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# INERMINOSIDES A AND B, TWO NOVEL COMPLEX IRIDOID GLYCOSIDES FROM *CLERODENDRUM INERME*[1]

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ABSTRACT.—The leaves of *Clerodendrum inerme* have yielded two new iridoid biglycosides which have been characterized as 2′-*O*-[5″-*O*-(8-hydroxy-2,6-dimethyl-2(*E*)-octenoyl)-β-D-apiofuranosyl]-mussaenosidic acid (inerminoside A) [**1**], and 2′-*O*-[5″-*O*-(8-hydroxy-2,6-dimethyl-2(*E*),6(*E*)-octadienoyl)-β-D-apiofuranosyl]-8-*epi*-loganic acid (inerminoside B [**2**]), respectively. Structure elucidation was carried out both chemically and spectroscopically.

The genus *Clerodendrum* belongs to the subfamily Viticoideae, and is the largest genus of the Verbenaceae. Plants of the genus *Clerodendrum* are well known for their pesticidal properties (1). In East Africa they are used as army-worm antifeedants (2) and in West Africa the leaf extract is used for arresting bleeding from cuts and other wounds as well as for stopping post-partum hemorrhage. Several *Clerodendrum* species have been reported to contain phenylpropanoid glycosides (2,3), flavonoids (4,5), diterpenes (5,6), and iridoids (7,8).

Our current research into the secondary metabolite content of *Clerodendrum inerme* Gaertn. leaves has resulted in the isolation of several iridoids, phenylpropanoids, and flavonoids. The current report describes results relating to the isolation and structure elucidation of two new iridoid biglycosides, inerminosides A [**1**] and B [**2**].

## RESULTS AND DISCUSSION

Inerminoside A [**1**] was obtained as an amorphous colorless powder. The fabms of **1** exhibited a peak at *m/z* 699 $[M+Na]^+$, compatible with the molecular formula $C_{31}H_{48}O_{16}$. The uv (228 nm) and ir (3350, 1700, 1670, and 1630 $cm^{-1}$) absorptions and $^1$H-nmr data for H-3 (δ 7.37 s) indicated the presence of a 4-substituted enol ether system typical of iridoids. Consistent with these data was the $^1$H-nmr spectrum of **1** (Table 1) that exhibited signals for a $C_{10}$-iridoid biglycosidic moiety as well as for an open-chain monoterpene unit. Two signals for anomeric protons at δ 4.77 (d) and at δ 5.41 (br s), were assigned to β-D-glucose and β-D-apiose, respectively. The $^1$H-nmr spectrum also contained resonances at δ 4.27 and 4.22 (AB system, $J_{AB}$ = 11.3 Hz) which were assigned to $H_2$-5″ of the apiose unit, indicating the site of acylation. The $^{13}$C-nmr data (Table 3) contained resonances that could be assigned to an iridoid moiety very similar in structure to mussaenosidic acid (9) as well as to the monoterpene 6,7-dihydrofoliamenthic acid (10). Alkaline hydrolysis of **1** yielded **3**, clearly indicating the monoterpene unit to be attached to C-5″ of the apiose moiety.

To resolve all of the connectivities between the four discrete molecular fragments within **1**, an amount of the compound was acetylated to yield the hexaacetate, **1a**. Extensive $^1$H,$^1$H-homonuclear and $^1$H,$^{13}$C-heteronuclear-correlated 2D nmr spectral measurements permitted all $^1$H- and $^{13}$C-nmr resonances of **1a** to be assigned (Tables 1

[1]Presented at the poster session of the "40th Annual Congress on Medicinal Plant Research," Trieste, Italy, September 1–5, 1992.

