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TWO SECOIRIDOID GLUCOSIDES FROM *JASMINUM MESNYI**

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Key Word Index—*Jasminum mesnyi*; Oleaceae; secoiridoid glucoside; jasminin; jasmoside; jasmesoside; ^{1}H NMR; ^{13}C NMR; structure elucidation.

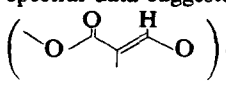
Abstract—Besides the known glucoside jasminin and an unidentified glucoside, two new secoiridoid glucosides, jasmoside and jasmesoside have been isolated from the leaves of *Jasminum mesnyi* and their structures elucidated.

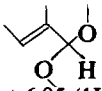
INTRODUCTION

As a part of our studies on the secoiridoid glucosides of oleaceous plants [1, and references therein], we re-investigated the constituents of the leaves of *Jasminum mesnyi* Hance (= *J. primulinum* Hemsley, Japanese name, Unnan-ōbai), which is known to contain jasminin (**1**) [2], and isolated three new secoiridoid glucosides in addition to **1**. This paper deals with the structure elucidation of two of these new glucosides.

RESULTS AND DISCUSSION

The methanolic extract of the fresh leaves of *J. mesnyi* was fractionated as described in the Experimental to give the new glucosides jasmoside (**2**) and jasmesoside (**3**) along with an unidentified glucoside and jasminin (**1**).

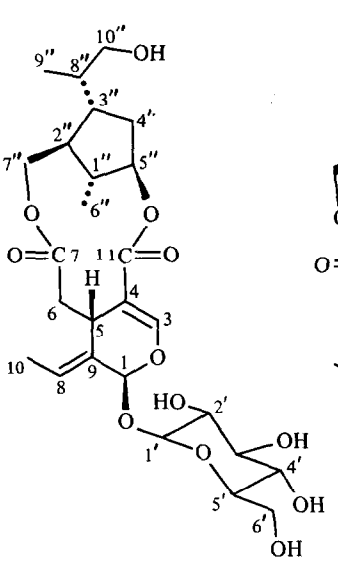
Jasmoside (**2**) was obtained as a white powder, $C_{43}H_{60}O_{22}\cdot 2H_2O$, $[\alpha]_D^{18} - 236.4°$ (MeOH). It showed a UV maximum (MeOH) at 237 nm (log ε4.36) and IR bands (KBr) at 3380, 1700 and 1630 cm^{-1}. These spectral data suggested the presence of a chromophore  characteristic of iridoid glucosides.

The ^{1}H NMR spectrum of **2** showed signals for two protons of this chromophore at δ7.47 (1H, *s*) and 7.53 (1H, *s*), two methyl groups at 1.01 (3H, *d*, J = 7.5 Hz) and 1.09 (3H, *d*, J = 7.0 Hz), two vinyl methyl groups at 1.76 (6H, *d* (*br*), J = 7.0 Hz), a carbomethoxy group at 3.71 (3H, *s*), two protons of  at 5.95 (2H, *s*, *br*) and two olefinic protons at 6.05 (1H, *q* (*br*), J = 7.0 Hz) and 6.11 (1H, *q* (*br*), J = 7.0 Hz). These ^{1}H NMR signals of jasmoside (**2**) were similar to those of jasminin (**1**). However, the signals observed at δ7.53, 6.11 and 3.71 in the spectrum of **2** were absent in that of **1**. Furthermore, the intensities of the signals at δ1.76 and 5.95 of **2** were twice as strong as those of **1**. The signals observed only in the spectrum of **2** suggested the presence of an additional oleoside methyl ester moiety in the molecule, whereas the chemical shift (3.71 ppm) of the carbomethoxy group indicated its location at 11-position.

