An Iridoid Glucoside from *Jasminum hemsleyi*

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A new iridoid glucoside, jashemsloside E, was isolated from the leaves of *Jasminum hemsleyi*. Its structure was elucidated on the basis of chemical and spectral data.

We have previously reported the isolation of six new iridoid glucosides, jashemslosides A, B, C (**1**), and D (**2**), 6′-*O*-*trans*-*p*-coumaroylloganin, and 6′-*O*-*cis*-*p*-coumaroylloganin from the leaves of *Jasminum hemsleyi* Yamamoto (Oleaceae), which grows in Taiwan.[1] In a continuation of this study, we have examined this species further and isolated an additional minor iridoid glucoside. This paper reports the structure elucidation of this new compound (**3**).

The novel glucoside **3**, named jashemsloside E, was obtained as an amorphous powder. HRSIMS established a molecular formula for **3** of $C_{38}H_{58}O_{21}$. The compound showed a UV maximum at 224 nm and IR bands at 3439, 1716, 1705, 1699, 1647, and 1636 cm^{-1}. Its ^{1}H- and ^{13}C-NMR spectra gave characteristic signals corresponding to loganin (**4**), a menthiafolic acid [**5**, (2*E*)-6-hydroxy-2,6-dimethyl-2,7-octadienoic acid] moiety, and a glucose unit, indicating the structural similarity of **3** to jashemsloside C (**1**) and jashemsloside D (**2**).[1] Furthermore, its ^{1}H-NMR spectrum showed two coupled doublets at δ 4.97 and 3.87 (J = 2.5 Hz), an AB system at δ 3.76 and 3.96 (J = 9.5 Hz), and a two-proton singlet at δ 3.58, suggesting the presence of an apiose unit in the molecule. Conventional acetylation of **3** with Ac_2O-pyridine gave the nonaacetate **3a** and the decaacetate **3b**, confirming an apiose unit with a tertiary hydroxyl group.[2] The anomeric configuration of apiose in **3** was determined to be β from the coupling constant (d, J = 2.5 Hz) of the anomeric proton and from the ^{13}C-NMR chemical shifts of C-1′′′′, C-2′′′′, and C-3′′′′ of the apiose moiety.[3,4]

Detailed comparison of the ^{1}H- and ^{13}C-NMR data of **1**−**3** showed that the chemical shifts of proton signals for H-7′′, H_2-8′′, and H_3-10′′, as well as the chemical shifts of carbon signals for C-5′′, C-8′′, and C-10′′ of **3**, were in good accord with those of **1** [δ 41.2 (C-5′′), δ 116.1 (C-8′′), δ 23.6 (C-10′′)] but differed from those of **2** [δ 39.9 (C-5′′), δ 115.3 (C-8′′), δ 24.0 (C-10′′)].[1] These results indicated the absolute configuration of C-6′′ of the menthiafolic acid moiety in **3** to be *S*, as is the case for **1**.[5]

A remaining point of ambiguity was the site of linkage of the apiose moiety. Glycosylation shifts were observed for C-6′ or C-6′′′ (+6.0 ppm) and C-5′ or C-5′′′ (−1.1 ppm), when compared with the ^{13}C-NMR data of **1**.[2] However, it was rather difficult to differentiate between C-6′ and C-6′′′ by spectroscopic methods. In order to solve this problem, compound **3** was subjected to methanolysis with NaOMe, giving loganin (**4**) and a monoterpene glycoside (**6**). The ^{1}H-NMR and SIMS spectra of **6** demonstrated that an apiosyl group as well as a glucose unit were attached to a menthiafolic acid methyl ester skeleton. Accordingly, the structure of jashemsloside E was established as (6′′*S*)-7-*O*-{6-*O*-[β-D-apiofuranosyl-(1→6)-β-D-glucopyranosyl]menthiafolioyl}loganin (**3**) (Chart 1).

