Three Secoiridoid Glucosides Esterified with a Linear Monoterpene Unit and a Dimeric Secoiridoid Glucoside from *Jasminum polyanthum*

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Reinvestigation of the dried flowers of *Jasminum polyanthum* has led to the isolation of four new secoiridoid glucosides, namely, jaspofoliamosides A (**1**) and B (**2**), jaspolinaloside (**3**), and neopolyanoside (**4**). The structures of new compounds were elucidated on the basis of chemical and spectroscopic evidence.

Jasminum polyanthum Franch. is a shrub belonging to the family Oleaceae. Its dried flowers have been used as the crude drug "Ye su xin" in Chinese folk medicine.[1] In the course of our chemical studies on the secoiridoid glucosides from oleaceous plants,[2] we have previously investigated the constituents of this crude drug and isolated 12 new secoiridoid glucosides and characterized eight of these.[3,4] Recently, a Taiwanese group reported the isolation of several secoiridoid glucosides, including a novel representative from the leaves of the same plant.[5,6] In a continuation of our study, we report here the structure elucidation of the remaining four glucosides, that is, three secoiridoid glucosides (**1**−**3**), each of which was esterified with a linear monoterpene unit, and one dimeric secoiridoid glucoside (**4**) (Chart 1).

Jaspofoliamoside A (**1**) was isolated as an amorphous powder and gave an octaacetate (**1a**) on conventional acetylation. The HRSIMS of **1** established an elemental composition of $C_{33}H_{50}O_{18}$. It showed a UV maximum at 225.5 nm and IR bands at 3421 (OH), 1715 (COO), and 1636 (C=C) cm^{-1}. Its distinctive ^{1}H-NMR spectral features [H-3 at δ 7.53, OMe at δ 3.72 (s), H-8 at δ 6.11 (br q, J = 7.0 Hz), H-1 at δ 5.94 (br s), H-1′ at δ 4.81 (d, J = 7.5 Hz), H_3-10 at δ 1.74 (dd, J = 7.0, 1.0 Hz)] indicated that **1** possessed an oleoside 11-methyl ester (**5**) moiety in its structure. The ^{1}H-NMR spectrum, moreover, displayed additional signals for an anomeric proton at δ 5.53 (d, J = 8.0 Hz), a secondary methyl group at δ 0.96 (d, J = 6.5 Hz), a vinyl methyl group at δ 1.87 (br s), a pair of oxygenated methylene protons at δ 4.06 (dt, J = 11.0, 6.0 Hz) and 4.13 (dt, J = 11.0, 7.0 Hz), and an olefinic proton at δ 6.91 (tq, J = 7.0, 1.5 Hz). The ^{13}C-NMR spectrum of **1** showed, besides the signals corresponding to the oleoside 11-methyl ester, resonances of 16 carbons, of which six were assignable to a 1-*O*-acyl-β-glucose unit.[7] With the aid of ^{1}H−^{1}H COSY, HMQC, and HMBC experiments, the remaining 10 carbon signals were evaluated as a 6,7-dihydrofoliamenthic acid [**6**, 8-hydroxy-2,6-dimethyl-2(*E*)-octenoic acid] moiety, which is also contained in other iridoid glucosides such as 6″*R*, 7″-dihydro-10-*O*-foliamenthoylaucubin.[8] An *E*-configuration of the olefinic bond at C-2″ was deduced from the chemical shift of the olefinic proton[9] and an NOE interaction between the vinyl methyl and methylene proton at δ 2.26 observed in the NOESY spectrum of **1**. The downfield shift of H_2-8″ and C-8″ and the upfield shift of C-7″ in **1** relative to the corresponding signals in (β-D-glucopyranosyl)-8-hydroxy-2,6-dimethyloct-2-enoate[7] showed an acylation of the hydroxyl group at C-8″. These findings suggested that, in the structure of jaspofoliamoside A (**1**), the C-7 carboxyl group of its oleoside 11-methyl ester moiety was linked to the C-8″ hydroxyl group of the 6,7-dihydrofoliamenthic acid unit, whose C-1″ carboxyl group was esterified with the C-1‴ hydroxyl group of β-glucose. The esterification linkages were further substantiated by significant HMBC correlations between H-1‴ and C-1″ and between H-8″ and C-7. Finally, alkaline hydrolysis of **1** yielded dihydrofoliamenthic acid (**6**) along with oleoside (**7**). The negative sign of the optical rotation of **6** was in agreement with that reported for (6*S*)-dihydrofoliamenthic acid, implying the absolute configuration at C-6″ in **1** to be *S*.[10] However, this result could not completely rule out the possibility that **1** contained a small portion of the 6″-epimer as seen in **3** mentioned below, because the optical purity of **6** could not be determined by chromatographic procedures.

