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A SECOIRIDOID GLUCOSIDE OF *JASMINUM HUMILE* VAR. *REVOLUTUM**

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Key Word Index—*Jasminum humile* var. *revolutum*; Oleaceae; secoiridoid glucoside; jasminoside; 10-cinnamoyloxyoleoside 7-methyl ester.

Abstract—The structure of jasminoside, a new secoiridoid glucoside isolated from *Jasminum humile* var. *revolutum*, was elucidated to be 10-cinnamoyloxyoleoside 7-methyl ester.

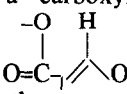
INTRODUCTION

Several plants of the family Oleaceae have been reported to contain iridoid and secoiridoid glucosides [1]. With regard to the plants of the genus *Jasminum*, no report has appeared except for the isolation and structure elucidation of jasminin (**1**) from *Jasminum primulinum* Hemsl (= *J. mesnyi* Hance, Japanese name, Unnan-obai) [2]. As a part of our studies on the monoterpene glucosides of oleaceous plants, we examined the constituents of *Jasminum humile* L. var. *revolutum* (Sims) Stokes (Japanese name, Kisokei). This paper deals with the isolation and structure elucidation of a new glucoside of the plant.

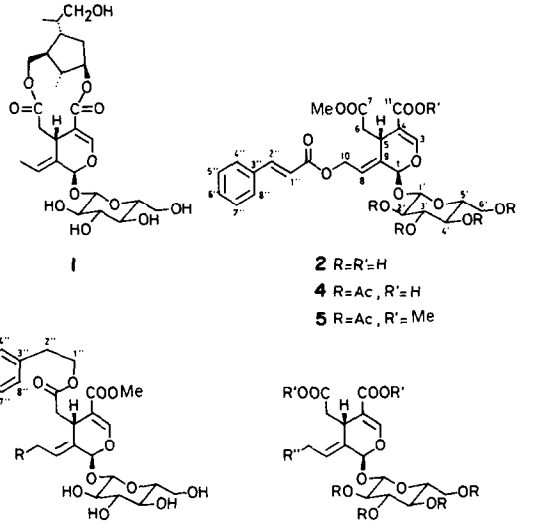
RESULTS AND DISCUSSION

An aq. extract of the fresh leaves of *J. humile* var. *revolutum* was subjected to CC as described in the Experimental to isolate a new glucoside jasminoside (**2**).

Jasminoside (**2**) was obtained as colourless needles, $C_{26}H_{30}O_{13}\cdot 3/2H_2O$, mp 116.5–118°, $[\alpha]_D$ −194.7° (MeOH). It showed UV absorptions (MeOH) at 217, 222, 233 and 276 nm (log ε 4.35, 4.35, 4.11 and 4.36) and IR bands (KBr) at 3370, 2700–2600, 2500, 1725, 1700, 1690, 1680, 1640, 1580, 1500 and 770 cm^{-1}. These spectral data suggested the presence of a cinnamoyl and a carboxyl group together with a



chromophore O=C–C=C–O– characteristic of iridoid glucosides. Furthermore, the ^{1}H NMR spectrum of **2** showed signals for a proton of the above-mentioned chromophore at δ 7.54 (1H, *s*), a carbomethoxy group at 3.64 (3H, *s*), an olefinic proton at 6.21 (1H, *br t*, J = 7.0 Hz) and an allylic acetal proton at 5.99 (1H, *br s*), besides signals at 7.22–7.66 (5H, *m*) and 6.49 and 7.69 (each *d*, J = 16.0 Hz) assignable to aromatic protons and two *trans* olefinic protons of a *trans*-cinnamoyl group. From the comparison of these ^{1}H NMR data with those of 10-acetoxyoleuropein (**3**), it was revealed that the secoiridoid glucoside moiety of **2** is very similar to that of **3**. Jasminoside (**2**) should thus be assumed to be 10-cinnamoyloxyoleoside methyl ester. This assumption was further supported by the near-coincidence of the ^{13}C NMR spectrum of 10-acetoxyoleuropein (**3**) with that of **2**, except for the signals owing to the *trans*-cinnamoyl, acetyl and phenethyl group (Table 1).



