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# GERMACRA-12,6β-OLIDES FROM *MONTANOA REVEALII* AND *M. MOLLISSIMA**

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**Key Word Index**—*Montanoa revealii*; *Montanoa mollissima*; Asteraceae; Heliantheae; sesquiterpene lactones; germacranolides.

**Abstract**—*Montanoa revealii* and *M. mollissima* yielded a series of germacra-12,6β-olides similar to those previously reported from *M. hibiscifolia* and *M. pteropoda*.

## INTRODUCTION

Germacra-12,6β-olides have previously been reported from three *Montanoa* taxa, *M. pteropoda* S. F. Blake [1, 2], *M. hibiscifolia* Benth. in Oerst. [2] and *M. atriplicifolia* (Pers.) Schultz Bip. in Seeman [3], *Ursinia anthemoides* (L.) Poiret (Anthemideae) [4] and *Pegolettia senegalensis* Cass. (Inuleae) [5]. X-Ray analysis of the *M. hibiscifolia* compounds established the novel *trans,trans*-germacra-1(10),4-dien-12,6β-olide structure. In continuation of our biochemical systematic study of *Montanoa*, the terpenes of *M. revealii* H. Robinson and *M. mollissima* Brongniart ex Groenland were investigated and both taxa found to produce germacra-12,6β-olides; *Montanoa revealii* yielded compounds **1**, **2**, **3**, **5** and **6** and *M. mollissima* produced structures **7**, **8**, **9** and **10**.

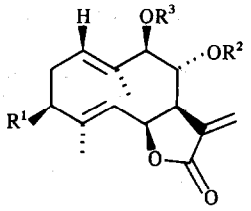
## RESULTS AND DISCUSSION

$^1$H NMR spectra of the *M. revealii* compounds **1–3** resembled spectra of the structures (e.g. **4**) reported from *M. pteropoda* and *M. hibiscifolia* [2]. Compounds **1–3** share with these structures the small $J_{7,13}$ (1 Hz) and large $J_{5,6}$ (approx. 11 Hz) and $J_{6,7}$ values (*ca* 6 Hz) typical of germacra-12,6β-olides. Further, the large $J_{7,8}$ (8 Hz) and $J_{8,9}$ (9 Hz) values of **1–3** indicate that these compounds also share a common stereochemistry at C-8 and C-9 with the *M. pteropoda* and *M. hibiscifolia* constituents.

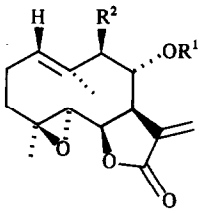
8α-Hydroxy-9β-angeloyloxy-*trans,trans*-germacra-1(10),4-dien-12,6β-olide (**1**) $C_{20}H_{26}O_5$ (HRMS) and 8α-hydroxy-9β-(2-methylbutanoyloxy)-*trans,trans*-germacra-1(10),4-dien-12,6β-olide (**2**) $C_{20}H_{28}O_5$ (HRMS) were isolated as a mixture. The $^1$H NMR spectra (Table 1) of **1** and **2** displayed a pair of downfield broadened singlets (H-13a, δ 5.77; H-13b, δ 6.42) and an upfield broad doublet of a doublet (H-7, δ 3.18) typical of α,β-unsaturated γ-lactones. Irradiation at δ 3.18 sharpened the H-13a and H-13b signals to finely split doublets (geminal coupling, $J$ < 0.5 Hz), collapsed a doublet of a doublet at δ 5.17 (H-6) to a doublet ($J$ = 11 Hz) and a doublet of a doublet at δ 4.10 (H-8) to a doublet ($J$ = 9 Hz). Irradiation of this signal at δ 4.10 collapsed a doublet at δ 4.78 (H-9) to a singlet and simplified the H-7 signal. A broadened apparent triplet at δ 5.35 (H-1, $J$ = 7 Hz) when irradiated, sharpened the broad methyl singlet at δ 1.67 (H-14). Low resolution EIMS of **1** and **2** showed molecular ions at $m/z$ 346 and 348, respectively, and a common ion at $m/z$ 246 resulting from the loss of the C-9 side chain acids. Loss of water ($m/z$ 228) from the $m/z$ 246 ion indicates the presence of a free hydroxyl function in both **1** and **2**. EIMS sidechain acylium ions and other fragments (**1**, $m/z$ 83, 55; **2**, $m/z$ 85, 57) support the assigned structures, and the CIMS (isobutane) confirms the molecular formulas for **1** and **2** (Experimental).

