New Secoiridoid Glucosides from *Jasminum lanceolarium*

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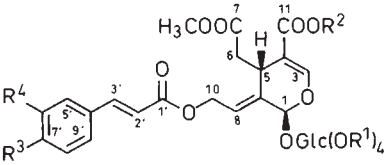
Abstract: **Two new secoiridoid glucosides, the *trans-p*-coumaroyl and *trans*-feruloyl esters of 10-hydroxyoleoside, jaslanceosides A (2) and B (3), were isolated from the leaves and stems of *Jasminum lanceolarium* (Oleaceae) in addition to jasminoside (1) and 10-hydroxyoleoside dimethyl ester (8). The structures of these compounds have been elucidated on the basis of spectral and chemical methods.**

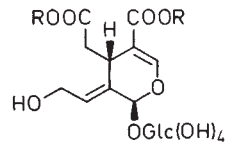
Key words: *Jasminum lanceolarium*, Oleaceae, secoiridoid glycosides, jaslanceosides A, B.

Introduction

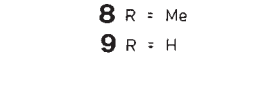
Secoiridoids of oleaceous plants have been extensively investigated in recent years (1–5). Multiflorin and several bioactive secoiridoid glucosides were found in *Jasminum multiflorum* (6–8). Five new secoiridoid glucosides, molihuasides A–E have been isolated from the flowers of *J. sambac* (9). Moreover, six novel iridoid glucosides, jashemslosides A–D, 6′-*O*-*trans*-*p*-coumaroylloganin and 6′-*O*-*cis*-*p*-coumaroylloganin were isolated from the leaves of *J. hemsleyi* Yamamoto (10). As part of our studies on the constituents of oleaceous plants we have undertaken the phytochemical investigation of *J. lanceolarium* Roxb. This plant is a climbing shrub distributed over thickets at low altitudes from southeastern China to India. Its compound leaves, comprising of 3 leaflets (8–9 cm long and 5–6 cm broad for a leaflet) are opposite. The white flowers of *J. lanceolarium* opening in June are noted for fragrance. Its globular fruits appearing in October are about 0.5–1 cm in diameter (11). The stems and the roots of *J. lanceolarium* are used in Chinese medicine for the treatment of fever and rheumatic pain. Its leaves are also used as an anti-inflammatory agent for infection and pain of the eyes (12). No previous phytochemical study on this plant has been reported. From the stems and the leaves of this plant two new secoiridoids, jaslanceosides A (**2**) and B (**3**) were isolated and characterized in addition to two kown secoiridoids, jasminoside (**1**) and 10-hydroxyoleoside dimethyl ester (**8**). Herein, we report the isolation and structure elucidation of these new compounds.



1 $R^1 = R^2 = R^3 = R^4 = H$
2 $R^1 = R^2 = H$, $R^3 = OH$, $R^4 = OMe$
3 $R^1 = R^2 = H$, $R^3 = OH$, $R^4 = H$
4 $R^1 = Ac$, $R^2 = H$, $R^3 = OAc$, $R^4 = OMe$
6 $R^1 = H$, $R^2 = Me$, $R^3 = R^4 = OMe$
5 $R^1 = Ac$, $R^2 = H$, $R^3 = OAc$, $R^4 = H$
7 $R^1 = H$, $R^2 = Me$, $R^3 = OMe$, $R^4 = H$



8 R = Me
9 R = H



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Materials and Methods

General experimental procedures

Optical rotations were recorded on a Jasco DIP-1000 polarimeter. IR and UV spectra were measured on Hitachi T-2001 and on Hitachi V-3210 spectrophotometers, respectively. EI-MS and FAB-MS were recorded on a VG Quattro 5022 mass spectrometer. The ^{1}H-, ^{13}C-NMR and COSY experiments were recorded on a Varian FT-300 spectrometer.