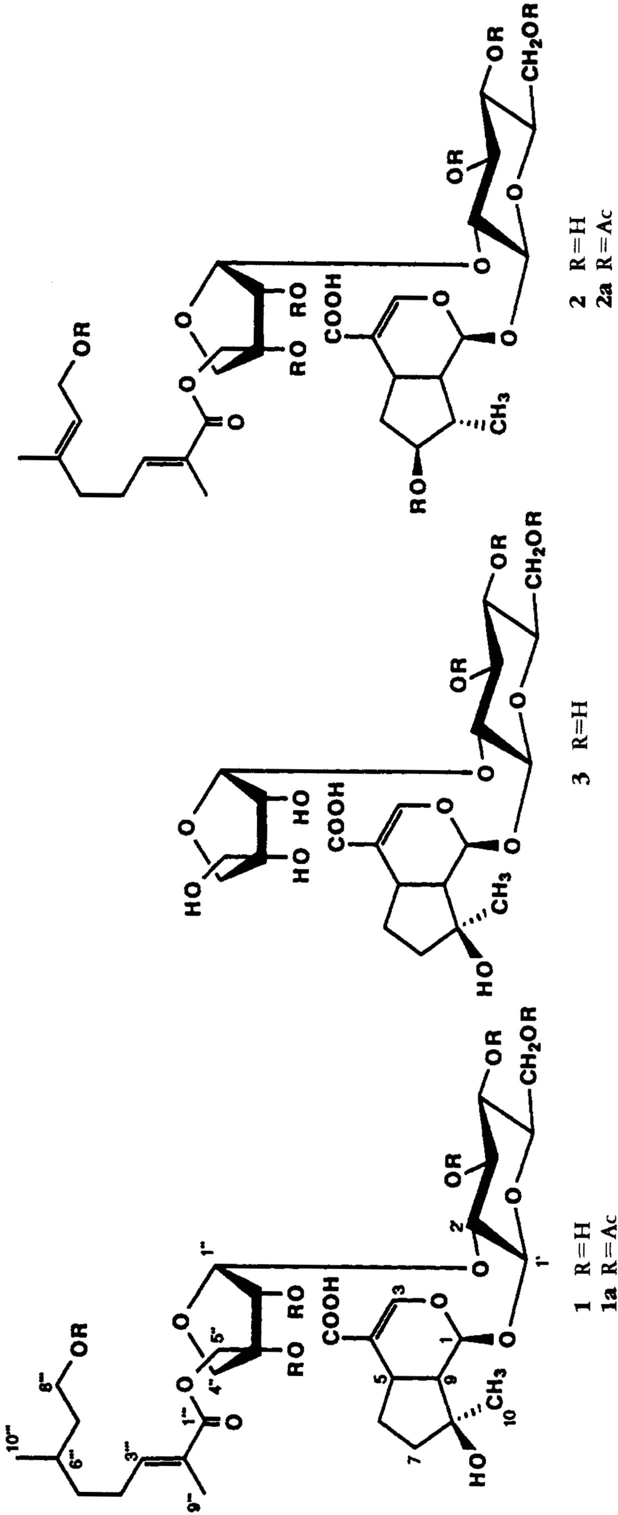
1 R=H
1a R=Ac
3 R=H
2 R=H
2a R=Ac

TABLE 1. $^1$H-Nmr Spectral Data for **1**, **1a**, and **3** (300 MHz; **1** and **3** in $CD_3OD$, **1a** in $CDCl_3$).