The second glucoside (**2**), $C_{33}H_{48}O_{18}$, was also isolated as an amorphous powder. A comparison of the spectra of **2** with those of **1** suggested a close relationship between their structures. The ^{1}H- and ^{13}C-NMR spectral features of **2** resembled those of **1** except that **2** demonstrated signals for a vinyl methyl group at δ 1.74 (d, J = 1.0 Hz) and an olefinic proton at δ 5.38 (tq, J = 7.5, 1.0 Hz), instead of a three-proton doublet at δ 0.96 as in **1**. These differences in their spectra could be accounted for by the introduction of a double bond between C-6″ and C-7″ of the dihydrofoliamenthoyl group in **1**. This received further support from the ^{13}C-NMR spectrum of **2**, where two sp^3 resonances observed at δ 30.86 and 36.60 in the spectrum of **1** were replaced by two sp^2 carbons (δ 142.28 and 120.53). The sequence of the oleoside 11-methyl ester, foliamenthic acid (**8**), and β-glucose units in **2** was confirmed to be the same as in **1** by comparative analysis of the ^{13}C-NMR spectra of both compounds and of 10-*O*-foliamenthoylaucubin,[8] as well as HMBC experiments with **2**. The *E*-configuration of the olefinic bonds at C-2″ and C-6″ was deduced from the NOE cross peaks between the vinyl methyl at δ 1.86 and H_2-4″ at δ 2.38, and between the vinyl methyl at δ 1.74 and H_2-8″ at δ 4.54 and 4.61 observed in the NOESY spectrum of **2**. Accordingly, compound **2** was formulated as shown and designated as jaspofoliamoside B.

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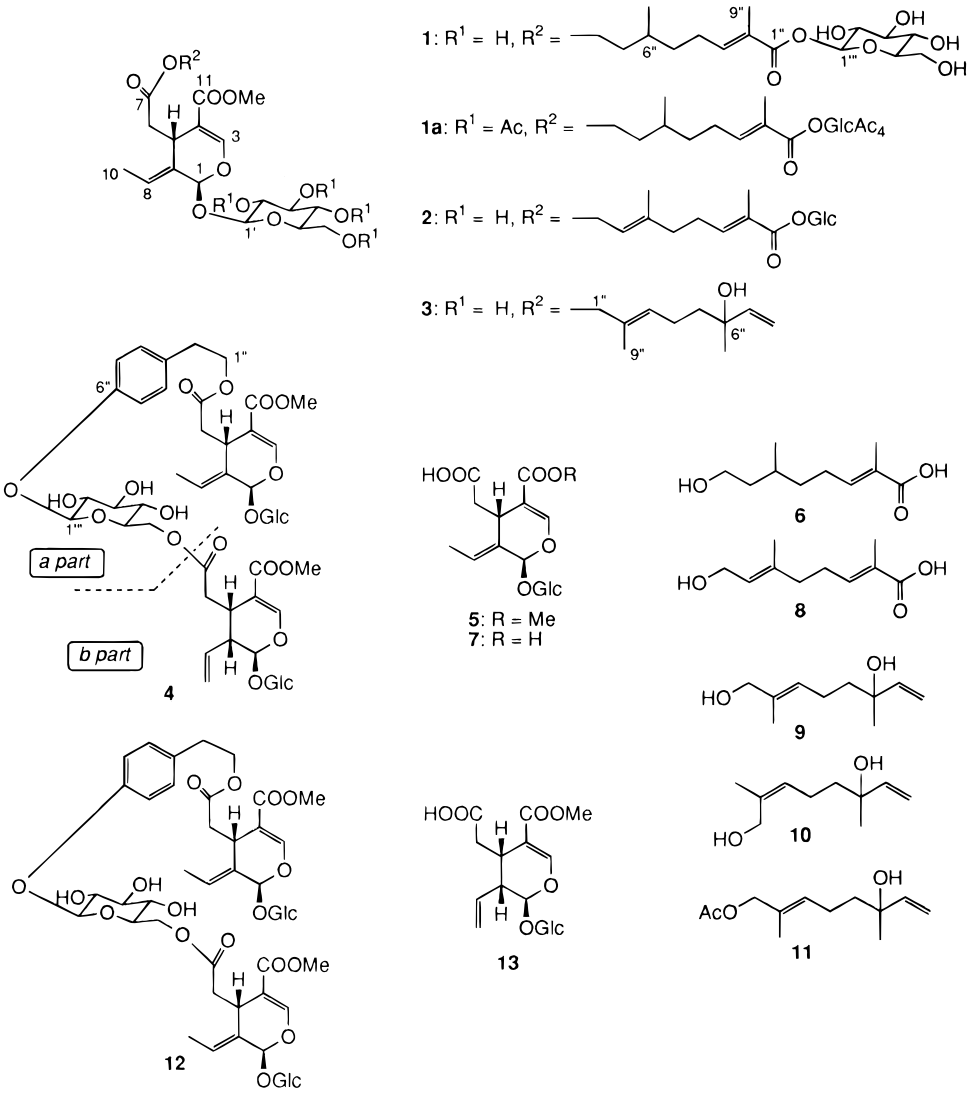
Chart 1