Plant material

Jasminum lanceolarium Roxb. was collected in June 1994, in Taichung County, Taiwan. This plant was identified by one of the authors (YCS) and a voucher specimen (TP 260-5) was kept in the Institute of Marine Resources, National Sun Yat-sen University.

Extraction and isolation

Fresh stems and leaves (2.1 kg) were ground and extracted with EtOH. The combined EtOH extracts were concentrated to a green tar. After diluting with H_2O (400 ml), the resulting suspension was partitioned with an equal volume of EtOAc. The H_2O soluble fraction was extracted thrice with *n*-BuOH. The *n*-BuOH soluble fraction was reduced under vacuum to give a secoiridoid containing residue (40 g), which was applied on a LH-20 column (10 × 50 cm, 500 g) and eluted with MeOH to give a residue (30 g). Part of the residue (15 g) was chromatographed on a silica gel column (4 × 60 cm, 250 g) and eluted

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with the lower layer of the mixture $CHCl_3$-MeOH-H_2O by increasing the polarity with the following ratios and volumes (540 : 135 : 120; 540 : 135 : 80; 540 : 135 : 50; 505 : 135 : 40; 450 : 150 : 40; 650 : 350 : 100, each 1000 ml) to give nine fractions, A (0.1 g), B (0.1 g), C (0.3 g), D (1.7 g), E (3 g), F (1.9 g), G (4.3 g), H (0.8 g), I (0.9 g). The major compound, 10-hydroxyoleoside dimethyl ester (**8**) was obtained directly from fractions D and E without further purification. Fraction G was rechromatographed on a silica gel column and eluted with the same solvent system as mentioned above to yield six fractions, G1 (**8**, 140 mg), G2 (jasminoside, **1**, 36 mg), G3 (1.7 g), G4 (0.4 g), G5 (0.65 g), and G6 (0.5 g). Fraction G4 was further purified by a silica gel column and eluted with a solvent mixture of EtOAc and diethyl ether (1 : 1) to furnish jaslanceoside A (**2**, 87 mg). Jaslanceoside B (**3**, 320 mg) was obtained from fraction G5 by using a silica gel column and $CHCl_3$/EtOAc/MeOH (4 : 2 : 1) as solvent system.

Jaslanceoside A (**2**): Isolated as an amorphous solid, $[\alpha]_D^{25}$: −129° (*c* 0.25, MeOH); IR (neat): ν_{max} cm^{-1} = 3470, 2930, 1710, 1635, 1520, 1445, 1275, 1165, 1074; UV (MeOH): λ_{max} nm (log ε) = 202 (4.24), 218 (4.13), 232 (4.04), 293 (3.75), 326 (3.94); The ^{1}H-NMR data are listed in Table **1**; FAB-MS: *m/z* = 619 {M + Na}$^+$, 597 {M + 1}$^+$; EI-MS: *m/z* (rel. int.) = 401 {M − $C_{10}H_9O_3$ − H_2O}$^+$ (0.3), 355 (3.6), 307 (3.3), 281 (3.4), 221 {M − $C_{10}H_9O_3$ − H_2O − Glu}$^+$ (5.8), 194 $\{C_{10}H_{10}O_4\}^+$ (29), 177 $\{C_{10}H_9O_3\}^+$ (62), 150 (47), 135 (34), 119 (14), 107 (27), 85 (28), 73 (63), 58 (100).