1

2 R=R'=H
4 R=Ac, R'=H
5 R=Ac, R'=Me

3 R=OAc, R'=OH
9 R=H, R'=OH
10 R=R'=H

6 R=Ac, R'=Me, R''=OAc
7 R=R'=R''=H
8 R=R'=H, R''=OH

Conventional acetylation of jasminoside (**2**) gave jasminoside tetraacetate (**4**), mp 94.5–96°, which was further methylated with diazomethane to give jasminoside methyl ester tetraacetate (**5**). In the ^{1}H NMR spectrum of **4**, a signal of the carbomethoxy

*Part 44 in the series "Studies on Monoterpene Glucosides and Related Natural Products". For Part 43 see Uesato, S., Ali, E., Nishimura, H., Kawamura, I. and Inouye, H. (1982) *Phytochemistry* **21**, 353.

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Table 1. ^{13}C NMR chemical shifts of the glucosides **2** and **3** in CD_3OD

C atom	2	3
1	94.2(*d*)	94.3(*d*)
3	154.8(*d*)	154.9(*d*)
4	109.2(*s*)	109.1(*s*)
5	32.4(*d*)	32.4(*d*)
6	40.8(*t*)	41.1(*t*)
7	173.2(*s*)	172.8[b](*s*)
8	124.2(*d*)	124.4(*d*)
9	134.1(*s*)	133.9(*s*)
10	61.9(*t*)	61.8(*t*)
11	169.4(*s*)	168.3(*s*)
1′	100.8(*d*)	100.9(*d*)
2′	74.6(*d*)	74.7(*d*)
3′	78.3(*d*)	78.4(*d*)
4′	71.3(*d*)	71.4(*d*)
5′	77.7(*d*)	77.9(*d*)
6′	62.6(*t*)	62.7(*t*)
OCH_3	52.3(*q*)	52.0(*q*)
CCO	168.1(*s*)	172.6[b](*s*)
$OCCH_3$	—	20.8(*q*)
1″	146.4(*d*)	35.4(*t*)
2″	118.5(*d*)	66.9(*t*)
3″	135.5(*s*)	130.7(*s*)
4″	129.9[a](*d*)	116.4(*d*)
5″	129.1[a](*d*)	146.2(*s*)
6″	131.4(*d*)	144.9(*s*)
7″	129.1[a](*d*)	117.1(*d*)
8″	129.9[a](*d*)	121.3(*d*)

Values with the same superscript are interchangeable.

group appeared at δ 3.65 (*s*), while in the spectrum of **5**, one more carbomethoxy signal appeared at 3.73 (*s*). Comparison of the chemical shifts of both carbomethoxy groups suggested that the newly formed carbomethoxy group in **5** originated from an α,β-unsaturated carboxy group. These data indicated the presence of a carboxy and a carbomethoxy group at C-11 and C-7 of jasminoside (**2**), respectively. The absolute configuration of **2** was confirmed in the following way. Alkali hydrolysis of **2** gave *trans*-cinnamic acid and a secoiridoid glucoside. Acetylation of the latter followed by methylation with diazomethane yielded the dimethyl ester pentaacetate, which was found to be identical with 10-hydroxyoleoside dimethyl ester pentaacetate (**6**) obtained from 10-acetoxyoleuropein (**3**) through the same work-up. It was thus established that jasminoside (**2**) is 10-cinnamoyloxyoleoside 7-methyl ester.

It is well known that an alcohol of a C_6–C_2 unit usually combines with the 7-carboxy group of oleoside (**7**) or 10-hydroxyoleoside (**8**) moiety in secoiridoid glucosides occurring in oleaceous plants. Jasminoside (**2**) is the first example of glucosides belonging to the 10-hydroxyoleoside series, in which the C-10 hydroxy group is esterified with an acid of a C_6–C_3 unit.

Other secoiridoid glucosides like jasminin (**1**), 10-acetoxyoleuropein (**3**), oleuropein (**9**) and ligstroside (**10**) which are the characteristic constituents of plants belonging to the Oleaceae were not detected even by HPLC.

