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SECOIRIDOID GLYCOSIDES FROM *JASMINUM MULTIFLORUM*

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Key Word Index—*Jasminum multiflorum*; Oleaceae; secoiridoid glycosides; multifloroside; multiroside; 10-hydroxyoleoside-11-methyl ester; coronary dilating activity.

Abstract—In addition to 10-hydroxyoleuropein and 10-hydroxyligustroside, three new secoiridoid glycosides, multifloroside, multiroside, and 10-hydroxyoleoside-11-methyl ester have been isolated from the water soluble fraction of *Jasminum multiflorum*. Their structures were established by spectroscopic analyses and chemical correlations. 10-Hydroxyoleuropein and multifloroside were found to possess coronary dilating and cardiotropic activities.

INTRODUCTION

Jasminum multiflorum (Burm. f.) Andr. (Oleaceae) is an evergreen ornamental shrub in Taiwan. Previously, we reported the isolation of four novel secoiridoid lactones, jasmolactone A (**13**), B (**14**), C (**15**), and D (**16**) from the ethanolic extract of aerial part of this plant [1], which demonstrated interesting cardiovascular activities. Further pharmacological evaluation revealed that the water-soluble fraction also possessed potent coronary dilating and cardiotropic activities. Continuing investigation of these active components has now resulted in the isolation of three new secoiridoid glycosides, multifloroside (**3**), multiroside (**4**), and 10-hydroxyoleoside-11-methyl ester (**5**), along with two known compounds 10-hydroxyoleuropein (**1**) and 10-hydroxyligustroside (**2**). This paper deals with the isolation, structure elucidation, as well as pharmacological activities of these secoiridoids.

RESULTS AND DISCUSSION

The ethanolic extract of aerial parts of *J. multiflorum* was fractionated by solvent partitioning, as described in the Experimental, and by chromatography to give five secoiridoid glycosides. Two known compounds were identified as 10-hydroxyoleuropein (**1**) [2] and 10-hydroxyligustroside (**2**) [3] by spectral comparisons and by preparation of respective heptaacetate (**1a**) [2] and hexaacetate (**2a**) [4], which confirmed further their identities. Compound **1** was previously isolated from *Ligustrum japonicum* [2], and **2** from *L. obtusifolium* [3].

Multifloroside (**3**), $[\alpha]_D$ −40.9° (MeOH), was obtained as a pale yellow powder. The IR and UV spectra suggested the presence of an enol ether system conjugated with a carbonyl group (1710, 1700, 1630 cm^{-1}; and 224 nm) that was typical of iridoid nucleus. In addition, absorptions due to catecholic function (1520, 1450 cm^{-1}; and 282.4 nm) were observed. The ^1H NMR spectrum of **3** (Table 1) closely resembled that of **1**, among those signals arising from the secoiridoid nucleus. In particular, it exhibited typical signals from vinylic protons at δ7.49 (*s*, H-3) and δ6.15 (*br t*, H-8), and a hemiacetalic proton at δ5.93 (*br s*, H-1). An additional hemiacetalic proton at δ4.83 (*d*, J = 7.7 Hz) was assignable to the anomeric proton of a β-D-glucopyranosyl moiety. While no methoxyl singlet was observed, a group of signals at δ6.55 (*dd*, J = 8.0, 1.9 Hz, H-8'), δ6.65–6.72 (*m*, H-4', 7'), and δ2.78 (*t*, J = 6.9 Hz, H-2') were attributable to a 3,4-dihydroxyphenethoxyl moiety. Reflecting this similarity, the ^{13}C NMR spectrum of **3** (Table 2) was almost superimposable with that of **1** in those signals arising from secoiridoid glucoside moiety. Moreover, additional set of carbon signals corresponding to a 3,4-dihydroxyphenethoxyl group were observed. The base fragment ion (**9**) at *m/z* 154 in the EI mass spectrum of **3** also attested to the presence of this side chain.

Acetylation of **3** provided a nonacetate (**3a**), $[\alpha]_D$ −83.2° ($CHCl_3$). Its EI mass spectrum showed characteristic fragment ions at *m/z* 331, suggesting a glucose tetraacetate unit (**11**), and at *m/z* 666, reflecting the loss of **11** and an acetic acid residue from the molecular ion. The ^1H NMR spectrum of **3a** revealed five aliphatic acetyl and four aromatic acetyl groups, confirming the presence of a C-10 hydroxyl group and two 3,4-dihydroxyphenethoxyl moieties. The latter side chains were ascertained further by spin decoupling which established two sets of ABX spin system in the aromatic region. In addition, two sets of ABX spin patterns originated from signals of H-10a, 10b, (δ4.67, 4.74) and H-8 (δ5.96), as well as H-6a, 6b (δ2.34, 2.69) and H-5 (δ3.90) were observed. The ^{13}C NMR spectrum of **3a** resembled strongly that of **1a** with additional set of signals from a 3,4-diacetoxyphenethoxyl group. Thus all spectral evidence points to structure **3** for multifloroside. The stereochemistry was elaborated further by the following series of reactions. Mild alkaline hydrolysis of **3** provided the 3,4-dihydroxyphenethyl alcohol (**7**) and the secoiridoid glucoside moiety. The former compound was methylated and identified as its dimethyl ether (**7a**). The latter residue was methylated with diazomethane and then acetylated to yield the

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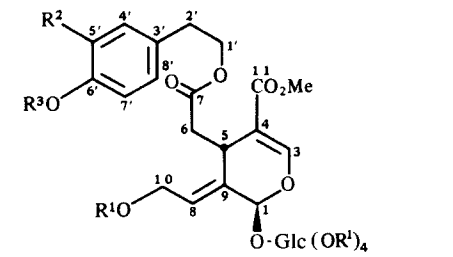

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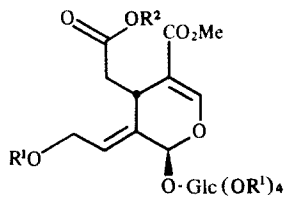
1a R^2 = OAc, R^1 = R^3 = Ac
2 R^2 = H, R^1 = R^3 = H
2a R^2 = H, R^1 = R^3 = Ac
4 R^1 = H, R^2 = OH, R^3 = Glc(OH)$_4$
4b R^1 = H, R^2 = OMe, R^3 = Glc(OH)$_4$



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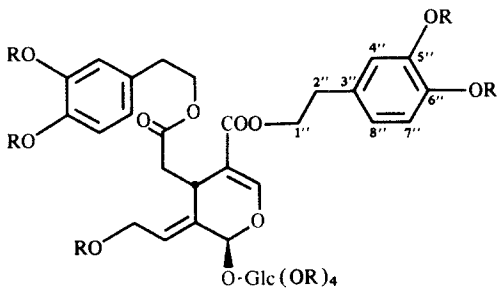
5a R^1 = Ac, R^2 = H
5b R^1 = Ac, R^2 = Me



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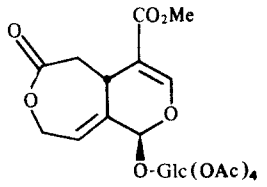

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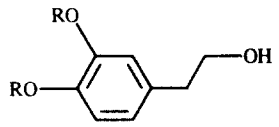

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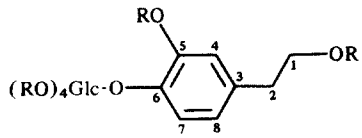
7a R = Me



8 R = H
8a R = Ac

dimethyl ester pentaacetate (**5b**). Spectral comparisons showed **5b** to be identical with 10-hydroxyoleoside 7,11-dimethyl ester pentaacetate, a known secoiridoid derivative prepared from 10-hydroxyligustroside [3] or 10-acetoxyoleuropein [4]. Thus, this conversion established the absolute structure of multifloroside as **3**.