Experimental Section

General Experimental Procedures. The UV spectrum was recorded on a Shimadzu UV-240 spectrophotometer and the IR spectrum on a Shimadzu FTIR-8200 infrared spectrophotometer. The optical rotation was measured on a Jasco DIP-370 digital polarimeter. SIMS and HRSIMS were obtained with a Hitachi M-4100 mass spectrometer, with glycerol or 3-NOBA as the matrix. The NMR experiments were performed with a Varian VXR-500 spectrometer, with Me_4Si as internal standard. HPLC was performed using a Waters system (600E Multisolvent Delivery System, 486 Tunable Absorbance Detector). Column chromatography was carried out with Si gel 60 (70−230 mesh, Nacalai Tesque, Kyoto, Japan). TLC was performed on precoated Kieselgel 60F_{254} plates (Merck), and spots were visualized under UV light.

Plant Material. The plant material used was published previously.[1]

Extraction and Isolation. Solvent extraction was carried out as reported previously.[1] Fraction V (2.38 g) was chromatographed on a Si gel column. Elution with EtOAc−C_6H_6−EtOH mixtures as eluents, with the EtOH content indicated in EtOAc−C_6H_6 (4:1) gave five fractions, V/1 (5−7%, 842 mg), V/2 (7−15%, 559 mg), V/3 (15%, 254 mg), V/4 (15−20%, 97.5 mg), and V/5 (20−50%, 230 mg). Fraction V/2 was purified by preparative HPLC (μBondasphere, 5 μM, C_{18} −100 Å, MeOH−H_2O, 1:1), affording **1** (50.9 mg) and **2** (43.6 mg) as briefly described.[1] Fractions V/3, V/4, and V/5 were separately purified by preparative HPLC (MeOH−H_2O, 1:1) to give **3** (10.3 mg, 8.1 mg, and 7.3 mg, respectively).

Jashemsloside E (3): amorphous powder; $[\alpha]^{20}_D$ −42.2° (*c* 1.01, MeOH); UV (MeOH) λ max (log ϵ) 224 (4.29) nm; IR (KBr) ν max 3439, 1716, 1705, 1699, 1647, 1636 cm^{-1}; ^{1}H NMR (CD_3OD) δ 1.07 (3H, d, J = 6.5 Hz, H_3-10), 1.40 (3H, s, H_3-10′′), 1.72 (2H, m, H_2-5′′), 1.76 (1H, ddd, J = 14.5, 8.0, 5.0 Hz, H-6), 1.83 (3H, d, J = 1.0 Hz, H_3-9′′), 2.10 (1H, td, J = 9.0, 4.5 Hz, H-9), 2.15 (1H, m, H-8), 2.28 (1H, ddd, J = 14.5, 8.0, 1.5 Hz, H-6), 2.32 (2H, m, H_2-4′′), 3.11 (1H, br q, J = 8.0 Hz, H-5),

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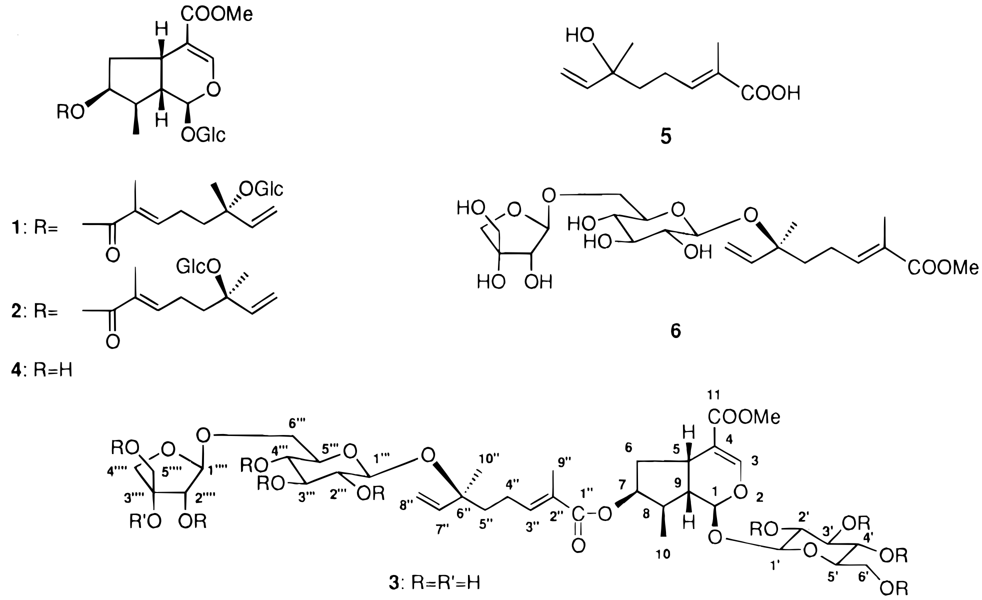
Chart 1