EXPERIMENTAL

General procedures. Mps were uncorr. Unless otherwise stated, ^1H NMR and ^{13}C NMR spectra were taken at 60 MHz and 50.31 MHz using TMS as the int. standard, respectively. Si gel GF_{254} was used for TLC and spots were visualized by irradiation under a UV light (254 nm), by exposure to I_2 vapour or by spraying with the anisaldehyde–H_2SO_4 reagent followed by heating. Si gel PF_{254} was used for prep. TLC and spots were detected under a UV light. Si gel (Wako) or carbon for chromatography (Wako) was used for CC. HPLC was carried out using μ Bondapak C_{18} column (30 cm × 3.9 mm, stainless steel) and H_2O–MeOH (1:1) as the mobile phase. Flow rate 0.5 ml/min; pressure 53.3 kg/cm^2; detection: UV absorption at 254 nm.

Plant material. Jasminum humile var. *revolutum* was collected at the Higashiyama Botanic Garden, Nagoya, in 1980, and the voucher specimen (H. Inouye and F. Murai No. 1) 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 jasminoside (**2**) *from* Jasminum humile *var.* revolutum. Fresh leaves (2.0 kg) of *J. humile* var. *revolutum* were extracted with hot H_2O (3 l × 3) and the combined extracts were conc *in vacuo* to 3 l. After washing with Et_2O, the aq. extract was conc *in vacuo* to give a residue (100 g), which was subjected to CC on active carbon (500 g) eluted successively with H_2O (30 l) and MeOH (30 l). The MeOH eluate was conc *in vacuo* to give a viscous residue (29.0 g), which was chromatographed on a Si gel column (200 g) with $CHCl_3$–MeOH as eluant with an increasing MeOH content. Combined fractions eluted with $CHCl_3$–MeOH (9:1) were conc *in vacuo* to give a crystalline residue which was recrystallized from MeOH, giving rise to jasminoside (**2**) (10.3 g), as colourless needles, mp 116.5–118°. $[\alpha]_D^{29}$ – 194.7° (MeOH; *c* 1.03); ^1H NMR (90 MHz; CD_3OD): δ 2.51 (1H, *dd*, *J* = 15.0, 9.5 Hz, 6-H), 2.88 (1H, *dd*, *J* = 15.0, 4.5 Hz, 6-H), 3.64 (3H, *s*, COOMe), 4.09 (1H, *dd*, *J* = 9.5, 4.5 Hz, 5-H), 5.99 (1H, *br s*, 1-H), 6.21 (1H, *br t*, *J* = 7.0 Hz, 8-H), 6.49 (1H, *d*, *J* = 16.0 Hz, –CH=CH–Φ), 7.22–7.66 (5H, *m*, ArH), 7.54 (1H, *s*, 3-H), 7.69 (1H, *d*, *J* = 16.0 Hz, –CH=CH–Φ). (Found: C, 54.18; H, 5.55. $C_{26}H_{30}O_{13}\cdot 3/2H_2O$ requires: C, 54.07; H, 5.76%.)

Acetylation of jasminoside (**2**). Jasminoside (**2**) (304.9 mg) was acetylated (Ac_2O–pyridine) and the product (414.3 mg) was recrystallized from EtOH–H_2O to give jasminoside tetraacetate (**4**) as colourless needles (398.0 mg), m.p. 94.5–96°. $[\alpha]_D^{22}$ – 178.2° ($CHCl_3$, *c* 1.00); UV λ_{max}^{EtOH} nm (log ϵ): 217 (4.39), 222 (4.38), 236 (inf.) (4.10), 277 (4.38); IR ν_{max}^{KBr} cm^{-1}: 2620, 2500, 1740, 1730, 1720, 1710, 1690, 1640, 1630, 1580, 1500, 770; ^1H NMR ($CDCl_3$): δ 2.02 (9H, *s*, 3× OCOMe), 2.08 (3H, *s*, OCOMe), 3.65 (3H, *s*, COOMe), 4.89 (2H, *br d*, *J* = 7.0 Hz, 10-H), 5.77 (1H, *br s*, 1-H), 6.12 (1H, *br t*, *J* = 7.0 Hz, 8-H), 6.42 (1H, *d*, *J* = 16.0 Hz, –CH=CH–Φ), 7.25–7.67 (5H, *m*, ArH), 7.55 (1H, *s*, 3-H), 7.70 (1H, *d*, *J* = 16.0 Hz, –CH=CH–Φ), 7.88 (1H, *m*, COOH, disappeared on treatment with D_2O). (Found: C, 55.94; H, 5.53. $C_{34}H_{38}O_{17}\cdot 1/2H_2O$ requires: C, 56.12; H, 5.40%.)