Multiroside (**4**) was obtained as a pale amorphous powder, $[\alpha]_D$ −108.6° (MeOH). The IR bands and UV absorptions indicated a conjugated enol-ether (1685 and 1635 cm^{-1}; and 226.4 nm) and catecholic function (1510 cm^{-1}; and 276.8 nm). The ^{1}H NMR spectrum showed signals arising from a secoiridoid ring, including those of hemiacetalic proton at δ5.89 (*br s*, H-1), vinylic protons at δ7.50 (*s*, H-3) and δ6.13 (*t*, H-8), and a methoxycarbonyl group at δ3.70 (*s*). In addition, two hemiacetalic proton doublets at δ4.81 (J = 7.6 Hz) and 4.74 (J = 7.5 Hz) suggested the presence of two β-D-glucopyranosyl moieties. Cross comparison between the ^{13}C NMR spectrum of **4** with that of 10-hydroxyoleuropein (**1**) revealed close correspondence of signals, except that **4** contained two sets of signals from a β-D-glucopyranosyl residue. In comparison with **1**, the signals of aromatic carbons C-5′, C-6′, and C-7′ in **4** underwent typical glycosidation shifts (C-5′ upfield by 0.64 ppm, C-6′ and C-7′ downfield by 3.62, 2.26 ppm, respectively), suggesting that the second glucosyl unit was attached at the C-6′ hydroxyl group. Substantiating this observation, the H-7′ signal also underwent a downfield shift of 0.39 ppm. The free hydroxyl group was clearly located at C-5′ position by the ^{1}H NMR shift studies of **4** under alkaline condition, in which the signals of H-4′ and 8′ exhibited more shielding effects than that of H-7′ (upfield by 0.3, 0.44, and 0.17 ppm, respectively). The EI mass spectrum of **4** exhibited fragment ion **12** at *m/z* 298, representing the glucosyl catecholic moiety, and ion **10** at *m/z* 241, indicating the loss of **12** together with a glucosyl moiety from the molecular ion. Methylation of **4** with diazomethane afforded a monomethylate (**4b**), which showed in its ^{1}H NMR spectrum additional aromatic methoxyl singlet at δ3.86. NOE difference study was performed on **4b**, in which irradiation of the methoxyl signal clearly enhanced the doublet of H-4′ at δ6.90, suggesting that the methoxyl group is at C-5′ and that C-6′ is indeed *O*-glucosylated. Thus, **4** is the 6′-*O*-glucosyl derivative of **1**.

The stereochemistry of **4** was established as follows. Mild alkaline hydrolysis of **4** provided two products. The first product, which retains the glucosyl iridoid nucleus, was further methylated and acetylated to yield the known

Table 1. ^{1}H NMR spectral data (300 MHz) for compounds **1–5**

H	1*	3*	4*	5†
1	5.94 *br s*	5.93 *br s*	5.89 *br s*	5.87 *br s*
3	7.52 *s*	7.49 *s*	7.50 *s*	7.44 *br s*
5			3.90‡	3.60 *dd* (9.1, 6.0)
6a	2.48 *dd* (14.8, 9.4)	2.43 *dd* (14.8, 9.6)	2.49 *dd* (14.8, 9.1)	2.14 *dd* (14.0, 9.1)
6b	2.71 *dd* (14.8, 4.1)	2.66 *dd* (14.8, 3.2)	2.70 *dd* (14.8, 4.4)	2.60 *dd* (14.0, 6.0)
8(X)	6.15 *br t* (6.3)	6.15 *br t* (6.3)	6.13 *t* (6.5)	6.01 *br t* (6.4)
10(A)	4.20	4.20	4.10 *dd*‡ (14.2, 6.2)	4.18 (J_{AB} = 12.9)
10(B)	4.20	4.20	4.27 *dd*‡	4.16
1′(AB)	4.20	4.20	4.17–4.23	
2′(X_2)	2.76 *t* (7.0)	2.76 *t* (7.4)	2.81 *t* (6.0)	
4′	6.69	6.65–6.72	6.75 *d* (2.1)	
7′	6.72 *d* (8.1)	6.65–6.72	7.11 *d* (8.4)	
8′	6.55 *d* (7.9)	6.55 *dd* (8.0, 1.9)	6.66 *dd* (8.4, 2.1)	
1″(AB)		4.24		
2″(X_2)		2.78 *t* (6.9)		
4″		6.65–6.72		
7″		6.65–6.72		
8″		6.55 *dd* (8.0, 1.9)		
OMe	3.68 *s*		3.70 s	3.63 *s*
Glc				
1‴	4.82 *d* (7.6)	4.83 *d* (7.7)	4.81 *d* (7.6)	4.84 *d* (7.7)
1⁗			4.74 *d* (7.5)	

*Measured in methanol-d_4.
†Measured in water-d_2.
‡Data were obtained from HETCOR.

dimethyl ester pentaacetate (**5b**) [3, 4], which was also prepared from hydrolysis of **3**. The second product was shown to be 6-*O*-glucosyl-5-hydroxyphenethanol (**8**) by acetylation to its hexaacetate (**8a**). Conventional acetylation of **4** at room temperature also provided two products. One contained the glucosyl iridoid nucleus and was shown to be the pentaacetate acid (**5a**), identified as 10-hydroxyoleoside-11-methyl ester pentaacetate prepared from **5** as follows, and the second was the hexaacetate **8a**. Combination of both structural units established unequivocally structure **4** for multiroside. Heteronuclear correlated spectrum (HETCOR) of **4** unambiguously located the hidden signal of H-5 at δ3.90, and the carbon signals of C-4′, 7′ and 8′ at δ117.12, 119.28 and 121.45, respectively. The long-range ^{1}H–^{13}C correlation studies (COLOC) of **4** (Table 3) revealed significant correlations of the carbonyl resonance at δ168.41 with protons of methoxyl singlet (δ3.70) and the vinylic singlet (δ7.50, H-3), which established unambiguously the position of methyl ester group at C-11. That the remaining carbonyl signal at δ172.99 was assigned to C-7 was secured by its correlation with one of the methylene proton H-6b (δ2.70). One of the glucosyl carbon signal at δ100.86 (C-1‴) showed weak correlation with the proton singlet of H-1 (δ5.89), suggesting the location of one sugar residue at C-1. All other correlations are in full agreement with structure **4** for multiroside.