| H | **1** | | **1a**[a] | | **3** | |
|---|---|---|---|---|---|---|
| | δ (ppm) | *J* (Hz) | δ (ppm) | *J* (Hz) | δ (ppm) | *J* (Hz) |
| 1 | 5.39 d | (5.6) | 5.14 d | (7.1) | 5.52 d | (2.8) |
| 3 | 7.37 s | | 7.39 s | | 7.30 s | |
| 5 | 3.16 ddd "q" | (8.5) | 3.20 ddd "q" | (7.7) | 3.16 m | |
| 6a | 1.51 m | | 1.50 m | | 1.56 m | |
| 6b | 2.34 m | | 2.36 m | | 2.31 m | |
| 7 | 1.76 m | | 1.73 t like | (7.6) | 1.73 m | |
| 9 | 2.14 dd | (8.5, 5.6) | 2.12 dd | (7.8, 6.5) | 2.27 dd | (9.8, 2.8) |
| 10 | 1.39 s | | 1.38 s | | 1.33 s | |
| 1′ | 4.77 d | (7.7) | 4.86 d | (7.8) | 4.73 d | (7.8) |
| 2′ | 3.46 dd | (9.1, 7.7) | 3.72 dd | (9.1, 7.8) | 3.44 dd | (9.2, 7.8) |
| 3′ | 3.55 t | (8.8) | 5.21 t | (9.5) | 3.55 t | (8.6) |
| 4′ | 3.27 dd "t" | (9.7, 8.3) | 4.99 dd "t" | (9.7, 9.6) | 3.28 t | (9.8) |
| 5′ | 3.35 m | | 3.69 m | | 3.32 m | |
| 6′a | 3.66[b] | | 4.08–4.20[b] | | 3.68 dd | (12.0, 5.8) |
| 6′b | 3.94 br d | (12.9) | 4.08–4.20[b] | | 3.93 dd | (12.0, 2.0) |
| 1″ | 5.41 br s | | 5.09 br s | | 5.43 br s | |
| 2″ | 3.92 br s | | 5.15 br s | | 3.93 br s | |
| 4″ | 3.79 d | (9.6) | 4.09 d | (10.2) | 4.01 d | (9.9) |
| 4″ | 4.23 d | (9.6) | 4.30 d | (10.2) | 3.75 d | (9.9) |
| 5″ | 4.27 d | (11.3) | 4.73 d | (12.7) | 3.62 br s | |
| 5″ | 4.22 d | (11.3) | 4.54 d | (12.7) | | |
| 3‴ | 6.86 br t | (7.5) | 6.75 dt | (7.2, 1.0) | | |
| 4‴ | 2.27 m | | 2.20 m | | | |
| 5‴ | 1.36 m | | 1.30 m | | | |
| 5‴ | 1.48 m | | 1.50 m | | | |
| 6‴ | 1.67 m | | 1.60 m | | | |
| 7‴ | 1.50 m | | 1.50 m | | | |
| 7‴ | 1.62 m | | 1.70 m | | | |
| 8‴ | 3.66[b] | | 4.20 d | (3.0) | | |
| 9‴ | 1.87 s | | 1.81 br s | | | |
| 10‴ | 0.99 d | | 0.94 d | (6.0) | | |

[a]Additional acetyl signals here observed at δ: 2.00, 2.02, 2.04 (each 3H), 2.06 (9H) (aliph.×6).
[b]Signal patterns were unclear due to overlapping.

and 3). As no downfield shift was observed for the signal of H-2′ of glucose (δ 3.72), an interglycosidic linkage must be present at C-2′, indicating the presence of a disaccharide moiety, 2-*O*-β-D-apiosyl-D-glucose (11). Actual connectivities between the iridoid, sugar, and monoterpene moieties were clearly identified from the results of a single HMBC experiment made with **1a** (Figure 1). From this spectrum, correlations between C-1 of the iridoid aglycone (δ 94.3) and H-1′ of β-D-glucose (δ 4.86), C-1″ of β-D-apiose (δ 106.2) and H-2′ of β-D-glucose (δ 3.72), and C-1‴ of 6,7-dihydrofoliamenthic acid (δ 167.4) and $H_2$-5″ of β-D-apiose (δ 4.54 and 4.73) were evident. All of these deductions were supported by the fabms of **1a** which displayed a $[M+Na]^+$ ion at *m/z* 951, consistent with the molecular formula $C_{43}H_{60}O_{22}$ and showed the typical fragments at *m/z* 715 and 427 for the apiosyl-glucose and apiose moieties esterified with 6,7-dihydrofoliamenthic acid, respectively. Compound **1** was thus established as 2′-*O*-[5″-*O*-(8-hydroxy-2,6-dimethyl-2(*E*)-octenoyl)-β-D-apiofuranosyl]-mussaenosidic acid, for which the trivial name inerminoside A is proposed.