Further evidence supporting this suggestion was obtained by comparison of the ^{13}C NMR spectrum of **1** with that of **2**, which contained signals corresponding to jasminin (**1**) and oleoside 11-methyl ester (**4**) (Table 1). The remainder of the signals of both glucosides **1** and **2** coincided except for those due to C-8″ and C-10″, which appeared in **2** at δ39.6 and 69.7, and in **1** at δ42.1 and 67.1, respectively. This difference can be explained by the esterification of the 10″-hydroxy group of **1** with the 7-carboxy group of oleoside 11-methyl ester (**4**). To corroborate this assumption, **2** was subjected to partial hydrolysis with sodium hydroxide (0.2 M), yielding jasminin (**1**) and oleoside 11-methyl ester (**4**). The acetate (**5**) of the latter was identified by comparison with the acetate of **4** obtained from oleuropein (**6**) [3] through partial hydrolysis. On the basis of these results, jasmoside was characterized as jasminyloleoside methyl ester (**2**).

The second glucoside, jasmesoside (**3**) was obtained as a white amorphous powder, $C_{27}H_{42}O_{13}\cdot H_2O$, $[\alpha]_D^{24} - 156.0°$ (MeOH). This glucoside showed UV absorption (MeOH) at 236 nm (log ε4.06) and IR bands (KBr) at 3380, 1705 and 1630 cm^{-1}. Furthermore, its ^{1}H NMR spectrum indicated along with the signal due to the characteristic chromophore of iridoids at δ7.53 (1H, *s*), signals of a vinyl methyl group at δ1.75 (3H, *dd*, J = 7.0 and 1.0 Hz), an allylic acetal proton at 5.92 (1H, *s*, *br*) and an olefinic proton at 6.12 (1H, *q* (*br*), J = 7.0 Hz). These spectral data suggested that jasmesoside (**3**) also has an oleoside (**7**) moiety in its structure. Moreover, the ^{1}H NMR spectrum of **3** showed signals of two methyl groups at δ0.96 (3H, *d*, J = 6.5 Hz) and 1.03 (3H, *d*, J = 6.0 Hz), suggesting the similarity of jasmesoside (**3**) to jasminin (**1**), which is composed of oleoside (**7**) and triol (**8**) moieties. The spectrum of **3**, however, showed the signal of a carbomethoxy group at δ3.72 (3H, *s*), which was absent in the spectrum of **1**. These findings led to an assumption that one of the two ester carbonyl groups in the oleoside moiety of **3** existed as a methyl ester and another as an ester with triol **8**. From the chemical shift of the signal due to the carbomethoxy group, it was further assumed that this group was located at the α,β-unsaturated position, i.e. the 11-position. On the other

*Part 53 in the series "Studies on Monoterpene Glucosides and Related Natural Products". For Part 52 see Uesato, S., Matsuda, S. and Inouye, H. (1984) *Yakugaku Zasshi* **104**, 1232.



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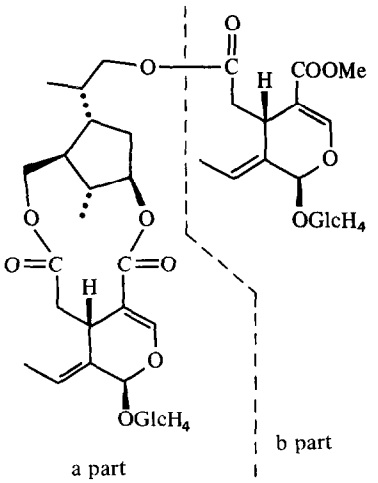

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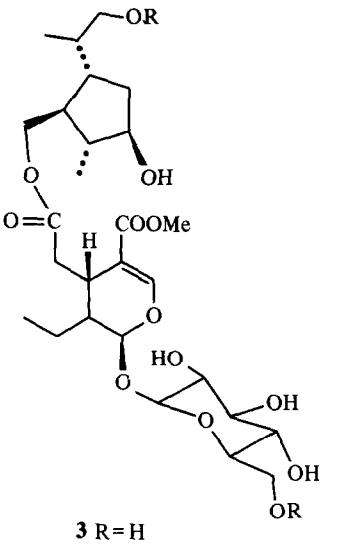
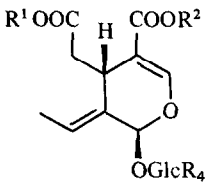
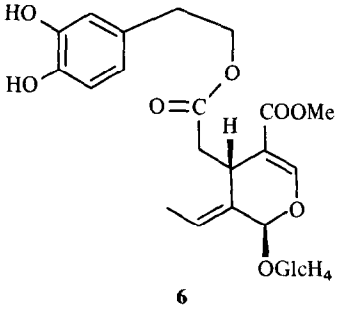