3: R=R'=H
3a: R=Ac, R'=H
3b: R=R'=Ac

Table 1. ^{13}C-NMR Spectral Data of Compound **3** in CD_3OD

carbon	δ_c		carbon	δ_c
C-1	97.5		C-1″	169.4
C-3	152.6		C-2″	128.9
C-4	113.4		C-3″	144.4
C-5	32.6		C-4″	24.5
C-6	40.5		C-5″	41.2
C-7	78.8^a		C-6″	81.1
C-8	41.1		C-7″	144.2
C-9	47.3		C-8″	116.1
C-10	13.8		C-9″	12.6
C-11	169.4		C-10″	23.7
OMe	51.8		C-1⁗	111.1
C-1′, C-1‴	100.2	99.6	C-2⁗	78.2^a
C-2′, C-2‴	74.8	75.3	C-3⁗	80.6
C-3′, C-3‴	78.1^a	78.5^a	C-4⁗	75.1
C-4′, C-4‴	71.7^b	71.9^b	C-5⁗	65.8
C-5′, C-5‴	78.3^a	76.6		
C-6′, C-6‴	62.8	62.9		

^{a,b} Values with the same superscript are interchangeable.

3.17 (1H, dd, J = 9.5, 8.0 Hz, H-2‴), 3.21 (1H, dd, J = 9.5, 8.0 Hz, H-2′), 3.25 (1H, t, J = 9.5 Hz, H-4‴), 3.26 (1H, t, J = 9.5 Hz, H-4′), 3.31 (1H, m, H-5‴ or H-5′), 3.32 (1H, t, J = 9.5 Hz, H-3‴), 3.33 (1H, m, H-5′ or H-5‴), 3.38 (1H, t, J = 9.5 Hz, H-3′), 3.54 (1H, dd, J = 11.5, 6.5 Hz, H-6‴), 3.58 (2H, s, H$_2$-5⁗), 3.67 (1H, dd, J = 11.5, 5.5 Hz, H-6′), 3.69 (3H, s, COOMe), 3.76 (1H, d, J = 9.5 Hz, H-4⁗), 3.87 (1H, d, J = 2.5 Hz, H-2⁗), 3.90 (1H, dd, J = 11.5, 1.5 Hz, H-6′), 3.94 (1H, dd, J = 11.5, 2.0 Hz, H-6‴), 3.96 (1H, d, J = 9.5 Hz, H-4⁗), 4.36 (1H, d, J = 8.0 Hz, H-1‴), 4.67 (1H, d, J = 8.0 Hz, H-1′), 4.97 (1H, d, J = 2.5 Hz, H-1⁗), 5.18 (1H, td, J = 5.0, 1.5 Hz, H-7), 5.23 (1H, dd, J = 11.0, 1.0 Hz, H-8″), 5.30 (1H, dd, J = 17.5, 1.0 Hz, H-8″), 5.31 (1H, d, J = 4.5 Hz, H-1), 5.94 (1H, dd, J = 17.5, 11.0 Hz, H-7″), 6.78 (1H, tq, J = 7.5, 1.0 Hz, H-3″), 7.43 (1H, d, J = 1.5 Hz, H-3); ^{13}C-NMR data, see Table 1; HRSIMS m/z [M + Na]$^+$ 873.3371 (calcd for $C_{38}H_{58}O_{21}Na$, 873.3365).