Glucoside **3**, named jaspolinaloside, was analyzed for $C_{27}H_{40}O_{12}$ from its HRSIMS. It was evident from its ^{1}H- and ^{13}C-NMR spectra that **3** possessed an oleoside 11-methyl ester moiety and a monoterpene unit, as in **1** and **2**, but no additional glucose. The ^{1}H-NMR spectrum of **3** demonstrated the presence in the monoterpene unit of two methyl groups (δ 1.26 and 1.65), a terminal vinyl group (δ 5.91, 5.20, 5.03), an olefinic proton (δ 5.47) adjacent to a methylene group, an oxygenated methylene group (δ 4.36, 4.48), and two methylene groups (δ 1.54 and 2.01), suggesting that the monoterpene unit in **3** should be 1-hydroxylinalool (**9**) or 9-hydroxylinalool (**10**). Inspection of the ^{13}C-NMR data of **3**, **9**, **10**, and 1-acetoxylinalool (**11**) indicated the monoterpene unit to be 1-hydroxylinalool with its C-1 hydroxyl group esterified.[11,12] The esterification pattern was elucidated by HMBC experiments, which showed ^3J interactions between H-1″ and C-7 (δ 173.06) and between the methoxyl and C-11 (δ 168.66). Accordingly, the structure of jaspolinaloside was elucidated as **3**, except for the absolute configuration at C-6″. In order to establish the stereochemistry at the chiral center, compound **3** was subjected to alkaline hydrolysis followed by acetylation to give 1-acetoxylinalool (**11**). Chiral HPLC analysis showed **11** to be a mixture of (6*S*)-1-acetoxylinalool and (6*R*)-1-acetoxylinalool in the ratio of 31:69. These results led to the conclusion that jaspolinaloside (**3**) was an inseparable mixture of diastereoisomers, similar to jashemslosides A and B, which are iridoid glucosides esterified with enantiomeric monoterpene units.[13]

Compound **4** was obtained as an amorphous powder. The HRSIMS measurement revealed a molecular formula of $C_{48}H_{64}O_{27}$. Its ^{1}H-NMR spectral features suggested that glucoside **4** was composed of two secoiridoid glucoside units [H-3a and H-3b (δ 7.48, 7.51), two anomeric protons (δ 4.80, 4.67) and two methoxyls (δ 3.71, 3.64)], a *p*-hydroxyphenethyl moiety, and an additional glucose unit in the same case as in a dimeric secoiridoid glucoside, polyanoside (**12**).[4] However, its ^{1}H-NMR spectrum showed only one set of signals corresponding to an ethylidene group at δ 6.06 (1H, qd) and 1.64 (3H, dd), but exhibited characteristic signals for a vinyl group at δ 5.07 (1H, dd, J = 10.0, 1.0 Hz), 5.14 (1H, dd, J = 17.0, 1.0 Hz), and 5.55 (1H, dt, J = 17.0, 10.0 Hz). These findings were indicative of the presence in **4** of one oleoside 11-methyl ester (**5**) (a part) and one secologanoside 11-methyl ester (**13**) (b part) unit, instead of two oleoside 11-methyl ester units as in **12**. Further support for this conclusion was obtained from its ^{13}C-NMR spectrum, which was very similar to that of **12**, except that one set of the carbon signals