Jaslanceoside A pentaacetate (**4**): Acetylation (Ac_2O: Py; 2 : 1; rt) of **2** (35 mg) gave **4** (30 mg) as a solid; $[\alpha]_D^{25}$: −115° (*c* 0.25, MeOH); IR (KBr): ν_{max} cm^{-1} = 2940, 1752, 1638, 1512, 1438, 1372, 1218, 1158, 1038; UV (MeOH): λ_{max} nm (log ε) = 202 (4.17), 216 (4.11), 223 (4.09), 280 (3.86), 316 (3.57); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.74 (1H, br. s, H-1), 7.53 (1H, s, H-3), 2.85 (1H, H-6α), 2.42 (1H, H-6β), 6.10 (1H, t, *J* = 7.5 Hz, H-8), 6.40 (1H, d, *J* = 15.8 Hz, H-2′), 7.66 (1H, d, *J* = 15.8 Hz, H-3′), 7.10 (1H, H-5′), 7.10 (1H, H-8′), 7.01 (1H, H-9′), 5.00–5.20 (3H, m, H-1″, 2″, 4″), 5.28 (1H, dd, *J* = 9.3, 9.0 Hz, H-3″), 3.80 (1H, m, H-5″), 4.12 (1H, dd, *J* = 10.8, 1.5 Hz, H-6″), 4.31 (1H, dd, *J* = 10.8, 3.0 Hz, H-6″), 3.64 (3H, COOMe), 3.86 (3H, s, OMe), 2.02, 2.03 ×2, 2.09 (12H, s, OAc), 2.32 (3H, s, OAc); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 92.9 (d, C-1), 151.4 (d, C-3), 111.3 (s, C-4), 29.7 (d, C-5), 123.2 (d, C-8), 133.3 (s, C-9), 169.3 (s, C-11), 51.8 (q, COOMe), 166.5 (s, C-1′), 117.9 (d, C-2′), 144.5 (d, C-3′), 127.7 (s, C-4′), 111.3 (d, C-5′), 151.4 (s, C-6′), 141.5 (s, C-7′), 127.6 (d, C-8′), 122.3 (d, C-9′), 97.1 (d, C-1″), 70.7 (d, C-2″), 72.5 (d, C-3″), 68.2 (d, C-4″), 72.2 (d, C-5″), 61.7 (t, C-6″), 56.0 (q, OMe), 20.6 ×5 (q, COMe), 168.7, 169.3, 169.4, 170.1, 170.6 (s, COMe); EIMS: *m/z* (rel. int.) = 429 (0.2), 419 (1.5), 375 (0.5), 331 (3.7), 307 (4.4), 289 (3.4), 219 (4.1), 190 (4.2), 176 (21), 169 (28), 154 (100), 136 (94), 109 (45).

Jaslanceoside A dimethyl ester (**6**): Jaslanceoside A (**2**) (38 mg) was treated with an excess of CH_2N_2 and allowed to react overnight at 0–5 °C. The reaction mixture was evaporated under vacuum and purified by PTLC (silica gel, 1 mm, developed with lower layer of $CHCl_3$/MeOH/H_2O, 65 : 35 : 10) to give **6** (15 mg); $[\alpha]_D^{25}$: −119° (*c* 0.2, MeOH); IR (neat): ν_{max} cm^{-1} = 3450, 2930, 1715, 1635, 1520, 1450, 1260, 1165, 1080; UV (MeOH): λ_{max} nm (log ε) = 203 (4.48), 220 (4.35), 233 (4.40), 295 (4.09), 322 (4.19); ^{1}H-NMR (300 MHz, CD_3OD): δ = 6.00 (1H, br. s, H-1), 7.55 (1H, s, H-3), 4.10 (1H, m, H-5), 2.80 (1H, dd, *J* = 15.6, 4.5 Hz, H-6α), 2.55 (1H, dd, *J* = 15.6, 9.6 Hz, H-6β), 6.20 (1H, t, *J* = 7.0 Hz, H-8), 6.40 (1H, d, *J* = 16.0 Hz, H-2′), 7.64 (1H, d, *J* = 16.0 Hz, H-3′), 7.21 (1H, d, *J* = 1.5 Hz, H-5′), 6.97 (1H, d, *J* = 8.4 Hz, H-8′), 7.17 (1H, dd, *J* = 8.4, 1.5 Hz, H-9′), 4.83 (1H, overlap, H-1″), 3.30–3.90 (6H, H-2″, 3″, 4″, 5″, 6″), 3.63 (3H, s, 7-COOMe), 3.72 (3H, s, 11-COOMe), 3.86 (6H, s, OMe); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 94.5 (d, C-1), 155.1 (d, C-3), 109.3 (s, C-4), 32.6 (d, C-5), 40.9 (t, C-6), 173.5 (s, C-7), 124.2 (d, C-8), 134.2 (s, C-9), 61.9 (t, C-10), 168.8 (s, C-11), 52.1, 52.5 (q, COOMe), 168.5 (s, C-1′), 116.3 (d, C-2′), 146.8 (d, C-3′), 128.9 (s, C-4′), 112.8 (d, C-5′), 150.9 (s, C-6′), 149.8 (s, C-7′), 115.4 (d, C-8′), 124.5 (d, C-9′), 101.1 (d, C-1″), 74.8 (d, C-2″), 78.7 (d, C-3″), 71.6 (d, C-4″), 78.1 (d, C-5″), 62.8 (t, C-6″), 56.6, 56.7 (q, OMe); FAB-MS: *m/z* = 647 {M + Na}$^+$; EI-MS: *m/z* (rel. int.) = 443 (1.5), 255 (6.3), 208 $\{C_{11}H_{12}O_4\}^+$ (79), 191 $\{C_{11}H_{11}O_3\}^+$ (70), 163 (31), 133 (48), 107 (26), 91 (58).