Acetylation of 3. Jashemsloside E (**3**) (5.1 mg) was treated with Ac_2O and pyridine (each 0.3 mL) at room temperature for 2 h, and the product (8.6 mg) was purified by preparative TLC with $CHCl_3$−MeOH (9:1) to afford jashemsloside E nonaacetate (**3a**) (4.4 mg) and jashemsloside E decaacetate (**3b**) (1.3 mg). **3a**: amorphous powder; ^{1}H NMR ($CDCl_3$) δ 1.03 (3H, d, J = 7.0 Hz, H$_3$-10), 1.35 (3H, s, H$_3$-10″), 1.68 (2H, m, H$_2$-5″), 1.80 (3H, d, J = 1.0 Hz, H$_3$-9″), 1.85 (1H, ddd, J = 15.5, 8.5, 5.0 Hz, H-6), 1.96 (1H, m, H-9), 1.91, 1.997, 2.004, 2.02, 2.03, 2.04, 2.10, 2.13, 2.15 (27H, each s, 9 × Ac), 2.20 (2H, m, H$_2$-4″), 2.24 (1H, m, H-8), 2.28 (1H, ddd, J = 15.5, 8.5, 1.5 Hz, H-6), 3.01 (1H, br q, J = 8.5 Hz, H-5), 3.51 (1H, dd, J = 11.0, 7.0 Hz, H-6‴), 3.60 (1H, ddd, J = 9.5, 7.0, 2.0 Hz, H-5‴), 3.69 (1H, dd, J = 11.0, 2.0 Hz, H-6‴), 3.69 (3H, s, COOMe), 3.75 (1H, ddd, J = 9.5, 4.5, 2.0 Hz, H-5′), 3.89 (1H, d, J = 10.0 Hz, H-4⁗), 3.97 (1H, d, J = 10.0 Hz, H-4⁗), 4.14 (1H, dd, J = 12.0, 2.0 Hz, H-6′), 4.22 (1H, d, J = 11.5 Hz, H-5⁗), 4.33 (1H, dd, J = 12.0, 4.5 Hz, H-6′), 4.37 (1H, d, J = 11.5 Hz, H-5⁗), 4.58 (1H, d, J = 8.0 Hz, H-1‴), 4.87 (1H, d, J = 8.0 Hz, H-1′), 4.91 (1H, t, J = 9.5 Hz, H-4‴), 4.95 (1H, d, J = 1.5 Hz, H-2⁗), 4.98 (1H, dd, J = 9.5, 8.0 Hz, H-2‴), 5.00 (1H, dd, J = 9.5, 8.0 Hz, H-2′), 5.09 (1H, d, J = 1.5 Hz, H-1⁗), 5.11 (1H, t, J = 9.5 Hz, H-4′), 5.18 (1H, br t, J = 5.0 Hz, H-7), 5.18 (1H, t, J = 9.5 Hz, H-3‴), 5.23 (1H, t, J = 9.5 Hz, H-3′), 5.24 (1H, dd, J = 17.5, 1.0 Hz, H-8″), 5.26 (1H, d, J = 2.5 Hz, H-1), 5.30 (1H, dd, J = 11.0, 1.0 Hz, H-8″), 5.72 (1H, dd, J = 17.5, 11.0 Hz, H-7″), 6.66 (1H, tq, J = 7.5, 1.0 Hz, H-3″), 7.26 (1H, br s, H-3); SIMS m/z [M + Na]$^+$ 1251, 331, 217, 193; HRSIMS m/z [M + Na]$^+$ 1251.4324 (calcd for $C_{56}H_{76}O_{30}Na$, 1251.4322). **3b**: amorphous powder; ^{1}H-NMR ($CDCl_3$) δ 1.03 (3H, d, J = 7.0 Hz, H$_3$-10), 1.36 (3H, s, H$_3$-10″), 1.68 (2H, m, H$_2$-5″), 1.80 (3H, d, J = 1.0 Hz, H$_3$-9″), 1.85 (1H, ddd, J = 15.5, 8.5, 5.0 Hz, H-6), 1.95 (1H, m, H-9), 1.91, 1.996, 2.004, 2.02, 2.029, 2.032, 2.04, 2.09, 2.10, 2.12 (30H, each s, 10 × Ac), 2.18 (2H, m, H$_2$-4″), 2.23 (1H, m, H-8), 2.27 (1H, ddd, J = 15.5, 8.5, 1.5 Hz, H-6), 3.01 (1H, br q, J = 8.5 Hz, H-5), 3.54 (1H, dd, J = 11.0, 7.5 Hz, H-6‴), 3.60 (1H, ddd, J = 9.5, 7.5, 2.0 Hz, H-5‴), 3.67 (1H, dd, J = 11.0, 2.0 Hz, H-6‴), 3.69 (3H, s, COOMe), 3.75 (1H, ddd, J = 9.5, 5.0, 2.5 Hz, H-5′), 4.15 (1H, dd, J = 12.5, 2.5 Hz, H-6′), 4.15 (1H, d, J = 10.5 Hz, H-4⁗), 4.22 (1H, d, J = 10.5 Hz, H-4⁗), 4.33 (1H, dd, J = 12.5, 5.0 Hz, H-6′), 4.52 (1H, d, $J = 12.5$ Hz, H-5′′′′), 4.58 (1H, d, $J = 8.0$ Hz, H-1′′′), 4.78 (1H, d, $J = 12.5$ Hz, H-5′′′′), 4.87 (1H, d, $J = 8.0$ Hz, H-1′), 4.88 (1H, t, $J = 9.5$ Hz, H-4′′′), 4.97 (1H, dd, $J = 9.5$, 8.0 Hz, H-2′′′), 5.00 (1H, dd, $J = 9.5$, 8.0 Hz, H-2′), 5.02 (1H, br s, H-1′′′′), 5.10 (1H, t, $J = 9.5$ Hz, H-4′), 5.18 (1H, br t, $J = 5.0$ Hz, H-7), 5.18 (1H, t, $J = 9.5$ Hz, H-3′′′), 5.23 (1H, t, $J = 9.5$ Hz, H-3′), 5.25 (1H, dd, $J = 17.5$, 1.0 Hz, H-8′′), 5.26 (1H, d, $J = 2.5$ Hz, H-1), 5.30 (1H, dd, $J = 11.0$, 1.0 Hz, H-8′′), 5.33 (1H, br s, H-2′′′′), 5.72 (1H, dd, $J = 17.5$, 11.0 Hz, H-7′′), 6.66 (1H, tq, $J = 7.5$, 1.0 Hz, H-3′′), 7.26 (1H, br, s, H-3); SIMS *m/z* $[M + Na]^+$ 1293, 331, 259, 193; HRSIMS *m/z* $[M + Na]^+$ 1293.4393 (calcd for $C_{58}H_{78}O_{31}Na$, 1293.4427).