Table 1. ^{13}C-NMR Spectral Data of Compounds **1**−**4** in CD_3OD

carbon	**1**		**2**		**3**	**4** a part		**4** b part
1	95.18		95.21		95.21	95.21		97.67
3	155.16		155.16		155.16	155.19		153.81
4	109.46		109.45		109.43	109.41		109.92
5	31.93		31.92		31.92	31.88		28.68
6	41.30		41.26		41.28	41.26		35.60
7	173.33		173.17		173.06	173.18		173.90
8	124.75		124.84		124.84	124.92		134.08
9	130.76		130.60		130.67	130.52		45.01
10	13.69		13.74		13.70	13.64		121.10
11	168.67		168.69		168.66	168.66		168.86
OMe	51.97		51.95		51.93	51.98		51.81
1′, 1‴	100.85	95.98	100.92	95.99	100.90	100.91	102.38	100.06
2′, 2‴	74.81	74.03	74.05[b]	74.82[b]	74.82	74.53[c]	74.73	74.81[c]
3′, 3‴	77.97[a]	78.15[a]	77.98[b]	78.17[b]	77.99	78.12[c]	77.88	77.97[c]
4′, 4‴	71.14[a]	71.59[a]	71.12[b]	71.56[b]	71.49	71.48[c]	71.32	71.56[c]
5′, 5‴	78.48[a]	78.82[a]	78.49[b]	78.84[b]	78.48	78.37	75.34	78.49
6′, 6‴	62.39[a]	62.87[a]	62.84[b]	62.38[b]	62.86	62.84	64.27	62.59
1″	168.19		168.08		71.58	66.70		
2″	128.28		128.68		131.30	35.25		
3″	145.61		144.68		130.87	133.39		
4″	27.27		28.08		23.53	131.03		
5″	36.43		38.98		42.77	118.07		
6″	30.86		142.28		73.75	157.78		
7″	36.60		120.53		146.22	118.07		
8″	64.10		62.43		112.21	131.03		
9″	12.47		12.52		14.09			
10″	19.68		16.56		27.74			

[a−c] Assignments may be reversed horizontally.

attributable to the oleoside 11-methyl ester was replaced by the signals assignable to the secologanoside 11-methyl ester unit.[14] It was evident from the coupling constant (J = 7.5 Hz) of the anomeric proton H-1‴ at δ 4.87, an HMBC correlation between H-1‴ and the aromatic carbon at δ 157.78, and the chemical shifts of aromatic carbons comparable to those of **12**, that an additional glucose was connected to the hydroxyl group of the aromatic ring with a β-linkage. The ester linkages of an oleoside methyl ester, a secologanoside methyl ester and a *p*-glucosyloxyphenethyl alcohol moiety were determined by a combination of 2D-NMR experiments, which permitted the assignment of almost all of the ^{1}H- and ^{13}C-NMR signals. Significant HMBC cross peaks were observed between the methoxyl signal (δ 3.71) and C-11a (δ 168.66), between the methoxyl signal (δ 3.64) and C-11b (δ 168.86), between H_2-1″ (δ 4.140 and 4.25) and C-7a (δ 173.18), and between the proton signal at δ 4.137 and C-7b (δ 173.90). The proton signal at δ 4.137 was assigned at H-6‴ rather than H-6′a on the basis of a COSY correlation with H-5‴ at δ 3.63, which showed a NOESY interaction with H-1‴ as well as an HMBC cross peak with C-1‴ at δ 102.38. These results suggested that an oleoside 11-methyl ester unit was esterified with the C-1″ hydroxyl of a *p*-glucosyloxyphenethyl alcohol moiety, while a secologanoside 11-methyl ester unit was connected to the hydroxyl group at C-6‴ of the glucose attached to the aromatic ring in the isolated glucoside. Consequently, the structure of the new compound is represented by **4**, and this compound designated as neopolyanoside.

