-20 (3 g), eluting successively with H_2O (50 ml) and MeOH (100 ml). The residue (25.8 mg) obtained from the MeOH eluate through concn was purified by prep. TLC (C_6H_6–EtOAc–EtOH, 1:4:1) to afford the starting material (**3**) (12.9 mg) and jasminin (**10**) (9.2 mg).

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