Alkaline hydrolysis of jaslanceoside A (**2**): Hydrolysis (0.5 M NaOH, 2 ml; rt) of **2** (50 mg) provided after work-up as described in previous papers (2, 3) *trans*-ferulic acid (**10**, 14 mg) and a secoiridoid glucoside (**9**). The latter was further methylated with CH_2N_2/Et_2O to give **8**, identical (^{1}H-NMR, [α], and TLC) with 10-hydroxyoleoside 7,11-dimethyl ester (3). Compound **10**, ^{1}H-NMR (CD_3OD, 300 MHz): δ = 6.32 (1H, d, *J* = 15.9 Hz, H-2′), 7.57 (1H, d, *J* = 15.9 Hz, H-3′), 7.17 (1H, d, *J* = 1.5 Hz, H-5′), 6.80 (1H, d, *J* = 8.2 Hz, H-8′), 7.05 (1H, dd, *J* = 8.2 Hz, 1.5 Hz, H-9′), 3.89 (3H, s, OMe); ^{13}C-NMR (75 MHz, CD_3OD): δ = 171.4 (s, C-1′), 114.5 (d, C-2′), 146.4 (d, C-3′), 127.9 (s, C-4′), 111.7 (d, C-5′), 150.4 (s, C-6′), 149.3 (s, C-7′), 116.5 (s, C-8′), 123.9 (d, C-9′), 56.4 (q, OMe).

Jaslanceoside B (**3**): Isolated as an amorphous powder, $[\alpha]_D^{25}$: −171° (*c* 0.2, MeOH); IR (neat): ν_{max} cm^{-1} = 3240, 2900, 1708, 1694, 1636, 1606, 1514, 1446, 1204, 1168, 1078, 1042, 992, 838; UV (MeOH): nm (log ε) λ_{max} = 201 (4.15), 212 (4.71), 229 (4.26), 299 (4.17), 314 (4.24); the ^{1}H- and ^{13}C-NMR data are listed in Tables **1** and **2**, respectively; FAB-MS: *m/z* = 589 {M + NA}$^+$, 567 {M + 1}$^+$; EI-MS: *m/z* (rel. int.) = 442 (0.5), 360 (0.2), 312 (0.4), 269 (0.8), 241 (1.3), 197 (1.8), 180 (2.1), 164 $\{C_9H_7O_3\}^+$ (24), 147 $\{C_9H_8O_2\}^+$ (100), 120 (41), 91 (55), 73 (47).