Oleoside-type secoiridoid glucosides with a linear mototerpene unit, **1**−**3**, and dimeric secoiridoid glucosides such as neopolyanoside (**4**) and polyanoside (**12**) are characteristic of the flowers of *J. polyanthum*, while monomeric secoiridoid glucosides coupled with a phenethyl moiety, oleuropein and ligstroside, are major constituents common to the flowers and leaves of this species.[3,4,6]

Experimental Section

General Experimental Procedures. These were as described previously.[4]

Plant Material and Isolation of Glucosides. The crude drug, identified as "Ye su xin", from the dried flowers of *J. polyanthum*, was obtained from Sunstar Bai Yunshan Co., Ltd., in Guangzhou, China. Voucher specimens (KPFY-862) are deposited in the laboratory of Kobe Pharmaceutical University. Isolation of glucosides were described in a previous publication.[4] Compounds **I**, **II**, **III**, and **IV** in Tanahashi *et al.*[4] correspond to **2**, **1**, **4**, and **3**, respectively.

Jaspofoliamoside A (1): colorless amorphous powder; $[\alpha]^{27}_D$ −125° (*c* 0.76, MeOH); UV (MeOH) λ_{max} (log ϵ) 225.5 (4.31) nm; IR (KBr) ν_{max} 3421, 1715, 1636, 1076, 816 cm^{-1}; ^{1}H NMR (CD_3OD) δ 0.96 (3H, d, J = 6.5 Hz, H_3-10″), 1.48 (2H, m, H-5″, H-7″), 1.59 (1H, m, H-6″), 1.70 (2H, m, H-5″, H-7″), 1.74 (3H, dd, J = 7.0, 1.0 Hz, H_3-10), 1.87 (3H, br s, H_3-9″), 2.26 (2H, m, H_2-4″), 2.48 (1H, dd, J = 14.5, 9.0 Hz, H-6), 2.71 (1H, dd, J = 14.5, 4.5 Hz, H-6), 3.66 (1H, dd, J = 12.0, 4.5 Hz, H-6‴ or H-6′), 3.68 (1H, dd, J = 12.0, 4.5 Hz, H-6′ or H-6‴), 3.72 (3H, s, OMe), 3.84 (1H, dd, J = 12.0, 1.5 Hz, H-6′ or H-6‴), 3.89 (1H, dd, J = 12.0, 2.0 Hz, H-6‴ or H-6′), 3.99 (1H, dd, J = 9.0, 4.5 Hz, H-5), 4.06 (1H, dt, J = 11.0, 6.0 Hz, H-8″), 4.13 (1H, dt, J = 11.0, 7.0 Hz, H-8″), 4.81 (1H, d, J = 7.5 Hz, H-1′), 5.53 (1H, d, J = 8.0 Hz, H-1‴), 5.94 (1H, br s, H-1), 6.11 (1H, br q, J = 7.0 Hz, H-8), 6.91 (1H, tq, J = 7.0, 1.5 Hz, H-3″), 7.53 (1H, s, H-3); ^{13}C NMR, see Table 1; HRSIMS *m/z* 757.2893 [M + Na]$^+$, calcd for $C_{33}H_{50}O_{18}Na$ 757.2897.

Jaspofoliamoside B (2): colorless amorphous powder; $[\alpha]^{28}_D$ −118° (*c* 0.37, MeOH); UV (MeOH) λ_{max} (log ϵ) 226 (4.29) nm; IR (KBr) ν_{max} 3423, 1729, 1709, 1634, 1076, 818 cm^{-1}; ^{1}H NMR (CD_3OD) δ 1.73 (3H, dd, J = 7.0, 1.5 Hz, H_3-10), 1.74 (3H, d, J = 1.0 Hz, H_3-10″), 1.86 (3H, d, J = 1.5 Hz, H_3-9″), 2.19 (2H, br t, J = 7.0 Hz, H_2-5″), 2.38 (2H, br q, J = 7.0 Hz, H_2-4″), 2.46 (1H,