10-Hydroxyoleoside-11-methyl ester (**5**) was obtained as a powder, $[\alpha]_D$ −113.3° (MeOH). The UV spectrum revealed a maximum band at 235.2 nm, indicating a carbomethoxyl enol-ether chromophore. The IR absorptions at 3500–2500, 1695, 1640 and 775 cm^{-1}, not only support the above function, but also suggested the presence of acidic and pyranose functions. The ^{1}H NMR spectrum (Table 1) showed characteristic signals of iridoid nucleus, including vinylic protons at δ7.44 (*br s*, H-3) and δ6.01 (*br t*, H-8), and an hemiacetalic proton at δ5.87 (*br s*, H-1). Cross comparison of proton and carbon spectra of **5** with those of **1** showed strong similarity in every aspect, except that the signals of 3,4-dihydroxyphenethoxyl group were missing from **5**. Compound **5** was, therefore, assumed to be a 11-methyl ester of 10-hydroxyoleoside. To verify this, **5** was subjected to methylation, followed by acetylation to yield a dimethyl

Table 2. ^{13}C NMR spectral data (75.47 MHz) for compounds **1–5** (CD_3OD)

C	1*	2	3	4†	5
1	94.56 *d*	94.55 *d*	94.57 *d*	94.65 *d*	94.94 *d*
3	155.03 *d*	155.00 *d*	155.02 *d*	155.06 *d*	154.73 *d*
4	109.05 *s*	109.11 *s*	109.26 *s*	109.06 *s*	109.93 *s*
5	32.16 *d*	32.19 *d*	32.17 *d*	32.23 *d*	32.67 *d*
6	41.14 *t*	41.13 *t*	41.07 *t*	41.14 *t*	43.16 *t*
7	173.05 *s*	172.99 *s*	173.07 *s*	172.99 *s*	177.54 *s*
8	129.34 *d*	129.36 *d*	129.33 *d*	129.40 *d*	128.73 *d*
9	130.86 *s*	129.89 *s*	130.64 *s*	130.92 *s*	131.80 *s*
10	59.12 *t*	59.14 *t*	59.19 *t*	59.13 *t*	59.19 *t*
11	168.43 *s*	168.37 *s*	167.96 *s*	168.41 *s*	168.70 *s*
1′	66.84 *t*	66.84 *t*	66.88 *t*	66.57 *t*	
2′	35.23 *t*	35.04 *t*	35.29 *t*[a]	35.32 *t*	
3′	130.81 *s*	130.90 *s*	130.90 *s*[b]	135.15 *s*	
4′	116.43 *d*	130.90 *d*	116.46 *d*[c]	117.12 *d*†	
5′	146.02 *s*	116.27 *d*	146.10 *s*[d]	145.38 *s*	
6′	144.71 *s*	156.87 *s*	144.78 *s*	148.33 *s*	
7′	117.02 *d*	116.27 *d*	117.04 *d*[e]	119.28*d*†	
8′	121.29 *d*	130.90 *d*	121.32 *d*	121.45 *d*†	
1″			66.39 *t*		
2″			35.39 *t*[a]		
3″			130.92 *s*[b]		
4″			116.35 *d*[c]		
5″			146.14 *s*[d]		
6″			144.78 *s*		
7″			116.97 *d*[e]		
8″			121.32 *d*		
1‴	100.78 *d*	100.79 *d*	100.82 *d*	100.86 *d*	100.92 *d*
2‴	74.58 *d*	74.64 *d*	74.78 *d*	74.81 *d*[a]	74.61 *d*
3‴	78.22 *d*	78.28 *d*	78.30 *d*[f]	78.26 *d*[b]	78.16 *d*
4‴	71.22 *d*	71.36 *d*	71.37 *d*	71.30 *d*[c]	71.40 *d*
5‴	78.02 *d*	77.78 *d*	78.14 *d*[f]	78.11 *d*[b]	77.72 *d*
6‴	62.58 *t*	62.67 *t*	62.40 *t*	62.70 *t*[d]	62.61 *t*
1⁗				104.52 *d*	
2⁗				74.64 *d*[a]	
3⁗				77.78 *d*[b]	
4⁗				71.27 *d*[c]	
5⁗				77.49 *d*[b]	
6⁗				62.33 *t*[d]	
OMe	52.03 *q*	51.98 *q*		52.02 *q*	52.00 *q*

*Previously reported by Inoue *et al.* [2].

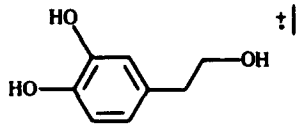
†Assignments and multiplicities were obtained from HETCOR.

[a–f]May be interchanged within each column.

ester pentaacetate (**5b**), identical in all aspects with the known 10-hydroxyoleoside 7,11-dimethyl ester pentaacetate [3, 4].

Direct acetylation of **5** yielded two products. The first is a pentaacetate acid (**5a**), which showed IR absorption at 3500–2600 and 1745 cm^{-1}, reflecting the acidic function. Its ^1H and ^{13}C NMR spectra resembled those of parent compound **5** besides those signals of five acetyl groups, indicating a pentaacetyl derivative of parent compound. The second compound (**6**) exhibited UV bands at 240.4 nm, and IR absorptions at 1745, 1700, 1630 cm^{-1}, suggesting the presence of carboalkoxy enol-ether and lactone functions. The ^1H NMR of spectrum of **6** exhibited only four acetyl singlets, two double doublets for H-6α and H-6β at rather low field (δ3.08 and δ3.33), and two triple doublets for H-10α and H-10β (δ4.75 and δ4.68). Cross comparison of the ^{13}C NMR spectra of **6** with that of **5a** revealed significant upfield shifts for resonances of C-5, C-6, and C-7, while downfield shifts were observed for signals of C-8, C-9 and C-10. As the signal of allylic acetoxyl group at C-10 was missing, these spectral data would be appropriately accommodated by an ene-lactone B-ring, which accounts for the additional unsaturation required. The formation of the lactone **6** and the pentaacetate **5a** supports further the structure of the parent acid as **5**.

Pharmacological studies revealed that both **1** and **3** possess strong coronary dilating and cardiotropic (negative inotropy) activities as performed on isolated guinea pig heart preparations. The minimum effective concentrations (MEC) of these bioactive secoiridoid glucosides are shown in the Experimental.