3 R = H
13 R = trityl



4 R = R¹ = H, R² = Me
5 R = Ac, R¹ = H, R² = Me
7 R = R¹ = R² = H
14 R = Ac, R¹ = R² = Me



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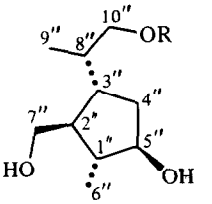
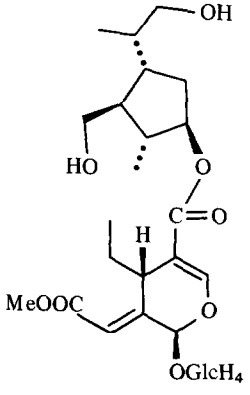


8 R = H
12 R = trityl



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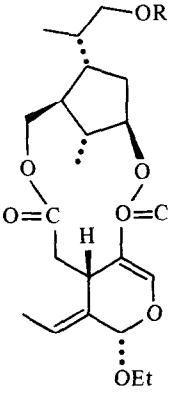


10 R = H
11 R = trityl

hand, the ^{13}C NMR signals due to the oleoside 11-methyl ester moiety of jasmesoside (3) also coincided with those ascribable to the same part of jasmoside (2). However, the location of the esterified hydroxy group of the triol (8) moiety could not be assigned from the spectral data so far obtained. To solve this problem, the ^{13}C NMR signals of the triol 8 assigned by the selective decoupling method were first compared with those of the ester 9, which was obtained from jasminin (1) through partial hydrolysis using sodium hydroxide (0.5 M) followed by methylation with diazomethane (Table 1). Due to esterification of the 5″-hydroxy group, the spectrum of 9 showed lower field

Table 1. ^{13}C NMR chemical shifts of the compounds **1**, **2**, **3**, **8** and **9** in CD_3OD*

Comp. C atom	1†	2‡ a	2‡ b	3	8	9
1	94.9 *d*	95.0 *d*	95.1 *d*	95.0 *d*		95.5 *d*
3	154.8 *d*	154.9 *d*	155.1 *d*	155.2 *d*		155.2 *d*
4	109.7 *s*	109.6 *s*	109.4 *s*	109.4 *s*		110.1 *s*
5	31.6 *d*	31.6 *d*	31.9 *d*	32.0 *d*		31.9 *d*
6	44.0 *t*	44.0 *t*	41.3 *t*	41.3 *t*		41.2 *t*
7	173.3 *s*	173.2 *s*	173.2 *s*	173.3 *s*		173.8 *s*
8	123.7 *d*	123.6 *d*	124.7 *d*	124.8 *d*		125.0 *d*
9	131.3 *s*	131.3 *s*	130.7 *s*	130.7 *s*		130.9 *s*
10	13.2 *q*	13.3 *q*	13.8 *q*	13.7 *q*		13.6 *q*
11	167.8 *s*	167.6 *s*	168.5 *s*	168.6 *s*		168.2 *s*
OMe	—	—	52.5 *q*	52.0 *q*		52.3 *q*
1″	44.8 *d*	44.8 *d*		46.8 *d*	46.5 *d*	44.1 *d*
2″	52.4 *d*	52.0 *d*		48.1 *d*	51.2 *d*	51.5 *d*
3″	42.7 *d*^{x}	42.4 *d*		42.2 *d*	41.7 *d*	42.9 *d*
4″	36.1 *t*	36.1 *t*		37.8 *t*	38.4 *t*	35.8 *t*
5″	82.7 *d*	82.5 *d*		79.7 *d*	79.9 *d*	83.3 *d*
6″	20.8 *q*	20.8 *q*		18.4 *q*	18.7 *q*	19.1 *q*
7″	67.6 *t*^{y}	67.4 *t*		69.1 *t*	66.4 *t*	66.3 *t*
8″	42.1 *d*^{x}	39.6 *d*		41.1 *d*	41.3 *d*	40.9 *d*
9″	16.0 *q*	16.4 *q*		15.9 *q*	15.7 *q*	15.8 *q*
10″	67.1 *t*^{y}	69.7 *t*		66.5 *t*	66.7 *t*	66.7 *t*

*The glucosides **1**, **2**, **3** and **9** show signals of C-1′ to C-6′ of glucose moiety at 100.8 (*d*), 74.7 (*d*), 78.4 (*d*), 71.5 (*d*), 77.9 (*d*) and 62.7 (*t*) or closed to them, respectively.