dd, J = 14.0, 9.5 Hz, H-6), 2.72 (1H, dd, J = 14.0, 4.5 Hz, H-6), 3.66, 3.68 (each 1H, dd, J = 12.0, 6.0 Hz, H-6′ and H-6‴), 3.72 (3H, s, OMe), 3.83 (1H, dd, J = 12.0, 2.0 Hz, H-6‴ or H-6′), 3.89 (1H, dd, J = 12.0, 2.5 Hz, H-6′ or H-6‴), 4.00 (1H, dd, J = 9.5, 4.5 Hz, H-5), 4.54, 4.61 (each 1H, dd, J = 12.0, 7.0 Hz, H_2-8″), 4.80 (1H, d, J = 8.0 Hz, H-1′), 5.38 (1H, tq, J = 7.5, 1.5 Hz, H-7″), 5.52 (1H, d, J = 8.0 Hz, H-1‴), 5.94 (1H, br s, H-1), 6.10 (1H, qd, J = 7.0, 2.0 Hz, H-8), 6.89 (1H, tq, J = 7.0, 1.5 Hz, H-3″), 7.52 (1H, s, H-3); ^{13}C NMR, see Table 1; HRSIMS m/z 731.2753 $[M - H]^-$, calcd for $C_{33}H_{47}O_{18}$ 731.2764.

Jaspolinaloside (3): colorless amorphous powder; $[\alpha]^{29}_D$ −147° (c 0.39, MeOH); UV (MeOH) λ_{max} (log ϵ) 237.5 (4.08) nm; IR (KBr) ν_{max} 3423, 1731, 1711, 1636, 1078, 818 cm^{-1}; ^{1}H NMR (CD_3OD) δ 1.26 (3H, s H_3-10″), 1.54 (2H, m, H_2-5″), 1.65 (3H, br t, J = 0.5 Hz, H_3-9″), 1.73 (3H, dd, J = 7.0, 1.5 Hz, H_3-10), 2.01 (2H, m, H_2-4″), 2.49 (1H, dd, J = 14.5, 9.0 Hz, H-6), 2.73 (1H, dd, J = 14.5, 4.5 Hz, H-6), 3.66 (1H, dd, J = 12.0, 6.0 Hz, H-6′), 3.71 (3H, s, OMe), 3.88 (1H, dd, J = 12.0, 2.0 Hz, H-6′), 4.00 (1H, dd, J = 9.0, 4.5 Hz, H-5), 4.36, 4.48 (each 1H, br d, J = 12.0 Hz, H_2-1″), 4.80 (1H, d, J = 8.0 Hz, H-1′), 5.03 (1H, dd, J = 11.0, 1.5 Hz, H-8″), 5.20 (1H, dd, J = 17.5, 1.5 Hz, H-8″), 5.47 (1H, tq, J = 7.0, 1.0 Hz, H-3″), 5.91 (1H, dd, J = 17.5, 11.0 Hz, H-7″), 5.94 (1H, br s, H-1), 6.11 (1H, qd, J = 7.0, 1.0 Hz, H-8), 7.52 (1H, s, H-3); ^{13}C NMR, see Table 1; HRSIMS m/z 579.2431 $[M + Na]^+$, calcd for $C_{27}H_{40}O_{12}Na$ 579.2419.