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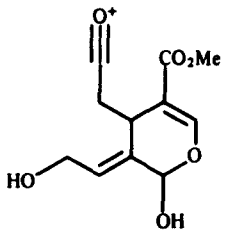

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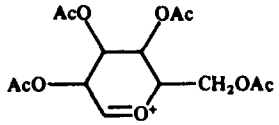

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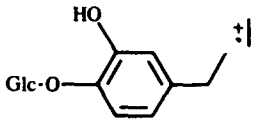

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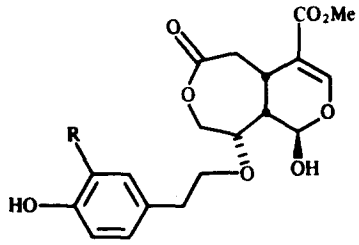

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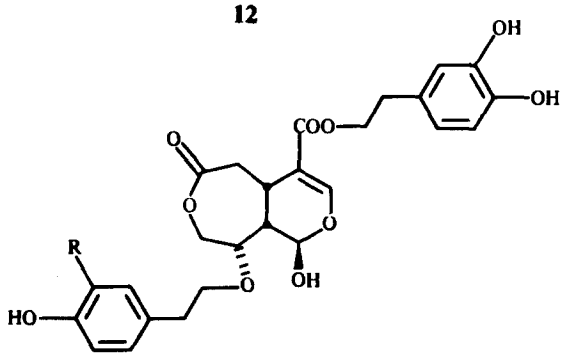
14 R = OH



15 R = H
16 R = OH

Table 3. Long-range ^{1}H–^{13}C correlation (COLOC) data of compound **4**

C	^{1}H–^{13}C connectivities*
1	(H-3)
4	H-3, (H-6b)
5	H-3, (H-6b)
7	H-6b
9	H-6b
11	–OMe, (H-3)
2′	(H-4′)
3′	(H-4′)
5′	H-4′
6′	H-4′
1‴	(H-1)

*^{1}H–^{13}C cross-peaks corresponding to two-bond or three-bond C–H connectivities. Weaks cross peaks are listed in parentheses.

Secoiridoid glucosides are commonly encountered in the oleaceous plants [5, 6], their presence being considered as a valuable systematic characteristic. Certain species of *Jasminum* have been examined for their secondary metabolites, e.g. jasminin from *J. primulinum* [7, 8] and two jasminin analogues, jasmesoside and jasmoside, from *J. mesnyi* [9]. Our finding of 10-hydroxyoleoside type secoiridoids, **1**–**5**, in *J. multiflorum* is of chemotaxonomic significance. Biogenetic consideration suggested that these 10-hydroxyoleoside type secoiridoids may be derived from secologanin [10]. The coexistence of these compounds along with jasmolactone A (**13**), B (**14**), C (**15**) and D (**16**), which possess a novel 2-oxo-oxepano[4,5-c]pyran ring system [1], in the same plant is. quite unusual.

EXPERIMENTAL

The general instrumental and experimental methods were described in previous paper [1]. NOE, HETCOR and COLOC spectra were recorded on a 300 MHz instrument, using standard pulse sequences. For the HETCOR and COLOC experiments, the measurements were optimized to coupling constants of 125 and 8 Hz, respectively. In addition to silica gel, RP C-18 (Merck) and Sephadex LH-20 (Pharmacia) were used in column chromatography.

Plant material. The plant of *J. multiflorum* were collected in a suburb of Taipei in December 1985 and July 1986. A voucher specimen is kept in the School of Pharmacy, National Taiwan University.

Extraction and isolation. In one batch of plant material, fresh aerial parts were extracted and fractionated as described pre-

viously [1]. The known jasmolactones **13–16** [1] were isolated from the $CHCl_3$-soluble and the *n*-BuOH-soluble fractions. Part of the *n*-BuOH-soluble fraction (75 g) was chromatographed on a silica gel column (750 g) and eluted with increasing polarity of $CHCl_3$–MeOH mixture to yield frs 1–14. Frs 1–8 (10–15% MeOH–$CHCl_3$) provided additional quantities of compounds **14–16**. Fr. 9 (20% MeOH–$CHCl_3$) was concd to give a residue (1.9 g), part of which (0.44 g) was chromatographed on a reverse phase C-18 column (15 g) using MeOH–H_2O (1:1) as eluent to yield 10-hydroxyligustroside (**2**) (81 mg). The residue from frs 11 (6.2 g) and 13 (4 g) (both eluted with 25% MeOH–$CHCl_3$) were repeatedly chromatographed on silica gel (250 g, 300 g) columns and eluted with *n*-BuOH (satd with H_2O). Final purification with a Sephadex LH-20 (45 g) column using MeOH as eluent, yielded 10-hydroxyoleuropein (**1**) (0.7 g) and multifloroside (**3**) (1.1 g).

In another batch of plant material, the dry powdered leaves (4.4 kg) was extracted 95% EtOH (10 l × 3). The alcoholic extract was concd *in vacuo* to give an aq. suspension (2 l) which was extracted with an equal vol. of $CHCl_3$. The aq. layer was then exhaustively extracted with *n*-BuOH. To the lower aqueous layer was added active charcoal (200 g) and stirred well to make a suspension, which was subsequently filtered through a Gooch funnel. The charcoal layer was washed successively with H_2O (2 l), 5% EtOH (2 l), and 90% EtOH (4 l). The secoiridoid fractions were obtained from concn of the *n*-BuOH-soluble fraction (30 g) and 90% EtOH extract (35 g). From the *n*-BuOH-soluble fraction additional quantities of **1** and **3** were isolated. Part of the 90% EtOH extract (6 g) was chromatographed on a silica gel column (180 g) eluted with the lower layer of the solvent mixture $CHCl_3$–MeOH–H_2O to afford frs I (1.0 g) (18:5:2), II (0.125 g) (45:15:4), and III (0.13 g) (13:7:2). Final purification of frs I and II on Sephadex LH-20 columns (30 and 15 g) eluted with MeOH yielded **3** (650 mg) and 10-hydroxyoleoside 11-methyl ester (**5**) (75 mg), respectively. Similar purification of fr. II with a Sephadex LH-20 column (30 g) yielded multiroside (**4**) (82 mg).