†Values with the same superscript are interchangeable.

‡a, jasminin part; b, methyl oleosidate part: see the formula **2**.

shift of the signal of C-5″ and upper field shift of the signals of C-1″ and C-4″ in comparison to the corresponding signals of **8**. In the same manner, the spectrum of jasmesoside (**3**) showed lower field shift of the signal of C-7″ and upper field shift of C-2″ as compared to the signals of **8**. These findings can only be explained by the esterification of the 7″-hydroxy group of the triol **8** with the carboxy group of oleoside methyl ester (**4**). This was also verified in the following chemical way: jasminogenin ethyl ether (**10**) [2] was converted to the trityl ether **11** and then reduced with lithium aluminium hydride to give the 10″-trityltriol (**12**). The same compound was also obtained through alkaline hydrolysis of the trityl ether of **3**, demonstrating the free primary hydroxy group at the 10″-position in the triol (**8**) part. Moreover, alkaline hydrolysis of jasmesoside (**3**) followed by acetylation and methylation afforded oleoside dimethyl ester tetraacetate (**14**). The structure of jasmesoside was therefore established as **3**.

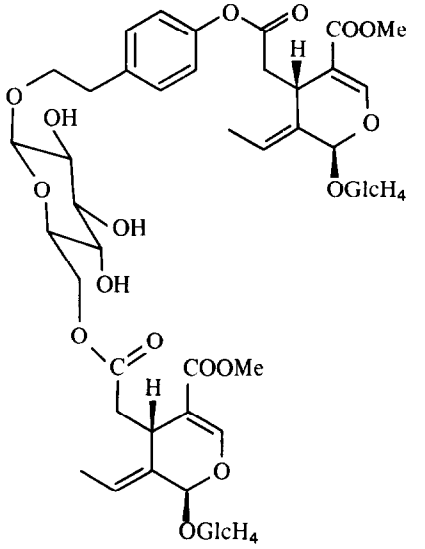
As glucosides consisting of two oleoside units like jasmoside (**2**), Gl 3 (**15**) and Gl 5 (**16**) have already been isolated from a member of the Oleaceae, *Fraxinus americana* [4], the occurrence of these glucosides seems to suggest that, on the biosynthetic pathway of these glucosides from secologanin (**17**), the esterification of the 7-carboxy group occurs after the formation of the ethylidene group. Furthermore, the occurrence of jasmesoside (**3**) suggests the possibility that jasminin (**1**) is formed through transesterification at the 11-position after the formation of **3** through esterification at C-7 of oleoside methyl ester (**4**).

EXPERIMENTAL

General procedures. Mps: uncorr; NMR: ^1H, 100 or 200 MHz, ^{13}C 50.31 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; CC: silica gel AR-100 (Mallinckrodt): medium pressure CC: silica gel PF_{254}.

Plant material. Jasminum mesnyi Hance was collected at the Botanical Garden of Osaka City University in September and October. A voucher specimen (H. Inouye No. 4) is deposited in the Herbarium of the Institute of Botany, Faculty of Science, Kyoto University, Kitashirakawa-oiwake-cho, Sakyo-ku, Kyoto 606, Japan.

Isolation of glucosides. Fresh leaves (1.18 kg) of *J. mesnyi* were cut into small pieces and extracted with hot MeOH (3 l × 3). After concentration of the combined extracts *in vacuo*, H_2O (0.5 l) was added and the insoluble material was filtered off through a Celite layer, which was washed with H_2O (0.2 l × 3). The combined filtrate and washings were concentrated *in vacuo* to 0.5 l. The resulting soln was successively extracted with $CHCl_3$ (0.3 l × 2) and *n*-BuOH (0.5 l × 3). The *n*-BuOH layer was concentrated *in vacuo* to give a viscous residue (134.08 g), which was chromatographed on a silica gel column (1.8 kg), eluting with $CHCl_3$–MeOH of increasing MeOH content. Combined frac-