Inerminoside B [**2**] was obtained as amorphous colorless powder. From the fabms of its methyl ester derivative, which displayed a $[M+Na]^+$ ion at *m/z* 711, a molecular formula of $C_{31}H_{46}O_{16}$ was proposed for **2**. Uv (227.5 nm) and ir absorptions (3350, 1700,

TABLE 2. $^{1}$H-Nmr Spectral Data for **2** and **2a** (**2** in $CD_3OD$; 300 MHz, **2a** in $CDCl_3$ at 500 MHz).

| H | **2** | | **2a**[a] | |
|---|---|---|---|---|
| | δ (ppm) | *J* (Hz) | δ (ppm) | *J* (Hz) |
| 1 | ca. 5.43[b] | | 5.21 d | (5.3) |
| 3 | 7.38 s | | 7.40 d | (1.0) |
| 5 | 3.02 "q" like | (7.4) | 2.97 "q" like | (8.2) |
| 6a | 1.90 m | | 1.87 m | |
| 6b | 2.10 m | | 2.26 m | |
| 7 | 3.93[b] | | 4.74 m | |
| 8 | 2.14 m | | 2.32 m | |
| 9 | 2.43 m | | 2.43 m | |
| 10 | 1.13 d | (7.2) | 1.07 d | (7.1) |
| 1′ | 4.76 d | (7.6) | 4.78 d | (7.9) |
| 2′ | 3.47 dd | (9.0, 7.6) | 3.65 dd | (9.6, 7.9) |
| 3′ | 3.55 t | (9.0) | 5.14 t | (9.5) |
| 4′ | 3.28–3.43[b] | | 4.92 dd "t" | (9.8, 9.7) |
| 5′ | 3.28–3.43[b] | | 3.63 m | |
| 6′a | 3.66 dd | (12.9, 2.0) | 4.18 dd | (12.4, 2.4) |
| 6′b | ca. 3.90[b] | | 4.08 dd | (12.4, 4.8) |
| 1″ | ca. 5.42 | | 5.01 br s | |
| 2″ | 3.93 s | | 5.11 br s | |
| 4″ | 3.80 d | (9.8) | 4.03 d | (10.3) |
| 4″ | 4.24 d | (9.8) | 4.17 d | (10.3) |
| 5″ | 4.26 br s | | 4.54 br s | |
| 3‴ | 6.85 br t | (7.0) | 6.68 dt | (7.3, 1.5) |
| 4‴ | 2.39 m | | 2.24 m | |
| 5‴ | 2.24 m | | 2.10 m | |
| 7‴ | ca. 5.44[b] | | 5.31 dt | (7.1, 1.3) |
| 8‴ | 4.14 d | (6.6) | 4.52 d | (7.1) |
| 9‴ | 1.87 br s | | 1.75 d | (1.3) |
| 10‴ | 1.74 s | | 1.66 d | (0.7) |

[a]Additional acetyl signals were observed at δ 1.95, 1.969, 1.996 (each 3H), 2.00, 2.01 (each 6H) (aliph.×7).

[b]Signal patterns were unclear due to overlapping.

1670, and 1630 $cm^{-1}$) were similar to those of **1**. Its $^{1}$H- and $^{13}$C-nmr spectral data (Tables 2 and 3) showed a close resemblance to those of **1**, with some important exceptions. The signals for the biosidic sugar moiety were clearly similar to those of **1** indicating the presence of the same glycobiose, esterified at the same location as in **1**. The assignments of the methyl resonances—a broad singlet at δ 1.87 for an olefinic methyl, a singlet at δ 1.74 for a tertiary methyl and a doublet at δ 1.13 (d, $J$=7.2 Hz)—based on 2D $^{1}$H,$^{1}$H-homonuclear COSY, indicated the secondary methyl group belongs to the iridoid skeleton, hence differing from **1**. In addition, the $^{1}$H-nmr spectrum of **2** showed resonances for two olefinic protons at δ 6.86 and 5.44. The $^{13}$C-nmr spectrum exhibited four resonances for $sp^2$ carbons at δ 128.8, 144.0, 138.5, and 125.7. These and associated carbon and proton resonances were indicative of the presence of a foliamenthoyl (8-hydroxy-2,6-dimethyl-2(*E*),6(*E*)-octadienoic acid) moiety in **2**, as reported for similar iridoids (8,10).