Methylation of jasminoside tetraacetate (**4**). Jasminoside tetraacetate (**4**) (150.4 mg) was dissolved in Et_2O and methylated with ethereal CH_2N_2. The reaction product (156.7 mg) was subjected to prep. TLC (Et_2O) to give jasminoside methyl ester tetraacetate (**5**) as a white powder. $[\alpha]_D^{23}$ – 168.9° ($CHCl_3$; *c* 1.02); UV λ_{max}^{EtOH} nm (log ϵ): 217

(4.33), 222 (4.34), 236 (4.17), 277 (4.35); IR ν_{max}^{KBr} cm^{-1}: 1750, 1740, 1705, 1630, 1575, 1495, 765; ^1H NMR ($CDCl_3$): δ 2.03 (9H, *s*, 3×OCOMe), 2.09 (3H, *s*, OCOMe), 3.65 (3H, *s*, COOMe), 3.73 (3H, *s*, COOMe), 4.91 (2H, *br d*, J = 7.0 Hz, 10-H), 5.75 (1H, *br s*, 1-H), 6.12 (1H, *br t*, J = 7.0 Hz, 8-H), 6.43 (1H, *d*, J = 16.0 Hz, -CH=CH-Φ), 7.07–7.73 (5H, *m*, ArH), 7.45 (1H, *s*, 3-H), 7.70 (1H, *d*, J = 16.0 Hz, -CH=CH-Φ). (Found: C, 56.60; H, 5.35. $C_{35}H_{40}O_{17}\cdot 1/2H_2O$ requires: C, 56.68; H, 5.57%.)

Alkali hydrolysis of jasminoside (**2**). A soln of jasminoside (**2**) (70.0 mg) in 0.5 N NaOH (2 ml) was stirred at room temp. for 5 hr. After acidifying the soln by the dropwise addition of 1 N HCl under ice-cooling, the mixture was extracted with EtOAc (15 ml×3). The EtOAc layer was washed with H_2O, dried and conc *in vacuo*. The resulting crystalline residue (21.7 mg) was recrystallized from H_2O to give plates (15.9 mg), mp 133.5–135.5°. This substance was identical with an authentic sample of *trans*-cinnamic acid (mmp, IR and ^1H NMR).

On the other hand, the aq. layer was chromatographed on an active carbon (3 g) column, eluting successively with H_2O (100 ml) and MeOH (300 ml). The MeOH eluate was conc *in vacuo* and the resulting residue (50.0 mg) was acetylated (Ac_2O–pyridine). The acetate (68.6 mg) obtained was methylated with CH_2N_2 and purified by prep. TLC (Et_2O), giving rise to dimethyl ester tetraacetate (**6**) (61.5 mg) as a white powder. This substance was identical with 10-hydroxyoleoside dimethyl ester tetraacetate (**6**) (IR and ^1H NMR). $[\alpha]_D^{23}$ − 156.3° ($CHCl_3$; *c* 1.02) (lit. − 149.8° [1]). (Found: C, 51.98; H, 5.48. Calc. for $C_{28}H_{36}O_{17}$: C, 52.17; H, 5.63%.)

Search for other glucosides in the leaves of J. humile *by HPLC.* Fresh leaves of *J. humile* (10 g) were cut into pieces and extracted with hot H_2O (50 ml×3). After removal of the insoluble materials by filtration, the aq. extract was conc *in vacuo* and an aliquot (100 mg) of the residue was subjected to prep. TLC ($CHCl_3$–MeOH, 3:1). A band around R_f 0.1–0.7 was scraped off and eluted with $CHCl_3$–MeOH (3:1, 50 ml). The eluate was conc *in vacuo* to give a foamy residue. An aliquot (2 mg) of the residue dissolved in MeOH (0.5 ml) was examined by HPLC. Substances **1**, **2**, **3**, **9** and **10** (each 1 mg) dissolved in MeOH (each 0.5 ml) were used as standard samples, and a 5-μl aliquot of each sample was injected. The chromatogram showed the presence of only **2** in the *J. humile* extract. Retention time: jasminin (**1**) 14.1 min, jasminoside (**2**) 10.3 min, 10-acetoxyoleuropein (**3**) 11.7 min, oleuropein (**9**) 12.7 min, ligstroside (**10**) 17.6 min.

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