Jaslanceoside B pentaacetate (**5**): Acetylation (Ac_2O: Py; 2 : 1; rt) of **3** (40 mg) gave after work-up **5** (38 mg) as a solid; $[\alpha]_D^{25}$: −105° (*c* 0.25, MeOH); IR (KBr): ν_{max} cm^{-1} = 1754, 1636, 1510, 1434, 1372, 1220, 1164, 1042, 914; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.76 (1H, br. s, H-1), 7.55 (1H, s, H-3), 2.80 (1H, H-6α), 2.42 (1H, H-6β), 6.05 (1H, t, *J* = 6.6 Hz, H-8), 6.40 (1H, d, *J* = 16.2 Hz, H-2′), 7.68 (1H, d, *J* = 16.2 Hz, H-3′), 7.11 (2H, d, *J* = 8.7 Hz, H-6′, 8′), 7.52 (2H, d, *J* = 8.7 Hz, H-5′, 7′), 5.00–5.20 (3H, m, H-1″, 2″, 4″), 5.28 (1H, dd, *J* = 9.1, 9.0 Hz, H-3″), 3.78 (1H, m, H-5″), 4.13 (1H, d, *J* = 11 Hz, H-6″), 4.30 (1H, dd, *J* = 11, 2.0 Hz, H-6″), 3.64 (3H, s, COMe), 2.09, 2.06, 2.03, 2.01 (× 2) (15 H, s, OAc), 2.30 (3H, s, OAc); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 92.9 (d, C-1), 154.1 (d, C-3), 108.2 (s, C-4), 30.8 (d, C-5), 39.8 (t, C-6), 124.2 (d, C-8), 133.3 (s, C-9), 60.7 (t, C-10), 51.8 (q, COOMe), 166.5 (s, C-1′), 117.8 (d, C-2′), 144.0 (d, C-3′), 132.1 (s, C-4′), 131.3 (d, C-5′), 122.1 (s, C-6′), 152.1 (s, C-7′), 122.1 (d, C-8′), 131.3 (d, C-9′), 97.1 (d, C-1″), 70.6 (d, C-2″), 72.4 (d, C-3″), 68.1 (d, C-4″), 72.2 (d, C-5″), 61.7 (t, C-6″), 20.6 × 3, 20.8, 21.1 (q, COMe), 169.3, 169.4, 170.1, 170.6, 171.3 (s, COMe); FAB-MS: *m/z* = 799 {M + Na}$^+$; Ei-MS: *m/z* (rel. int.) = 447 (0.2), 331 (8.9), 208 (4.1), 169 (51), 109 (52), 43 (100).

Jaslanceoside B dimethyl ester (**7**): Jaslanceoside B (**3**) (40 mg) was treated with an excess of CH_2N_2 and allowed to react over-