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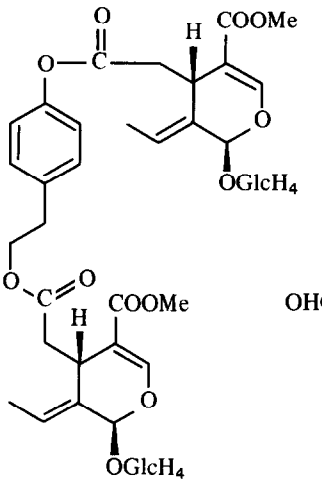

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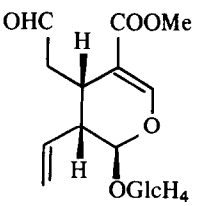

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tions eluted with $CHCl_3$–MeOH (23:2 and 9:1) were concentrated *in vacuo* to afford a residue (R-1, 53.83 g). Likewise, eluates with $CHCl_3$–MeOH (9:1, 22:3 and 17:3) and $CHCl_3$–MeOH (17:3 and 4:1) gave on concentration *in vacuo* residues R-2 (7.76 g) and R-3 (23.91 g), respectively. R-1 gave jasminin (**1**) (27.19 g) on repeated recrystallization from EtOH. The mother liquor gave more **1** (13.56 g) on medium pressure CC. R-2 gave jasminin (**1**) (2.58 g) and a fraction containing jasmesoside (**3**) and an unidentified glucoside on medium pressure CC. The latter fraction was subjected to prep. TLC (EtOAc–C_6H_6–EtOH, 4:1:1). Of the two major bands, the more mobile one gave the unidentified glucoside* (267.1 mg) as a white powder. The less mobile band afforded jasmesoside (**3**) (491.2 mg) as a white powder. R-3 was purified by medium pressure CC and prep. TLC (EtOAc–C_6H_6–EtOH, 4:1:1) giving rise to jasmoside (**2**) (1.43 g) as a white powder.

Jasmoside (**2**). $[\alpha]_D^{18}$ −236.4° (MeOH, *c* 0.85); UV λ_{max}^{MeOH} nm (log ε): 237 (4.36); IR ν_{max}^{KBr} cm^{-1}: 3380, 1700, 1630; ^1H NMR (CD_3OD): δ1.01 (3H, *d*, *J* = 7.5 Hz, H_3-6″ or H_3-9″), 1.09 (3H, *d*, *J* = 7.0 Hz, H_3-9″ or H_3-6″), 1.76 (6H, *d* (*br*), *J* = 7.0 Hz, H_3-10a and H_3-10b)†, 3.71 (3H, *s*, COOMe), 5.95 (2H, *s* (*br*), H-1a and H-1b), 6.05 (1H, *q* (*br*), *J* = 7.0 Hz, H-8a), 6.11 (1H, *q* (*br*), *J* = 7.0 Hz, H-8b), 7.47 (1H, *s*, H-3a), 7.53 (1H, *s*, H-3b). (Found: C, 53.50; H, 6.64; $C_{43}H_{60}O_{22}\cdot 2H_2O$ requires: C, 53.52; H, 6.69%.)

Jasmesoside (**3**). $[\alpha]_D^{24}$ −156.0° (MeOH, *c* 0.73); UV λ_{max}^{MeOH} nm (log ε): 236 (4.06); IR ν_{max}^{KBr} cm^{-1}: 3380, 1705, 1630; ^1H NMR (CD_3OD): δ0.96 (3H, *d*, *J* = 6.5 Hz, H_3-6″ or H_3-9″), 1.03 (3H, *d*, *J* = 6.0 Hz, H_3-9″ or H_3-6″), 1.75 (3H, *dd*, *J* = 7.0 and 1.0 Hz, H_3-10), 2.46 (1H, *dd*, *J* = 14.0 and 8.8 Hz, H-6), 2.70 (1H, *dd*, *J* = 14.0 and 5.0 Hz, H-6), 3.72 (3H, *s*, COOMe), 5.92 (1H, *s* (*br*), H-1), 6.12 (1H, *q* (*br*), *J* = 7.0 Hz, H-8), 7.53 (1H, *s*, H-3). (Found: C, 54.87; H, 7.45. $C_{27}H_{42}O_{13}\cdot H_2O$ requires: C, 54.72; H, 7.48%.)