Neopolyanoside (4): colorless amorphous powder; $[\alpha]^{27}_D$ −137° (c 0.51, MeOH); UV (MeOH) λ_{max} (log ϵ) 224 (4.37), 236 sh (4.31), 272 sh (3.18), 278 (3.08) nm; IR (KBr) ν_{max} 3421, 1730, 1707, 1630, 1512, 1076, 818 cm^{-1}; ^{1}H NMR (CD_3OD) δ 1.64 (3H, dd, J = 7.0, 1.5 Hz, H_3-10a), 2.29 (1H, dd, J = 16.5, 9.0 Hz, H-6b), 2.44 (1H, dd, J = 14.0, 9.0 Hz, H-6a), 2.69 (1H, dd, J = 14.0, 4.5 Hz, H-6a), 2.86 (1H, ddd, J = 10.0, 5.5, 4.0 Hz, H-9b), 2.87 (2H, t, J = 7.0 Hz, H_2-2″), 3.03 (1H, dd, J = 16.5, 5.5 Hz, H-6b), 3.28 (1H, m, H-5′a), 3.32 (1H, m, H-5b), 3.34 (1H, m, H-5′b), 3.63 (1H, ddd, J = 9.0, 5.5, 2.0 Hz, H-5‴), 3.64 [3H, s, OMe(b)], 3.67, 3.72 (each 1H, dd, J = 12.0, 4.5 Hz, H-6′b and H-6′a), 3.71 [3H, s, OMe(a)], 3.88 (1H, dd, J = 12.0, 1.5 Hz, H-6′b or H-6′a), 3.90 (1H, dd, J = 12.0, 2.0 Hz, H-6′a or H-6′b), 3.95 (1H, dd, J = 9.0, 4.5 Hz, H-5a), 4.14 (1H, dd, J = 12.0, 5.5 Hz, H-6‴), 4.14, 4.25 (each 1H, dt, J = 11.0, 7.0 Hz, H_2-1″), 4.57 (1H, dd, J = 12.0, 2.0 Hz, H-6‴), 4.67 (1H, d, J = 7.5 Hz, H-1′b), 4.80 (1H, d, J = 7.5 Hz, H-1′a), 4.87 (1H, d, J = 7.5 Hz, H-1‴), 5.07 (1H, dd, J = 10.0, 1.0 Hz, H-10b), 5.14 (1H, dd, J = 17.0, 1.0 Hz, H-10b), 5.45 (1H, d, J = 4.0 Hz, H-1b), 5.55 (1H, dt, J = 17.0, 10.0 Hz, H-8b), 5.90 (1H, br s, H-1a), 6.06 (1H, qd, J = 7.5, 1.0 Hz, H-8a), 7.02 (2H, AA′BB′ pattern, J = 8.5 Hz, H-5″, H-7″), 7.17 (2H, AA′BB′ pattern, J = 8.5 Hz, H-4″, H-8″), 7.48 (1H, d, J = 1.5 Hz, H-3b), 7.51 (1H, s, H-3a); ^{13}C NMR, see Table 1; SIMS m/z 1071 $[M - H]^-$, 909; HRSIMS m/z 1071.3569 $[M - H]^-$, calcd for $C_{48}H_{63}O_{27}$ 1071.3559.

Acetylation of 1. Glucoside **1** (14.7 mg) was acetylated with Ac_2O−pyridine, and the crude acetate (22.2 mg) was purified by preparative TLC (Et_2O) to yield **1a** (15.5 mg). Colorless amorphous powder; $[\alpha]^{27}_D$ −94° (c 0.75, $CHCl_3$); UV (EtOH) λ_{max} (log ϵ) 226 (4.34) nm; IR (KBr) ν_{max} 1743, 1710, 1636, 1077, 818 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (3H, d, J = 6.5 Hz, H_3-10″), 1.44, 1.66 (each 1H, m, H_2-5″), 1.56 (1H, m, H-6″), 1.44, 1.66 (each 1H, m, H_2-7″), 1.75 (3H, dd, J = 7.0, 1.5 Hz, H_3-10), 1.83 (3H, d, J = 1.0 Hz, H_3-9″), 2.01, 2.026 (×2), 2.034, 2.037, 2.038, 2.085, 2.090 (24H, 8 × Ac), 2.18 (2H, m, H_2-4″), 2.41 (1H, dd, J = 14.5, 9.0 Hz, H-6), 2.72 (1H, dd, J = 14.5, 4.5 Hz, H-6), 3.73 (3H, s, OMe), 3.77 (1H, ddd, J = 10.0, 4.5, 2.0 Hz, H-5′ or H-5‴), 3.88 (1H, ddd, J = 10.0, 4.5, 2.0 Hz, H-5‴ or H-5′), 3.98 (1H, dd, J = 9.0, 4.5 Hz, H-5), 4.04 (1H, ddd, J = 11.0, 7.0, 6.0 Hz, H-8″), 4.08 (1H, dt, J = 11.0, 7.0 Hz, H-8″), 4.12 (2H, br dd, J = 12.5, 2.0 Hz, H-6′ and H-6‴), 4.31 (1H, dd, J = 12.5, 4.5 Hz, H-6‴ or H-6′), 4.32 (1H, dd, J = 12.5, 4.5 Hz, H-6′ or H-6‴), 5.04 (1H, d, J = 8.0 Hz, H-1′), 5.71 (1H, br t, J = 1.5 Hz, H-1), 5.74 (1H, d, J = 8.0 Hz, H-1‴), 6.01 (1H, qd, J = 7.0, 1.0 Hz, H-8), 6.84 (1H, tq, J = 7.5, 1.5 Hz, H-3″), 7.46 (1H, s, H-3); ^{13}C NMR ($CDCl_3$) δ 12.17 (C-9″), 13.59 (C-10), 19.19 (C-10″), 20.55, 20.59, 20.67, 20.72 (8 × $CO\underline{C}H_3$), 26.44 (C-4″), 29.85[a] (C-5), 30.20[a] (C-6″), 35.22[b] (C-5″), 35.41[b] (C-7″), 40.05 (C-6), 51.45 (OCH_3), 61.54[c] (C-6′), 61.80[c] (C-6‴), 62.96 (C-8″), 67.96[d] (C-4′), 68.29[d] (C-4‴), 70.16[e] (C-2′), 70.74[e] (C-2‴), 72.23[f] (C-3′), 72.53[f] (C-3‴), 72.68[g] (C-5′), 72.71[g] (C-5‴), 92.06[h] (C-1‴), 93.73[h] (C-1), 97.05 (C-1′), 108.76 (C-4), 124.74 (C-8), 126.30 (C-2″), 128.25 (C-9), 145.59 (C-3″), 153.01 (C-3), 165.72[i] (C-1″), 166.76[i] (C-11), 169.19, 169.35, 169.40, 169.43, 170.09, 170.17, 170.56, 170.63, 171.18 (C-7, 8 × $\underline{C}OCH_3$) ([a−i]values with same superscript are interchangeable); HRSIMS m/z 1071.3895 $[M + H]^+$, calcd for $C_{49}H_{67}O_{26}$ 1071.3923.