night at 0–5 °C. The reaction mixture was reduced under vacuum and purified by PTLC (silica gel, 1 mm, developed with $CHCl_3$/EtOAc/MeOH, 4 : 2 : 1) to give **7** (15 mg); $[\alpha]_D^{25}$: −106° (*c* 0.15, MeOH); IR (neat): ν_{max} cm^{-1} = 3400, 2930, 1715, 1635, 1610, 1515, 1445, 1260, 1165, 1080, 955, 835; UV (MeOH): λ_{max} nm (log ε) = 202 (4.13), 229 (4.08), 298 (3.89), 312 (3.95); ^{1}H-NMR (300 MHz, CD_3OD): δ = 6.00 (1H, br. s, H-1), 7.55 (1H, s, H-3), 4.10 (1H, m, H-5), 2.81 (1H, dd, *J* = 15.6, 3.9 Hz, H-6α), 2.56 (1H, dd, *J* = 15.6, 9.9 Hz, H-6β), 6.19 (1H, t, *J* = 6.6 Hz, H-8), 6.36 (1H, d, *J* = 16.1 Hz, H-2′), 7.59 (1H, d, *J* = 16.1 Hz, H-3′), 6.95 (2H, d, *J* = 8.4 Hz, H-6′, 8′), 7.55 (2H, d, *J* = 8.4, H-5′, 7′), 4.82 (1H, overlap, H-1″), 3.30–3.90 (6H, H-2″, 3″, 4″, 5″, 6″), 3.63 (3H, s, 7-COOMe), 3.72 (3H, s, 11-COOMe), 3.82 (3H, s, OMe); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 94.5 (d, C-1), 155.1 (d, C-3), 109.3 (s, C-4), 32.6 (d, C-5), 41.0 (t, C-6), 173.4 (s, C-7), 124.6 (d, C-8), 14.3 (s, C-9), 61.9 (t, C-10), 168.4 (s, C-11), 52.2, 52.5 (q, COOMe), 168.5 (s, C-1′), 114.6 (d, C-2′), 146.6 (d, C-3′), 128.0 (s, C-4′), 131.2 (d, C-5′), 117.4 (d, C-6′), 162.5 (s, C-7′), 117.4 (d, C-8′), 131.2 (d, C-9′), 101.1 (d, C-1″), 74.8 (d, C-2″), 78.7 (d, C-3″), 71.5 (d, C-4″), 78.1 (d, C-5″), 62.8 (t, C-6″), 56.0 (q, OMe); FAB-MS: *m/z* = 619 $\{M + Na\}^+$, 597 $\{M + 1\}^+$; EI-MS: *m/z* (rel. int.) = 575 (0.6), 545 (0.7), 531 (1.1), 501 (0.6), 487 (1.0), 443 (0.2), 412 (0.6), 399 (1.0), 398 (1.8), 396 (1.4), 344 (2.2), 255 (9.3), 223 (4.9), 208 (9.3), 178 $\{C_{10}H_{10}O_3\}^+$ (45), 161 $\{C_{10}H_9O_2\}^+$ (100), 133 (35), 89 (51), 45 (96).

Alkaline hydrolysis of jaslanceoside B (**3**): Hydrolysis (0.5 M NaOH, 2 ml; rt) of **3** (50 mg) provided after work-up as described above 10-hydroxyoleoside (**9**, 25 mg) and *p*-hydroxy-*trans*-cinnamic acid (9 mg).

Results and Discussion

The extract of *J. lanceolarium* foliage and stems gave, after extensive chromatography (see Materials and Methods), rise to the four compounds **1**, **2**, **3**, and **8**, of which **1** and **8** were identified by the spectral data (13, 14).

Jaslanceoside A (**2**), $[\alpha]_D$ −129° (MeOH), had the composition $C_{27}H_{32}O_{15}$ as derived from FAB-MS and ^{13}C-NMR data. The UV and IR spectra suggested the presence of a ferulic chromophore (293, 326 nm; and 1695, 1635, 1520 cm^{-1}), the phenolic function of which was indicated by a bathochromic shift (326 nm to 380 nm) in base conditions. The ^{1}H-NMR spectrum of **2** (Table **1**) displayed signals typical of a secoiridoid nucleus (15). The relationship between each proton in **2** was established by a COSY experiment. This study revealed not only the structural skeleton of **2** but also the location of the methylene protons H-10, which overlapped with water signal. Comparison of the ^{13}C-NMR data of **2** with that of **1** (Table **2**) revealed that they are quite similar except for those signals in the side chain moieties (C4′–C9′). Upon acetylation compound **2** provided a pentaacetate (**4**), the ^{1}H-NMR spectrum of which showed an aromatic acetyl singlet at δ = 2.32 and four aliphatic acetyl singlets at δ = 2.02, 2.03, 2.03 and δ = 2.09. The location of the phenolic hydroxy was determined at the C-7′ position due to the upfield shift (−8 ppm) of C-7′ and the downfield shift (+12 ppm) of C-8′ in **4** compared with the corresponding signals of **2** in the ^{13}C-NMR spectra. Methylation of **2** yielded a dimethyl ether (**6**), which showed an aromatic methoxy singlet at δ = 3.86 and a methoxycarbonyl singlet at δ = 3.72. The chemical shifts of both H-8′ and H-9′ in **6** were down shifted (+0.16 and +0.11, respectively), relative to those of **2**. Beside, the resonance of C-3 was downfield shifted from δ = 153.3 in **2** to δ = 155.1 in **6**. These observations established not only the carboxylic acid at C-11 position but also the aromatic hydroxy group at the C-7′ position in **2** and, in turn implied a 6′-

Table 1 ^{1}H-NMR spectral data* (300 MHz, CD_3OD) for compounds **1–3**.