10-Hydroxyoleuropein (**1**). Compound **1** was obtained as a powder, and was identified by spectral comparisons (UV, IR, ^{1}H NMR) as 10-hydroxyoleuropein [2]. The high resolution ^{1}H and ^{13}C NMR (CD_3OD) data are listed in Tables 1 and 2, respectively. Acetylation of **1** and usual work-up yielded **1a**, $[\alpha]_D^{28}$ −97.2° ($CHCl_3$; *c* 1.0). Its spectral data (UV, IR and ^{1}H NMR) also agreed with those reported for 10-hydroxyoleuropein heptaacetate [4]; ^{13}C NMR δ(75.47 MHz, $CDCl_3$): 92.73 (*d*, C-1), 152.81 (*d*, C-3), 108.19 (*s*, C-4), 30.73 (*d*, C-5), 39.80 (*t*, C-6), 170.10 (*s*, C-7), 124.15 (*s*, C-8), 131.04 (*s*, C-9), 60.56 (*t*, C-10), 166.25 (*s*, C-11), 64.57 (*t*, C-1′), 34.15 (*t*, C-2′), 136.37 (*s*, C-3′), 123.30 (*d*, C-4′), 141.85 (*s*, C-5′), 140.63 (*s*, C-6′), 123.74 (*d*, C-7′), 126.88 (*d*, C-8′), 96.94 (*d*, C-1‴), 70.59 (*d*, C-2‴), 72.39 (*d*, C-3‴), 67.98 (*d*, C-4‴), 72.14 (*d*, C-5‴), 61.49 (*t*, C-6‴), 51.50 (*q*, OMe), 20.50, 20.52, 20.54, 20.57, 20.80 (*q*, COMe), 168.14, 168.23, 169.22, 169.28, 170.52, 170.56, 170.61 (*s*, COMe); EIMS *m/z* (rel. int.): 850 $[M]^+$ (0.24), 790 $[M-HOAc]^+$ (0.2), 503 (2.2), 460 $[M-HOAc-330]^+$ (4.4), 443 (3.7), 400 (7.3), 330 $[Glc(OAc)_4]^+$ (60), 237 $[C_{12}H_{13}O_5]^+$ (51.2), 225 (70.7), 169 (100), 154 (7.4), 137 (14.6), 136 (22).

10-Hydroxyligustroside (**2**). Isolated as an amorphous powder, $[\alpha]_D^{28}$ −172.3° (EtOH; *c* 1.0), UV λ_{max}^{MeOH} nm (log ε): 203 (4.62), 226 (4.68), 277 (3.75); ^{1}H NMR δ(300 MHz, CD_3OD): 5.94 (1H, *br s*, H-1), 7.51 (1H, *s*, H-3), 3.66 (1H, *dd*, *J* = 9.4, 4.1 Hz, H-5), 2.47 (1H, *dd*, *J* = 14.9, 9.4 Hz, H-6α), 2.71 (1H, *dd*, *J* = 14.9, 4.1 Hz, H-6β), 6.14 (1H, *br t*, *J* = 6.2 Hz, H-8), 4.19 (2H, *m*, H-10), 4.15 (2H, *t*, *J* = 6.9 Hz, H-1′), 2.80 (2H, *t*, *J* = 6.9 Hz, H-2′), 6.72 (2H, *d*, *J* = 8.4 Hz, H-5′, 7′), 7.03 (2H, *d*, *J* = 8.4 Hz, H-4′, 8′), 4.83 (1H, *d*, *J* = 7.5 Hz, H-1″); the ^{13}C NMR spectral data are listed in Table 2. Acetylation of **2** (30 mg) and usual work-up yielded an amorphous hexaacetate **2a** (24 mg), identified by spectral comparisons (UV, IR and ^{1}H NMR) as 10-hydroxyligustroside hexaacetate [3]; ^{13}C NMR δ(75.47 MHz, $CDCl_3$): 92.88 (*d*, C-1), 152.72 (*d*, C-3), 108.47 (*s*, C-4), 30.88 (*d*, C-5), 39.92 (*t*, C-6), 170.24 (*s*, C-7), 124.17 (*d*, C-8), 131.37 (*d*, C-9), 60.44 (*t*, C-10), 166.15 (*s*, C-11), 64.88 (*t*, C-1′), 34.29 (*t*, C-2′), 135.09 (*s*, C-3′), 129.63 (*d*, C-4′, 8′), 121.48 (*s*, C-5′, 7′), 149.46 (*s*, C-6′), 97.02 (*d*, C-1″), 70.87 (*d*, C-2″), 72.30 (*d*, C-3″), 68.36 (*d*, C-4″), 72.53 (*d*, C-5″), 61.70 (*t*, C-6″), 51.31 (*q*, COOMe), 20.34 (× 4), 20.60, 20.58 (*q*, COMe), 169.03, 169.13 (× 2), 169.85, 170.34, 170.48 (*s*, COMe).

Multifloroside (**3**). $[\alpha]_D^{28}$ −40.9° (MeOH; *c* 1.0); UV λ_{max}^{MeOH} nm (log ε): 204 (4.73), 224 (4.36), 282.4 (3.92); EIMS *m/z* (rel. int.): 516 (0.12), 487 (0.24), 443 (0.19), 400 (0.25), 368 (0.44), 344 $[M-Glc-154-H_2O]^+$ (0.62), 318 (1.5), 316 $[344-CO]^+$ (0.88), 301 (8.9), 300 $[318-H_2O]^+$ (41.2), 279 (2.5), 224 (2.5), 182 (6.3), 167 (7.6), 165 (13.9), 164 (10.8), 163 (9.5), 155 (40), 154 $[C_8H_{10}O_3]^+$ (97.5), 153 (10.1), 140 (10.8), 137 (39.2), 136 (58.8), 124 (50.6), 123 $[154-MeO]^+$ (100), 73 (20.2), 61 (12.6), 60 (13.9). ^{1}H and ^{13}C NMR spectral data are listed in Tables 1 and 2, respectively.