Alkaline Hydrolysis of 1. A solution of **1** (28.6 mg) in 1 M NaOH (2.5 mL) was stirred for 1 h at room temperature. The reaction mixture was neutralized with Amberlite IR-120 (H^+ form) and concentrated *in vacuo*. The resulting residue (17.5 mg) was purified by preparative HPLC (μBondasphere, 5 μM, C_{18}-100 Å, MeOH−H_2O, 7:3, detection, 210 nm) to give **7** (11.1 mg) and **6** (5.1 mg), $[\alpha]^{25}_D$ −12.5° (c 0.6, MeOH). Compounds **6** and **7** were identified as dihydrofoliamenthic acid and oleoside, respectively (^{1}H NMR, SIMS).

HPLC Analysis of 11 Derived from 3. Standard (6*R*)- and (6*S*)-1-acetoxylinalools were prepared from (*RS*)-linalyl acetate according to the literature[12] and separated by chiral HPLC [column, CHIRALCEL OB (4.6 mm i.d. × 250 mm, Daicel Chemical Industries, Ltd.); mobile phase, *n*-hexane−*i*-PrOH (100:1); flow rate, 0.6 mL/min; detection, 210 nm; retention time, *S* form (53 min), *R* form (56 min)]. The ^{1}H-NMR data of both compounds were identical with those reported for 1-acetoxylinalool. An *R* configuration of (6*R*)-1-acetoxylinalool was deduced from the agreement of the negative sign of its specific optical rotation [$[\alpha]^{27}_D$ −14° (c 0.22, MeOH)] with those of similar compounds, such as (*R*)-linalool ($[\alpha]_D$ −20.1°) or (*R*)-1-hydroxylinalool ($[\alpha]_D$ −4°),[15] thereby requiring (6*S*)-1-acetoxylinalool [$[\alpha]^{27}_D$ +16° (c 0.31, MeOH)] to have a 6*S* configuration.

A solution of **3** (1.6 mg) in 1 M NaOH (0.2 mL) was stirred for 1 h at room temperature. The reaction mixture was worked up in the same way as for **1**, and the residue was acetylated as usual. The crude mixture of acetylation products was submitted to HPLC analysis in the same condition as described above, demonstrating **11** to be a mixture of (6″*S*)- and (6″*R*)-enantiomers with the ratio of 31:69.

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