H	1	2	3
1	5.94 brs	5.95 brs	5.95 brs
3	7.34 s	7.46 s	7.48 s
5	4.10 brd (8.7)	4.09 dd (9.8, 3.3)	4.08 dd (9.7, 3.5)
6α	2.90 dd (14.9, 2.4)	2.90 dd (15.3, 3.3)	2.82 dd (15.3, 3.5)
6β	2.51 dd (14.9, 10.6)	2.50 dd (15.3, 9.8)	2.51 dd (15.3, 9.7)
8	6.17 t (6.3)	6.17 t (6.5)	6.17 t (6.5)
10		4.95, 4.85	4.95, 4.87
2′	6.52 d (15.9)	6.34 d (16)	6.31 d (16)
3′	7.70 d (15.9)	7.62 d (16)	7.61 d (16)
5′	7.61 m	7.17 d (1.5	7.45 d (8.8)
6′	7.41 m		6.80 d (8.8)
7′	7.41 m		
8′	7.41 m	6.81 d (8.1)	6.80 d (8.8)
9′	7.61 m	7.06 dd (8.1, 1.5)	7.45 d (8.8)
1″	4.83 d (7.8)	4.81 overlap	4.82 overlap
2″–6″	3.30–3.90	3.30–3.90	3.30–3.90
COOMe	3.66 s	3.65 s	3.65 s
ArOMe		3.88 s	

* δ in ppm (*J* in Hz); TMS as internal standard.

Table 2 ^{13}C-NMR spectral data[a] (75 MHz) for compounds **1–3**.

C	1[b]	2	3
1	94.3 d	94.2 d	94.2 d
3	154.5 d	153.3 d	153.9 d
4	110.2 s	c	c
5	32.8 d	33.1 d	33.0 d
6	41.0 t	41.2 t	41.1 t
7	173.6 s	173.8 s	173.7 s
8	124.2 d	124.0 d	124.2 d
9	134.8 s	135.0 s	134.9 s
10	62.1 t	62.0 t	62.0 t
11	168.4 s	169.0 s	169.1 s
1′	168.4 s	168.1 s	168.2 s
2′	118.8 d	116.6 d	115.1 d
3′	146.7 d	147.2 d	146.9 d
4′	135.8 s	127.8 s	127.2 s
5′	130.2 d	112.0 d	131.3 d
6′	129.4 d	150.8 s	117.0 d
7′	131.1 d	149.5 s	161.4 s
8′	129.4 d	115.4 d	117.0 d
9′	130.2 d	124.2 d	131.3 d
1″	101.1 d	101.0 d	101.0 d
2″	74.9 d	74.8 d	74.8 d
3″	78.6 d	78.5 d	78.5 d
4″	71.6 d	71.5 d	71.5 d
5″	78.1 d	78.0 d	78.0 d
6″	62.8 t	62.8 t	62.8 t
COOMe	52.4 q	52.4 q	52.4 q
ArOMe		56.7 q	

[a] Measured in CD_3OD.
[b] Mulitplicities determined by DEPT (s = C, d = CH, t = CH_2, q = CH_3).
[c] Peaks are too small to be observed.

methoxy-7′-hydroxy-cinnamoyl moiety in **2** (16). The stereochemistry of **2** was further determined by comparison of the observed coupling constants with those of jasminoside (**1**) and the result of hydrolysis of **2**. Alkaline hydrolysis of **2** yielded compound **10** and the secoiridoid glucoside (**9**), which was methylated with CH_2N_2 to furnish the known dimethyl ester (**8**) (14). On the basis of spectral and chemical evidence, compound **2** was established as 10-*O*-(*trans*-feruloyl)-10-hydroxyoleoside 7-methyl ester.