Partial hydrolysis of jasmoside (**2**). A soln of **2** (80.3 mg) in 0.2 M NaOH (2 ml) was stirred for 6 hr at room temp. After acidifying with Amberlite IR-120 (H^+ form), the soln was concentrated *in vacuo* to give a residue (74.3 mg), which was subjected to prep. TLC ($CHCl_3$–MeOH, 7:3, 2 developments). Of the two major bands, the more mobile one afforded a crystalline residue, which was recrystallized from EtOH to give colourless needles (28.8 mg), mp 150–152°. This compound was identical with jasminin (**1**) (mmp, ^1H NMR, IR and $[\alpha]_D$). The substance obtained from the less mobile band was subjected to conventional acetylation (Ac_2O–pyridine). The acetate was purified by prep. TLC (Et_2O, 2 developments) to furnish a white powder (22.1 mg). This substance was identified as oleoside 11-methyl ester tetraacetate (**5**) (^1H NMR and IR).

Partial hydrolysis of oleuropein (**6**). A soln of **6** (80.6 mg) in 0.2 M NaOH (2 ml) was stirred for 6 hr at room temp. After acidifying the soln with 1 M HCl, the mixture was chromatographed on active charcoal (4.0 g) eluting with H_2O (100 ml) and MeOH (200 ml) successively. The MeOH eluate was concentrated *in vacuo* and the resulting residue (33.9 mg) was subjected to acetylation (Ac_2O–pyridine). The product (52.1 mg) was purified by prep. TLC (Et_2O) to furnish oleoside 11-methyl ester tetraacetate (**5**) (22.1 mg) as a white powder. $[\alpha]_D^{17}$ −165.1° ($CHCl_3$, *c* 0.28); UV λ_{max}^{MeOH} nm (log ε): 236 (4.09); IR ν_{max}^{KBr} cm^{-1}: 3230, 1755, 1705, 1630; ^1H NMR ($CDCl_3$): δ1.76 (3H, *d*, *J* = 7.0 Hz, H_3-10), 2.03, 2.08 (each *s*, 4 × OCOMe), 3.72 (3H, *s*, COOMe), 5.68 (1H, *s* (*br*), H-1), 6.03 (1H, *q* (*br*), *J* = 7.0 Hz, H-8), 7.43 (1H, *s*, H-3), 9.05 (1H, *m*, $W_{1/2}$ = 14.0 Hz, COOH, disappeared on addition of D_2O). (Found: C, 52.40; H, 5.72. $C_{25}H_{32}O_{15}$ requires: C, 52.45; H, 5.63%.)

Hydrolysis of jasminin (**1**). A soln of **1** (404.2 mg) in 0.5 M NaOH (10 ml) was stirred for 18 hr at room temp. After acidification with Amberlite IR-120 (H^+ form), the soln was concentrated *in vacuo*. The resulting residue (447.3 mg) was purified by prep. TLC ($CHCl_3$–MeOH, 3:1), giving triol **8** (114.2 mg) as a colourless syrup. ^1H NMR (C_5D_5N): δ1.13 (3H, *d*, *J* = 6.6 Hz, H_3-9″), 1.19 (3H, *d*, *J* = 6.8 Hz, H_3-6″), 1.80 (1H, *quintet*, *J* = 6.5 Hz, H-2″), 1.86–2.24 (4H, *m*, H-1″, H_2-4″ and H-8″), 2.51 (1H, *quintet*, *J* = 7.0 Hz, H-3″), 3.68 (1H, *dd*, *J* = 7.0 Hz and 10.5 Hz, H-10″), 3.91 (1H, *dd*, *J* = 5.5 and 10.5 Hz, H-10″), 3.96–4.10 (3H, *m*, H-5″ and H_2-7″); CIMS (*i*-butane) *m/z* (rel. int.):

*The details on this glucoside having a higher M_r than glucosides 1–3 will be reported later.

†a and b indicate the structural parts; see the formula **2**.

189 $[MH]^+$ (1.6), 153 $[MH-2H_2O]^+$ (100.0), 135 $[MH-3H_2O]^+$ (77.2), 123 (60.2).