Zemplen Reaction of 3. A solution of **3** (5.6 mg) in dry MeOH (0.5 mL) and 0.1 M NaOMe (0.5 mL) was heated for 8 h under reflux. The reaction mixture was neutralized with Amberlite IR-120 (H^+ form) and concentrated *in vacuo*. The resulting residue (7.6 mg) was purified by preparative HPLC (μBondasphere, 5 μM, C_{18} −100 Å, MeOH−H_2O, 1:1) to give **4** (0.6 mg) and **6** (1.4 mg). Compound **4** was identified as loganin[6] (^1H NMR, SIMS, HPLC). **6**: amorphous powder; ^1H NMR (CD_3OD) δ 1.40 (3H, s, H_3-10′′), 1.70 (2H, m, H_2-5′′), 1.81 (3H, d, $J = 1.0$ Hz, H_3-9′′), 2.29 (2H, m, H_2-4′′), 3.16 (1H, dd, $J = 9.0$, 8.0 Hz, H-2′′′), 3.57 (2H, s, H_2-5′′′′), 3.75 (1H, d, $J = 9.5$ Hz, H-4′′′′), 3.87 (1H, d, $J = 2.0$ Hz, H-2′′′′), 3.95 (1H, d, $J = 9.5$ Hz, H-4′′′′), 4.35 (1H, d, $J = 8.0$ Hz, H-1′′′), 4.97 (1H, d, $J = 2.0$ Hz, H-1′′′′), 5.22 (1H, dd, $J = 11.0$, 1.0 Hz, H-8′′), 5.29 (1H, dd, $J = 18.0$, 1.0 Hz, H-8′′), 5.93 (1H, dd, $J = 18.0$, 11.0 Hz, H-7′′), 6.77 (1H, tq, $J = 7.5$, 1.0 Hz, H-3′′); HRSIMS *m/z* $[M + Na]^+$ 515.2121 (calcd for $C_{38}H_{58}O_{21}Na$, 515.2103).

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