Acetylation of multifloroside (**3**). Compound **3** (55 mg) was acetylated with Ac_2O–pyridine at room temp. Usual work-up followed by purification with prep. TLC yielded multifloroside nonacetate (**3a**) (37 mg) as an amorphous powder, $[\alpha]_D^{28}$ −83.2° ($CHCl_3$; *c* 1.0); ^{1}H NMR δ(300 MHz, $CDCl_3$): 5.67 (1H, *br s*, H-1), 7.39 (1H, *s*, H-3), 3.90 (1H, *dd*, *J* = 9.4, 3.9 Hz, H-5), 2.34 (1H, *dd*, *J* = 15.4, 9.1 Hz, H-6α), 2.69 (1H, *dd*, *J* = 15.4, 3.9 Hz, H-6β), 5.96 (1H, *br t*, *J* = 6.4 Hz, H-8), 4.74, 4.67 (2H, J_{AB} = 13.4 Hz, H-10), 4.20, 4.22 (2H, H-1′), 2.88 (2H, *t*, *J* = 6.9 Hz, H-2′), 4.30 (2H, H-1″), 2.92 (2H, *t*, *J* = 6.7 Hz, H-2″), 7.02–7.11 (6H, H-4′, 4″, 7′, 7″, 8′, 8″), 5.00 (1H, *d*, *J* = 7.5 Hz, H-1‴), 5.10 (1H, *dd*, *J* = 7.5, 9.3 Hz, H-2‴), 5.24 (1H, *dd*, *J* = 9.3, 9.4 Hz, H-3‴), 5.10 (1H, *dd*, *J* = 9.4, 10.0 Hz, H-4‴), 3.74 (1H, *dm*, *J* = 10 Hz, H-5‴), 4.25 (1H, H-6‴), 4.07 (1H, *dd*, *J* = 12.4, 2.0 Hz, H-6‴), 2.00, 2.01, 2.03 (15H, *s*, OAc), 2.25 (12H, *s*, OAc); ^{13}C NMR δ(75.47 MHz, $CDCl_3$): 92.71 (*d*, C-1), 153.01 (*d*, C-3), 108.11 (*s*, C-4), 30.75 (*d*, C-5), 39.74 (*t*, C-6), 170.13 (*s*, C-7), 124.20 (*d*, C-8), 130.89 (*d*, C-9), 60.60 (*t*, C-10), 165.65 (*s*, C-11), 64.57 (*t*, C-1′), 34.16 (*t*, C-2′), 136.38 (*s*, C-3′), 123.33 (*d*, C-4′), 141.88 (*s*, C-5′), 140.64 (*s*, C-6′), 123.75 (*d*, C-7′), 126.91 (*d*, C-8′), 64.31 (*t*, C-1″), 34.40 (*t*, C-2″), 136.68 (*s*, C-3″), 123.33 (*d*, C-4″), 141.91 (*s*, C-5″), 140.64 (*s*, C-6″), 123.69 (*d*, C-7″), 126.96 (*d*, C-8″), 96.94 (*d*, C-1‴), 70.58 (*d*, C-2‴), 72.42 (*d*, C-3‴), 67.98 (*d*, C-4‴), 72.15 (*d*, C-5‴), 61.49 (*t*, C-6‴), 20.52 (× 2), 20.57 (× 5), 20.83 (× 2) (*q*, COMe), 168.16, 168.26, 168.29, 169.26, 169.31, 170.56, 170.61 (*s*, COMe); EIMS *m/z* (rel. int.): 745 (0.73), 701 (0.8), 666 $[M-331-HOAc]^+$ (0.53), 657 (1.7), 644 (0.7), 617 (1.1), 587 (1.0), 573 (1.5), 529 (1.3), 487 $[M-331-238]^+$ (1.2), 485 (1.2), 444 (4.7), 431 (57.3), 331 $[Glc(OAc)_4]^+$ (8.0), 202 (8), 200 (8), 184 (18), 169 (14.7), 167 (9.3), 157 (26.7), 154 (18.7), 149 (29.3), 136 (14.7), 115 (32), 112 (26.7), 103 (24), 98 (40), 97 (20), 87 (34.7), 58 (100).

Alkaline hydrolysis of multifloroside (**3**). A soln of **3** (300 mg) in 0.5 M NaOH (15 ml) was stirred for 3.5 hr at room temp. The mixture was acidified with Amberlite IR-20 (H^+ form) and extracted with EtOAc (30 ml × 4). The combined EtOAc extract was dried and evapd to give a syrup (56 mg), which showed identical behaviour (^{1}H NMR and TLC) with 2-(3,4-dihydroxyphenyl)ethyl alcohol (**7**). Methylation with CH_2N_2–Et_2O at 0° for 24 hr gave, on crystallization from Et_2O, needles (**7a**) (28 mg), mp 40–42°, identical with an authentic sample of 2-(3,4-dimethoxyphenyl)ethyl alcohol (mmp, ^{1}H NMR, IR and TLC). The aq. layer was concd to dryness to give a residue (260 mg) which was treated with CH_2N_2–Et_2O at 0° for 24 hr. The reaction mixture was chromatographed on a LH-20 column (20 g) and eluted with MeOH. The methylated product (110 mg) was acetylated with Ac_2O–pyridine at room temp. Usual work-up followed by purification with a silica gel (10 g) column (eluting with 5% MeOH in $CHCl_3$) yielded compound **5b** (95 mg). The spectral data (UV, IR, ^{1}H NMR) of

this compound are identical with that of 10-hydroxyoleoside dimethyl ester pentaacetate [3, 4], and also identical with the same compound prepared from **5**.

Multiroside (**4**). $[\alpha]_D^{28}$ −108.6° (MeOH; *c* 1.0); UV λ_{max}^{MeOH} nm (log ε): 203.2 (4.78), 226.4 (4.31), 276.8 (3.54); EIMS *m/z* (rel. int.): 298 (1.8), 285 (1.8), 241 $[M-2Glc-154]^+$ (25.4), 223 $[241-H_2O]^+$ (26.4), 209 $[241-MeOH]^+$ (21.8), 205 (11.8), 181 $[241-CO_2Me]^+$ (10.9), 155 (66.4), 154 $[C_8H_{10}O_3]^+$ (100), 136 (15.4), 127 (7.3), 123 (37.3), 97 (4.5), 91 (4.5), 85 (12.7), 73 (19.1), 69 (11), 57 (12); ^1H and ^{13}C NMR data are listed in Tables 1 and 2. The ^1H NMR δ(300 MHz, D_2O) showed the following aromatic signals: 7.15 (1H, *d*, *J* = 8.3 Hz, H-7′), 6.88 (1H, *d*, *J* = 1.8 Hz, H-4′), 6.83 (1H, *dd*, *J* = 1.8, 8.3 Hz, H-8′); with the addition of 5 drops of 0.5 M KOH in D_2O the same signals were: 6.98 (1H, *d*, *J* = 8.1 Hz, H-7′), 6.58 (1H, *d*, *J* = 2.0 Hz, H-4′), 6.39 (1H, *dd*, *J* = 8.1, 2.0 Hz, H-8′).

Alkaline hydrolysis of multiroside (**4**). A soln of **4** (32 mg) in 0.5 M NaOH (5 ml) was stirred at room temp. for 2 hr. The reaction mixture was acidified with Amberlite IR-20 (H^+ form) and evapd to dryness. The residue was chromatographed on a LH-20 column (10 g) and eluted with MeOH. The first eluate was treated with CH_2N_2–Et_2O at 0° C for 24 hr and then acetylated with a mixture of Ac_2O and pyridine at room temp. Usual work-up followed by purification with prep. TLC (C_6H_6–EtOAc 1:1) yielded **5b** (7 mg), the spectral data (UV, IR, ^1H NMR) are identical with that of 10-hydroxyoleoside dimethyl ester pentaacetate. [3, 4]. The second eluate from the LH-20 column was further acetylated with a mixture of Ac_2O and pyridine at room temp. A similar work-up and purification gave a hexaacetate (**8a**) (9 mg) of 6-*O*-glucosyl-5-hydroxyphenethanol (**8**). Compound **8a**, $[\alpha]_D^{27}$ −13.7° ($CHCl_3$; *c* 1.0), ^1H NMR δ(300 MHz, $CDCl_3$): 4.22 (2H, *t*, *J* = 7.0 Hz, H-1), 2.86 (2H, *t*, *J* = 7.0 Hz, H-2), 6.89 (1H, *d*, *J* = 2.1 Hz, H-4), 6.94 (1H, *d*, *J* = 8.3 Hz, H-7), 7.01 (1H, *dd*, *J* = 8.3, 2.1 Hz, H-8), 5.29 (1H, *d*, *J* = 5.9 Hz, H-1′), 5.08 (1H, H-2′), 5.26 (1H, H-3′), 5.15 (1H, *dd*, *J* = 9.9, 9.5 Hz, H-4′), 3.86 (1H, *ddd*, *J* = 9.9, 5.4, 2.4 Hz, H-5′), 4.27 (1H, *dd*, *J* = 12.4, 5.3 Hz, H-6′), 4.15 (1H, *dd*, *J* = 12.4, 2.3 Hz, H-6′), 1.98, 2.02, 2.06, 2.24 (18 Hz, *s*, OAc).