Partial hydrolysis of jasminin (**1**). A soln of **1** (600.4 mg) in 0.5 M NaOH was stirred for 5 hr at room temp. After acidifying the alkaline hydrolysate with Amberlite IR-120 (H^+ form), the soln was evaporated to dryness and the residue (603.6 mg) was subjected to prep. TLC ($CHCl_3$–MeOH, 7:3). The acidic compound (166.9 mg) obtained was methylated with CH_2N_2–Et_2O and the product (169.5 mg) purified by prep. TLC ($CHCl_3$–MeOH, 3:1), giving the ester **9** (140.2 mg) as a white powder. $[\alpha]_D^{24}$ −205.3° (MeOH, *c* 0.50); UV λ_{max}^{MeOH} nm (log ε): 238 (4.10); IR ν_{max}^{KBr} cm^{-1}: 3360, 1720, 1690, 1630; ^1H NMR (CD_3OD): δ0.98 (3H, *d*, *J* = 6.8 Hz, H_3-6″ or H_3-9″), 1.05 (3H, *d*, *J* = 7.1 Hz, H_3-9″ or H_3-6″), 1.73 (3H, *dd*, *J* = 7.1 and 1.2 Hz, H_3-10), 2.45 (1H, *dd*, *J* = 14.2 and 9.5 Hz, H-6), 2.76 (1H, *dd*, *J* = 14.2 and 4.2 Hz, H-6), 3.64 (3H, *s*, COOMe), 5.92 (1H, *s* (*br*), H-1), 6.11 (1H, *dq*, *J* = 0.7 and 7.1 Hz, H-8), 7.50 (1H, *s*, H-3). (Found: C, 54.46; H, 7.24. $C_{27}H_{42}O_{13}\cdot H_2O$ requires: C, 54.72; H, 7.48%.)

Tritylation of jasminogenin O-ethyl ether (**10**). Trityl chloride (200 mg) was added to a soln of **10** (100.5 mg) in pyridine (0.5 ml). It was allowed to stand for 48 hr at room temp. After concentration of the reaction mixture, the residue was subjected to prep. TLC (C_6H_6–EtOAc, 9:1), giving rise to the trityl ether **11** (115.8 mg) as a white powder. IR ν_{max}^{KBr} cm^{-1}: 1725, 1705, 1630, 1597, 1445, 730; ^1H NMR ($CDCl_3$): δ0.87 (3H, *d*, *J* = 7.5 Hz, H_3-6″ or H_3-9″), 1.17 (3H, *t*, *J* = 6.5 Hz, $-OCH_2CH_3$), 1.22 (3H, *d*, *J* = 7.0 Hz, H_3-9″ or H_3-6″), 1.64 (3H, *d*, *J* = 6.9 Hz, H_3-10), 4.83 (1H, *dd*, *J* = 2.0 and 12.0 Hz, H-7″), 4.86 (1H, *d*, *J* = 2.5 Hz, H-5″), 5.17 (1H, *s* (*br*), H-1) 5.67 (1H, *q* (*br*), *J* = 6.8 Hz, H-8), 7.23–7.48 (16H, *m*, H-3 and arom H); FDMS *m/z* (rel. int.): 650 $[M]^+$ (16.4), 604 (12.5), 408 (15.5), 325 (6.1), 243 (100.0), 122 (5.8). (Found: C, 73.93; H, 6.99. $C_{41}H_{46}O_7\cdot H_2O$ requires: C, 73.63; H, 7.23%.)