Jaslanceoside B (**3**), $[\alpha]_D$ −171° (MeOH), showed the molecular formula $C_{26}H_{30}O_{14}$ as deduced by FAB-MS and DEPT spectra. The UV absorptions (299, 314 nm), the IR bands (1694, 1636, 1606, 1514 cm^{-1}) and the ^{1}H-NMR data (Table **1**) of **3** resembled those of **2**, suggesting a close analogy. However, the aromatic ABX spin system in **2** was missing. Instead, a typical A_2B_2 pattern was observed at δ = 7.45 and 6.80 (J = 8.8 Hz) in compound **3**. The ^{13}C-NMR data of **3** were similar to those of **1** and **2** except for the signals in aromatic side chain. Upon acetylation **3** provided a pentaacetate (**5**) which exhibited four aliphatic acetyl singlets and one aromatic acetyl singlet (δ = 2.30) in the ^{1}H-NMR spectrum. Methylation of **3** yielded a dimethyl ester (**7**), which showed an aromatic methoxy singlet (δ = 3.82) and a methoxycarbonyl singlet (δ = 3.72) similar to those in the ^{1}H-NMR spectrum of **6**. Alkaline hydrolysis of **3** provided a known secoiridoid (**9**) and *p*-hydroxy-*trans*-cinnamic acid. Comparison of specific rotation and coupling constants of **3** with those of **2** indicated identical stereochemistry for **2** and **3**. Thereby, compound **3** was established as 10-*O*-(*p*-hydroxy-*trans*-cinnamoyl)-10-hydroxy oleoside 7-methyl ester.

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References

1 Shen, Y.-C., Chen, C.-H. (1993) J. Nat. Prod. 56, 1905–1911.
2 Shen, Y.-C., Chen, C.-H., Lee, K.-H. (1993) Phytochemistry 33, 1531–1533.
3 Shen, Y.-C., Chen, C.-Y. (1995) Plant Med. 61, 281–283.
4 He, Z.-D., Ueda, S., Inoue, K., Akaji, M., Fujita, T., Yang, C.-R. (1994) Phytochemistry 35, 177–181.
5 Damtoft, S., Franzyk, H., Jensen, S. R. (1992) Phytochemistry 31, 4197–4201.
6 Shen, Y.-C., Chen, C.-H. (1994) J. Chin. Chem. Soc. 41, 473–476.
7 Shen, Y.-C., Lin, C.-Y., Chen, C.-H. (1990) Phytochemistry 29, 2905–2912.
8 Shen, Y.-C., Chen, C.-H. (1989) J. Nat. Prod. 52, 1060–1070.
9 Zhang, Y. J., Liu, Y. Q., Pu, X. Y., Yang, C.-R. (1995) Phytochemistry 38, 899–903.
10 Tanahashi, T., Shimada, A., Nagakura, N., Inoue, K., Ono, M., Fujita, T., Chen, C.-C. (1995) Chem. Pharm. Bull. 43, 729–733.
11 Li, H. L., Liu, T. S., Huang, T. C., Koyama, T., DeVol, C. E. (1981) Flora of Taiwan, Epoch Publishing Co., Ltd., Taipei, Vol. IV, pp. 138–140.
12 Chiu, N.-Y., Chang, K.-H. (1995) The Illustrated Medicinal Plants of Taiwan, Vol. 4, SMC Publishing, INC., Taipei, p. 171.
13 Inoue, K., Tanahashi, T., Inouye, H., Murai, F., Tagawa, H. (1982) Phytochemistry 21, 359–361.
14 Inoue, H., Inoue, K., Nishioka, T., Kaniwa, M. (1975) Phytochemistry 14, 2029–2032.
15 Boros, C. A., Stermitz, F. R. (1991) J. Nat. Prod. 54, 1173–1246.
16 Nishimura, H., Sasaki, H., Morota, T., Chin, M., Mitsuhashi, H. (1989) Phytochemistry 28, 2705–2709.