Acetylation of multiroside (**4**). Acetylation of **4** (16 mg) in a mixture of Ac_2O and pyridine was carried out at room temp. Usual work-up followed by purification with prep. TLC (C_6H_6–EtOAc 1:1) yielded two compounds **5a** (6 mg) and **8a** (7 mg). Compound **5a** was identical (UV, IR, and ^1H NMR) with one of the acetylation products of compound **5**. Compound **8a** was identical (IR and ^1H NMR) with the same product obtained above from compound **4**.

Methylation of multiroside (**4**). Compound **4** (12 mg) was reacted with freshly prepared CH_2N_2–Et_2O at 0° for 3 days. The reaction mixture was purified on prep. TLC plate (1 mm thickness, developed with lower layer of $CHCl_3$–MeOH–H_2O, 13:7:2) to yield compound **4b** (5.8 mg), ^1H NMR δ(300 MHz, CD_3OD): 5.94 (1H, *br s*, H-1), 7.52 (1H, *s*, H-3), 3.90 (1H, H-5), 2.49 (1H, *dd*, *J* = 15.0, 9.5 Hz, H-6α), 2.72 (1H, *dd*, *J* = 15.0, 4.1 Hz, H-6β), 6.12 (1H, *br t*, *J* = 6.2 Hz, H-8), 4.07 (2H, *dd*, *J* = 4.8, 13.1 Hz, H-10), 4.26, 4.21 (2H, H-1′), 2.88 (2H, *t*, *J* = 6.8 Hz, H-2′), 6.90 (1H, *d*, *J* = 1.9 Hz, H-4′), 7.10 (1H, *d*, *J* = 8.2 Hz, H-7′), 6.79 (1H, *dd*, *J* = 1.9, 8.3 Hz, H-8′), 4.80 (1H, *d*, *J* = 7.6 Hz, H-1‴), 3.70, 3.86 (6H, *s*, OMe). The NOED of **4b** with irradiation at δ3.86 (*s*, OMe) enhanced signal at δ6.90 (*d*, H-4′) by 5%.

10-*Hydroxyoleoside* 11-*methyl ester* (**5**). Powder, $[\alpha]_D^{28}$ −113.3° (MeOH; *c* 1.0); UV λ_{max}^{MeOH} nm (log ε): 201 (3.94), 235.2 (3.95). The ^1H and ^{13}C NMR spectral data are listed in Tables 1 and 2.

Acetylation of 10-*hydroxyoleoside* 11-*methyl ester* (**5**). Usual acetylation of 10-hydroxyoleoside 11-methyl ester (60 mg) provided a mixture of two compounds which were sepd by prep. TLC (2 mm thickness, developed with C_6H_6–EtOAc, 2:3) to yield **5a** (21 mg) and **6** (18 mg). Compound **5a** $[\alpha]_D^{28}$ −151.9° ($CHCl_3$; *c* 1.0); UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 244.8 (4.31); ^1H NMR δ(300 MHz, $CDCl_3$): 5.69 (1H, *br s*, H-1), 7.45 (1H, *s*, H-3), 3.97 (1H, *dd*, *J* = 9.2, 3.9 Hz, H-5), 2.43 (1H, *dd*, *J* = 15.5, 9.2 Hz, H-6α), 2.82 (1H, *dd*, *J* = 15.5, 3.9 Hz, H-6β), 6.01 (1H, *br t*, *J* = 6.7 Hz, H-8), 4.75, 4.77 (2H, J_{AB} = 14.3, J_{AX} = J_{BX} = 6.8 Hz, H-10),* 5.02 (1H, *d*, *J* = 7.4 Hz, H-1‴), 5.11 (1H, *dd*, *J* = 7.4, 8.3 Hz, H-2‴), 5.25 (1H, *dd*, *J* = 8.3, 9.2 Hz, H-3‴), 5.11 (1H, *dd*, *J* = 9.4, 9.2 Hz, H-4‴), 3.77 (1H, *dm*, H-5‴), 4.27 (1H, *dd*, *J* = 12.6, 4.4 Hz, H-6‴), 4.14 (1H, *dd*, *J* = 12.6, 2.1 Hz, H-6‴), 3.72 (3H, *s*, OMe), 2.01, 2.02, 2.05, 2.07 (15H, *s*, OAc); ^{13}C NMR δ(75.47 MHz, $CDCl_3$): 92.7 (*d*, C-1), 152.71 (*d*, C-3), 108.06 (*s*, C-4), 30.74 (*d*, C-5), 39.99 (*t*, C-6), 174.59 (*s*, C-7), 124.06 (*s*, C-8), 130.87 (*s*, C-9), 60.6 (*t*, C-10), 166.03 (*s*, C-11), 96.92 (*d*, C-1‴), 70.66 (*d*, C-2‴), 72.37 (*d*, C-3‴), 68.09 (*d*, C-4‴), 72.12 (*d*, C-5‴), 61.52 (*t*, C-6‴), 51.90 (*q*, OMe), 20.52, 20.80 (*q*, COMe), 168.95, 169.83, 170.46 (*s*, COMe). Compound **6**: mp 195–197°; $[\alpha]_D^{28}$ −49.2° ($CHCl_3$; *c* 1.0); UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 240.4 (4.15); IR ν_{max}^{KBr} cm^{-1}: 1745, 1700, 1630, 905, 870, 770; ^1H NMR δ(300 MHz, $CDCl_3$): 5.54 (1H, *br s*, H-1), 7.37 (1H, *d*, *J* = 2.1 Hz, H-3), 3.70 (1H, *m*, H-5), 3.08 (1H, *dd*, *J* = 12.9, 9.6 Hz, H-6), 3.33 (1H, *dd*, *J* = 12.9, 3.7 Hz, H-6), 6.05 (1H, *m*, H-8), 4.75 (1H, *ddd*, *J* = 4.2, 3.3, 12.5 Hz, H-10), 4.68 (1H, *ddd*, *J* = 6.1, 2.3, 12.5 Hz, H-10), 4.85 (1H, *d*, *J* = 8.2 Hz, H-1‴), 4.95 (1H, *dd*, *J* = 8.2, 9.3 Hz, H-2‴), 5.20 (1H, *dd*, *J* = 9.3, 9.4 Hz, H-3‴), 5.08 (1H, *dd*, *J* = 9.4, 9.8 Hz, H-4‴), 3.7 (1H, H-5‴), 4.24 (1H, *dd*, *J* = 12.5, 4.3 Hz, H-6‴), 4.17 (1H, *dd*, *J* = 12.5, 2.4 Hz, H-6‴), 3.74 (3H, *s*, OMe), 1.87, 1.99, 2.00, 2.08 (12H, *s*, OAc); ^{13}C NMR δ(75.47 MHz, $CDCl_3$): 95.2 (*d*, C-1), 151.39 (*d*, C-3), 110.18 (*s*, C-4), 29.73 (*d*, C-5), 33.23 (*t*, C-6), 171.91 (*s*, C-7), 125.62 (*s*, C-8), 135.06 (*s*, C-9), 62.75 (*t*, C-10), 165.42 (*s*, C-11), 96.27 (*d*, C-1‴), 70.40 (*d*, C-2‴), 72.24 (*d*, C-3‴), 67.93 (*d*, C-4‴), 72.17 (*d*, C-5‴), 61.48 (*t*, C-6‴), 51.60 (*q*, OMe), 19.96, 20.51, 20.70 (*q*, COMe), 168.76, 169.27, 170.58, 170.13 (*s*, COMe); EIMS *m/z* (rel. int.): 347 (1.3), 332 (11.2), 331 (65.3), 271 (20.6), 260 (2.4), 246 (2.9), 229 (3.5), 224 (7.6), 212 (9.4), 181 (13.5), 178 (12.3), 170 (11.2), 169 (100), 157 (5.3), 145 (5.9), 139 (6.2), 128 (7.1), 109 (36.5).