Resonances for the iridoid aglycone unit were in good agreement with those for 8-*epi*-loganic acid (12). In order to confirm this deduction acetyl derivatives of **2** and 8-*epi*-loganin were prepared. Acetylation of **2** yielded a heptaacetate [**2a**], while acetylation of 8-*epi*-loganin yielded a pentaacetate. For both compounds extensive 2D nmr experiments, including HMQC and HMBC, enabled the complete assignment of all $^{1}$H- and

TABLE 3. $^{13}$C-Nmr Spectral Data for **1**, **1a**, **2**, **2a**, and **3**.[a]

| C | 1 | 1a[b] | 3 | 2 | 2a[b] |
|---|---|---|---|---|---|
| 1 | 94.5 d | 94.3 d | 94.4 d | 95.8 d | 94.5 d |
| 3 | 152.2 s | 152.0 s | 149.8 s | 153.0 s | 152.4 s |
| 4 | 113.4 s | 112.0 s | [c] | [c] | 111.6 s |
| 5 | 32.6 d | 31.9 d | 31.9 d | 31.1 d | 30.9 d |
| 6 | 30.8 t | 29.7 t | 30.6 t | 40.6 t | 38.1 t |
| 7 | 40.1 t | 39.4 t | 41.2 t | 79.2 d | 80.8 d |
| 8 | 80.9 s | 80.4 s | 80.9 s | 45.6 d | 41.9 d |
| 9 | 52.2 d | 51.2 d | 52.5 d | 43.5 d | 41.8 d |
| 10 | 25.1 q | 24.9 q | 24.4 q | 14.6 q | 13.7 q |
| 11 | 170.0 s | 169.1 s | [c] | 170.0 s | 169.1 s |
| 1′ | 98.4 d | 96.6 d | 98.2 d | 98.2 d | 96.6 d |
| 2′ | 77.9 d | 75.4 d | 77.8 d | 77.8 d | 75.8 d |
| 3′ | 78.3 d | 74.2 d | 78.2 d | 78.3 d | 74.2 d |
| 4′ | 71.9 d | 68.6 d | 71.9 d | 71.9 d | 68.6 d |
| 5′ | 78.3 d | 71.9 d | 78.5 d | 78.4 d | 71.9 d |
| 6′ | 63.0 t | 62.9 t | 63.0 t | 63.0 t | 61.8 t |
| 1″ | 110.2 d | 106.2 d | 110.5 d | 110.2 d | 106.3 d |
| 2″ | 78.9 d | 76.4 d | 79.1 d | 78.9 d | 76.4 d |
| 3″ | 79.2 s | 83.9 s | 80.3 s | 79.2 s | 83.7 s |
| 4″ | 75.5 t | 73.2 t | 75.4 t | 75.4 t | 72.9 t |
| 5″ | 68.7 t | 63.7 t | 66.1 t | 68.7 t | 63.4 t |
| 1‴ | 169.5 s | 167.4 s | | 169.5 s | 167.2 s |
| 2‴ | 128.4 s | 127.1 s | | 128.8 s | 127.5 s |
| 3‴ | 144.7 d | 143.4 d | | 144.0 d | 142.4 d |
| 4‴ | 27.3 t | 26.3 t | | 28.1 t | 26.9 t |
| 5‴ | 36.9 t | 35.3 t | | 36.9 t | 37.9 t |
| 6‴ | 30.6 d | 29.7 d | | 138.5 s | 142.1 s |
| 7‴ | 40.6 t | 35.2 t | | 125.7 d | 119.1 d |
| 8‴ | 61.0 t | 61.6 t | | 59.4 t | 61.3 t |
| 9‴ | 12.5 q | 12.3 q | | 12.5 q | 12.3 q |
| 10‴ | 19.8 q | 19.4 q | | 16.2 q | 16.4 q |

[a]At 75.5 MHz; in $CD_3OD$ [**1–3**] and $CDCl_3$ [**1a**, **2a**], and multiplicity by DEPT.