$LiAlH_4$ *reduction of trityl ether* **11**. A soln of **11** (70.1 mg) in dry THF (1.5 ml) was added to a stirred suspension of $LiAlH_4$ (20.4 mg) in dry THF (1.5 ml) within 10 min under ice cooling. The reaction was stirred for 1 hr at room temp, diluted with H_2O and extracted with $CHCl_3$ (20 ml × 3). The H_2O washed and dried $CHCl_3$ layer was evaporated to give a residue (77.3 mg), which was subjected to prep. TLC (C_6H_6–EtOAc, 7:3), giving **12** (42.1 mg) as a white powder. $[\alpha]_D^{24}$ −9.1° ($CHCl_3$, *c* 2.28) IR ν_{max}^{KBr} cm^{-1}: 3400, 1498, 1455, 1070, 765, 750, 710; ^1H NMR ($CDCl_3$): δ0.89 (3H, *d*, *J* = 7.1 Hz, H_3-6″ or H_3-9″), 1.00 (3H, *d*, *J* = 6.8 Hz, H_3-9″ or H_3-6″), 2.07 (1H, *quintet* (*br*), *J* = 8.0 Hz, H-3″), 2.54 (2H, *m*, 2 × OH), 2.89 (1H, *dd*, *J* = 7.0 and 9.5 Hz, H-10″), 3.02 (1H, *dd*, *J* = 5.5 and 9.5 Hz, H-10″), 3.44 (1H, *dd*, *J* = 4.0 and 10.5 Hz, H-7″), 3.56 (1H, *dd*, *J* = 3.5 and 10.5 Hz, H-7″), 3.63 (1H, *m*, H-5″), 7.12–7.46 (15H, *m*, arom H); FDMS *m/z* (rel. int.): 430 $[M]^+$ (15.9), 243 (100.0), 187 (1.7). (Found: C, 78.41; H, 7.78. $C_{29}H_{34}O_3$. 2/3 H_2O requires: C, 78.70; H, 8.05%.)

Tritylation of jasmesoside (**3**). Trityl chloride (200 mg) was added to a soln of **3** (100.1 mg) in py (2 ml). The mixture was left for 72 hr at room temp, and after evaporation of the solvent *in vacuo*, the residue was subjected to prep. TLC ($CHCl_3$–MeOH, 9:1) affording trityljasmesoside (**13**) (124.3 mg) as a white powder. ^1H NMR ($CDCl_3$): δ0.82 (3H, *d*, *J* = 6.2 Hz, H_3-6″ or H_3-9″), 0.94 (3H, *d*, *J* = 7.0 Hz, H_3-9″ or H_3-6″), 1.74 (3H, *dd*, *J* = 0.7 and 7.0 Hz, H_3-10), 2.37 (1H, *dd*, *J* = 8.8 and 14.5 Hz, H-6), 2.68 (1H, *dd*, *J* = 4.4 and 14.5 Hz, H-6), 2.86 (1H, *dd*, *J* = 6.6 and 8.8 Hz, H-10″), 2.98 (1H, *dd*, *J* = 5.1 and 8.8 Hz, H-10″), 3.69 (3H, *s*, COOMe), 4.81 (1H, *d*, *J* = 7.0 Hz, H-1′), 5.80 (1H, *s* (*br*), H-1), 6.09 (1H, *q* (*br*), *J* = 7.0 Hz, H-8), 7.19–7.49 (31H, *m*, H-3 and arom H). (Found: C, 71.34; H, 6.44. $C_{65}H_{70}O_{13}\cdot 2H_2O$ requires: C, 71.28; H, 6.81%.)

Alkaline hydrolysis of trityljasmesoside (**13**). Compound **13** was dissolved in a mixture of MeOH (2 ml), dioxane (2 ml) and 1 M NaOH (0.8 ml). After stirring for 12 hr at room temp, the reaction mixture was diluted with H_2O and extracted with $CHCl_3$ (30 ml × 3). The H_2O washed and dried $CHCl_3$ layer was evaporated to dryness. Prep. TLC of the resulting residue (50.9 mg) developed with C_6H_6–EtOAc (7:3) afforded **12** (14.9 mg), which was identified by comparison with an authentic sample derived from **10** [2] (^1H NMR, IR and $[\alpha]_D$).

Hydrolysis of jasmesoside (**3**). A soln of **3** (35.5 mg) in 0.2 M NaOH (0.5 ml) was stirred for 20 hr at room temp. After acidifying, the soln was evaporated to dryness *in vacuo* and the residue was acetylated (Ac_2O–pyridine). The product (36.7 mg) on purification by prep. TLC (Et_2O), followed by methylation with CH_2N_2–Et_2O afforded a white powder (16.2 mg). This substance was identified as oleoside dimethyl ester tetraacetate (**14**) (^1H NMR, IR and $[\alpha]_D$).

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