Methylation and acetylation of compound **5**. Compound **5** (100 mg) was treated with CH_2N_2–Et_2O to give a reaction product which was then acetylated with Ac_2O–pyridine. Usual work-up and purification on prep. TLC plates (1 mm thickness × 2, developed twice with Et_2O) provided **5b**, $[\alpha]_D^{28}$ −167.9° ($CHCl_3$; *c* 1.0). The spectral data (UV, IR, ^1H NMR) of this compound are identical with that of 10-hydroxyoleoside dimethyl ester pentaacetate [3, 4]. Additional data are shown as following. EIMS *m/z* (rel. int.): 399 (0.39), 369 (0.35), 355 (0.7), 332 (9.6), 331 (60.5), 311 $[M-331]^+$ (0.6), 303 (14), 299 (7.9), 271 (15.8), 265 (4.4), 243 (7.0), 223 (9.2), 211 (7.0), 173 (8.3), 169 (100), 141 (10.1), 109 (17.5). High resolution ^1H NMR δ(300 MHz, $CDCl_3$): 5.70 (1H, *br s*, H-1), 7.44 (1H, *s*, H-3), 3.96 (1H, *dd*, *J* = 9.3, 4.1 Hz, H-5), 2.41 (1H, *dd*, *J* = 15.3, 9.3 Hz, H-6), 2.79 (1H, *dd*, *J* = 15.3, 4.1 Hz, H-6), 6.00 (1H, *br t*, *J* = 6.6 Hz, H-8), 4.78, 4.71 (2H, J_{AB} = 13.6, J_{AX} = 7.2, J_{BX} = 6.0 Hz, H-10),* 5.02 (1H, *d*, *J* = 7.7 Hz, H-1‴), 5.11 (1H, *dd J* = 7.7, 8.4 Hz, H-2‴), 5.25 (1H, *dd*, *J* = 8.4, 9.3 Hz, H-3‴), 5.11 (1H, *dd*, *J* = 9.4, 9.3 Hz, H-4‴), 3.75 (1H, *dm*, H-5‴), 4.29 (1H, *dd*, *J* = 12.5, 4.7 Hz, H-6‴), 4.11 (1H, *dd*, *J* = 12.5, 1.8 Hz, H-6‴), 3.63, 3.72 (6H, *s*, OMe), 2.01, 2.02, 2.06, 2.08 (15H, *s*, OAc); ^{13}C NMR δ(75.47 MHz, $CDCl_3$): 92.97 (*d*, C-1), 152.85 (*d*, C-3), 108.53 (*s*, C-4), 30.98 (*d*, C-5), 39.91 (*t*, C-6), 169.25 (*s*, C-7), 124.23 (*s*, C-8), 131.07 (*s*, C-9), 60.57 (*t*, C-10), 166.29 (*s*, C-11), 97.17 (*d*, C-1‴), 70.92 (*d*, C-2‴), 72.95 (*d*, C-3‴), 68.45 (*d*, C-4‴), 72.39 (*d*, C-5‴), 61.84 (*t*, C-6‴), 51.46, 51.60 (*q*, OMe), 20.50 (×4), 20.73 (*q*, COMe), 169.17, 169.25, 170.00, 170.39, 171.03 (*s*, COMe).

*J values were calculated from second order analysis.

Pharmacological activities. Coronary dilating and cardiotropic activities were measured with an isolated guinea pig preparation in a system of modified Langendorff apparatus described in a previous paper [1]. Compound **1** exhibited MEC of both activities at 9.0×10^{-6} M, compound **3** at 3.7×10^{-6} and 1.5×10^{-6} M, respectively.

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REFERENCES

1. Shen, Y. C. and Chen, C. H. (1989) *J. Nat. Prod.* **52**, 1060.
2. Inoue, K., Nishioka, T. Tanahashi, T. and Inouye, H. (1982) *Phytochemistry* **21**, 2305.
3. Asaka, Y., Kamikawa, T., Kubota, T. and Sakamoto, H. (1972) *Chem. Letters* 141.
4. Inouye, H., Inoue, K., Nishioka, T. and Kaniwa, M. (1975) *Phytochemistry* **14**, 2029.
5. Plouvier, V. and Favre-Bonvin, J. (1971) *Phytochemistry* **10**, 1697.
6. El-Naggar, L. J. and Beal, J. L. (1980) *J. Nat. Prod.* **43**, 649.
7. Kubota, T., Ichikawa, N. and Kamikawa, T. (1968) *J. Chem. Soc. Jpn* **89**, 72.
8. Kamikawa, T., Inoue, K., Kubota, T. and Woods, M. C. (1970) *Tetrahedron* **26**, 4561.
9. Inoue, K., Tanahashi, T. and Inouye, H. (1985) *Phytochemistry* **24**, 1299.
10. Inouye, H. and Uesato, S. (1987) *Progr. Chem. Nat. Prod.* **50**, 169.