[b]Additional signals for **1a** were observed at δ 169.7–171.6 ($COCH_3$) and 20.6–21.1 ($COCH_3$), and for **2a** at δ 169.6–171.3 ($COCH_3$) and 20.6–21.2 ($COCH_3$).

[c]Not observed.

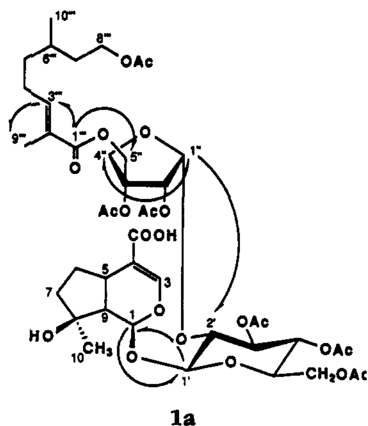


FIGURE 1. Schematic representation of diagnostic heteronuclear multiple bond correlations found for inerminoside A hexaacetate [**1a**]. Arrows point from carbon-to-proton resonances.

$^{13}$C-nmr resonances (see Table 2 and Experimental). The spectral data assigned to the aglycone (iridoid skeleton) moieties suggested the relative stereochemistry at C-8 to be the same. This deduction was also supported by the 2D NOESY data of **2a** and 8-*epi*-loganin pentaacetate which exhibited almost identical cross-peaks. These experiments clearly showed H-1, H-7, and Me-10 to be α. The existence of an 8-*epi*-loganic acid moiety in **2**, rather than its epimer, is also consistent with the chemotaxonomic data of family Verbenaceae (13). Finally, the long-range inverse-correlated spectrum (HMBC) of **2a** made clear all connectivities between the major molecular fragments. Once again all deductions made from the nmr spectral data were confirmed and supported by the fabms data of **2a**. Compound **2** was thus established as 2′-*O*-[5″-*O*-(8-hydroxy-2,6-dimethyl-2(*E*),6(*E*)-octadienoyl)-β-D-apiofuranosyl]-8-*epi*-loganic acid, for which the trivial name inerminoside B is proposed.

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—See Çaliş *et al.* (14).

PLANT MATERIAL.—*Clerodendrum inerme* Gaertn., was collected from Al-Orman Garden, Giza, Egypt, in May–June 1991, and identified by Dr. Nabil El-Hadidy, Faculty of Science, Cairo University. A voucher specimen (no. 701) has been deposited at the Herbarium of the Plant Taxonomy Department, Faculty of Science, Cairo University, Cairo, Egypt.

EXTRACTION AND ISOLATION.—The air-dried leaves (500 g) were extracted with MeOH at ca. 40°. The $H_2O$-soluble part of the MeOH extract was partitioned successively with petroleum ether, $Et_2O$, and BuOH. Fractionation of the BuOH extract over polyamide, eluting with $H_2O$ containing increasing amounts of MeOH in $H_2O$ gave five fractions A–E (frs. A, 8.5 g; B, 2.7 g; C, 1.6 g; D, 680 mg; E, 380 mg). Fraction A was chromatographed over Si gel with $CHCl_3$-MeOH-$H_2O$ (80:20:1, 70:30:3, and 60:40:4) to yield six main fractions, A1–A6 (A1, 325 mg; A2, 345 mg; A3, 775 mg; A4, 464 mg; A5, 550 mg; A6, 1.8 g). Fractions A3 and A5 were subjected separately to mplc (Sepralyte 40 μm, MeOH-$H_2O$ gradient, 5–45% MeOH) to give **1** (187 mg) and **2** (39 mg).

*Inerminoside A* [**1**].—Amorphous colorless powder; ir ν max 3350, 1700, 1670, and 1630 $cm^{-1}$; fabms $[M+Na]^+$ 699 (61); uv λ max 228 nm; $^1$H nmr (300 MHz, $CD_3OD$) see Table 1, $^{13}$C nmr (75.5 MHz, $CD_3OD$) see Table 3.

ALKALINE HYDROLYSIS OF INERMINOSIDE A [**1**].—Compound **1** (20 mg) was heated in aqueous 5% KOH (1 ml) at 80° for 2 h. After neutralization with aqueous 5% HCl, the solution was evaporated to dryness. The residue was purified over Si gel using $CHCl_3$-MeOH (9:1, 8:2) to afford **3** (9.5 mg).

*Deacyl-inerminoside A* [**3**].—$^1$H nmr (300 MHz, $CD_3OD$) see Table 1; $^{13}$C nmr (75.5 MHz, $CD_3OD$) see Table 3.

ACETYLATION OF **1** AND **2**.—Treatment of inerminosides A [**1**] and B [**2**] (each 15 mg) separately with $Ac_2O$ (0.5 ml) and pyridine (0.5 ml) at room temperature overnight followed by cc over Si gel using $C_6H_6$-$Me_2CO$ (9:1) gave **1a** and **2a**, respectively.

*Inerminoside A hexaacetate* [**1a**].—$^1$H nmr (300 MHz, $CDCl_3$) see Table 2; $^{13}$C nmr (75.5 MHz, $CDCl_3$) see Table 3; fabms $[M+Na]^+$ 951, 715, and 427.

*Inerminoside B* [**2**].—Amorphous colorless powder; ir ν max 3350, 1700, 1670, and 1630 $cm^{-1}$; fabms $[M+Na]^+$ 697 (calcd for $C_{31}H_{46}O_{16}$, 674); uv λ max 227.5 nm; $^1$H nmr (300 MHz, $CD_3OD$) see Table 2; $^{13}$C nmr (75.5 MHz, $CD_3OD$) see Table 3.

*Inerminoside B heptaacetate* [**2a**].—$^1$H nmr (500 MHz, $CDCl_3$) see Table 2; $^{13}$C nmr (125 MHz, $CDCl_3$) see Table 3; fabms $[M+Na]^+$ 991, 713, and 425.

8-epi-*Loganin pentaacetate*.—$^1$H nmr (300 MHz, $CDCl_3$) δ 5.33 (1H, d, $J$=2.6 Hz, H-1), 7.32 (1H, s, H-3), 3.01 (1H, m, H-5), 1.88 and 2.22 (2H, each m, H-6a and H-6b, respectively), 4.81 (1H, m, H-7), 2.32 (1H, m, H-8), 2.68 (1H, m, H-9), 0.99 (3H, d, $J$=7.5 Hz, Me-10), 3.70 (3H, s, COOMe), 4.86 (1H, d, $J$=8.1 Hz, H-1′), 4.99 (1H, dd, $J$=8.1 and 9.6 Hz, H-2′), 5.22 (1H, t, $J$=9.6 Hz, H-3′), 5.10 (1H, t, $J$=9.6 Hz, H-4′), 3.72 (1H, m, H-5′), 4.15 (1H, dd, $J$=12.5 and 2.4 Hz, H-6′a) and 4.29 (1H, dd, $J$=12.5 and 4.7 Hz, H-6′b), and 2.10, 2.03, 2.02, 2.00, and 1.92 (each 3H, s, aliph. acetyl×5); $^{13}$C nmr (75.5 MHz, $CDCl_3$) δ 94.3 d (C-1), 149.6 d (C-3), 113.9 s (C-4), 28.9 d (C-5), 37.4 t (C-6), 81.2 d (C-7), 41.2 d (C-8), 41.1 d (C-9), 13.6 q (Me-10), 167.1 s (C-11), 51.3 q (COO*Me*), 95.6 d (C-1′), 70.6 d (C-2′),

72.5 d (C-3′), 68.2 d (C-4′), 72.2 d (C-5′), 61.7 t (C-6′), 21.3, 20.7, 20.6 (×2), 20.2 (each s, CO*Me*×5), 170.6 (×2), 170.2, 169.4 and 169.2 (each s, *C*OMe×5) ppm.

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