$^1$H NMR spectra of **3** ($CDCl_3$; $CDCl_3$ and $C_6D_6$, 4:1) produced two broadened singlets at δ 5.54 (H-13a) and 6.25 (H-13b) and a broadened doublet of a doublet at δ 3.12 (H-7, $CDCl_3$) characteristic of α,β-unsaturated γ-lactone (Table 1). Irradiation at δ 3.12 sharpened the two signals at δ 5.54 and 6.25, simplified the doublet of a doublet at δ 5.10 (H-6) to a doublet ($J$ = 11 Hz) and the doublet of a doublet at δ 5.14 (H-8) to a doublet ($J$ = 9 Hz). Irradiation at δ 5.14 collapsed the doublet at δ 4.09 (H-9) to a singlet. Irradiation of one methyl doublet at δ 1.56 (H-15, $J$ = 1.0 Hz, $CDCl_3$ and $C_6D_6$) sharpened a downfield doublet at δ 5.12 (H-5, $J$ = 11 Hz); irradiation of the other methyl signal at δ 1.45 sharpened the broad triplet at δ 5.51 (H-1, $J$ = *ca* 8 Hz). Irradiation of the overlapping H-1 and H-3 signals at 5.62 ($CDCl_3$) affected only the two overlapping one-proton signals at δ 2.2–2.38 and the H-14 methyl signal. Upon addition of $C_6D_6$ to the $CDCl_3$ NMR sample solution of **3**, the two signals, H-1 and H-3, separated. Irradiation at δ 2.26 ($CDCl_3$:$C_6D_6$; 4:1) partially collapsed both the H-1 and H-3 signals to singlets centered at δ 5.57 (H-3) and 5.51 (H-1). Partial collapse seems to result from the incomplete irradiation of both H-2 protons. Examination of Dreiding models of **3** oriented in a conformation according to the results of the X-ray analysis of *M. hibiscifolia* compounds [2] demonstrates that the coupling between H-1 and H-2 ($J$ = *ca* 8 Hz) is consistent with the model and that the coupling

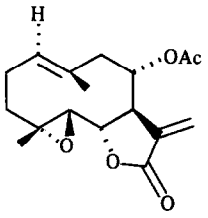
*Part 3 in the series "*Montanoa*—Terpenes".



**1** $R^1 = R^2 = H$, $R^3$ = Ang
**2** $R^1 = R^2 = H$, $R^3$ = 2 - Mebut
**3** $R^1$ = OAc, $R^2$ = Ang, $R^3 = H$
**4** $R^1 = H$, $R^2$ = Epoxyang, $R^3$ = Ac



**5** $R^1$ = Ang, $R^2 = H$
**6** $R^1$ = Sen, $R^2 = H$
**7** $R^1$ = 2-Mebut, $R^2 = H$
**8** $R^1 = H$, $R^2$ = OSen
**9** $R^1 = H$, $R^2$ = 02 - Mebut
**10** $R^1 = H$, $R^2$ = 0i - But



**11**

Table 1. $^1$H NMR signals for compounds **1, 2** and **3** at 200 MHz (TMS as internal standard, $CDCl_3$)

| | 1 | 2 | 3 | 3 ($CDCl_3$–$C_6D_6$, 4:1) |
|---|---|---|---|---|
| H-1 | 5.35 *br t* (8)* | 5.35 *br t* (8) | 5.58–5.70 | 5.51 *br t* (8.5) |
| H-2 | 2.0–2.5 | 2.0–2.5 | 2.0–2.5 | 2.05–2.20 |
| H-3 | — | — | — | 5.57 *dd* (5.5, 6) |
| H-5 | 4.96 *br d* (11) | 4.96 *br d* (11) | 5.21 *br d* (11) | 5.12 *br d* (11) |
| H-6 | 5.17 *dd* (11, 6) | 5.15 *dd* (11, 6) | 5.10 *dd* (11, 6) | 4.93 *dd* (11, 6) |
| H-7 | 3.18 *br dd* (6, 9) | 3.18 *br dd* (6, 9) | 3.12 *br dd* (6, 8) | 3.12 *br dd* (6, 8) |
| H-8 | 4.10 *dd* (9, 9) | 4.05 *dd* (9, 9) | 5.14 *dd* (8, 9) | 5.10 *dd* (8, 9) |
| H-9 | 4.78 *d* (9) | 4.70 *d* (9) | 4.09 *d* (9) | 4.09 *d* (9) |
| H-13a | 5.77 *br s* | 5.77 *br s* | 5.54 *br s* | 5.39 *br s* |
| H-13b | 6.42 *br s* | 6.42 *br s* | 6.25 *br s* | 6.20 *br s* |
| Me-10 | 1.67 *br s* | 1.67 *br s* | 1.62 *d* (1) | 1.45 *br s* |
| Me-4 | 1.71 *br s* | 1.71 *br s* | 1.73 *d* (1) | 1.56 *d* (1) |
| H-2′ | — | 2.40 *m* | — | — |
| C-2′-$CH_3$ | 1.92 *br s* | 1.14 *d* (7) | 1.87 *m* | 1.82 *m* |
| H-3′a | 6.09 *qq* (1, 7) | — | 6.08 *qq* (1, 7) | 5.97 *qq* (1, 7) |
| H-3′b | — | — | — | — |
| C-3′-Me | 1.99 *dq* (1, 7) | 0.92 *t* (7) | 1.97 *dq* (1.5, 7) | 1.95 *m* |
| -OAc | — | — | 2.17 *s* | 1.97 *s* |

*Numbers in parentheses are coupling constants or line separations in Hertz.

between H-2a, H-2b and H-3 ($J$ = 5.5, 6 Hz) is only in agreement with the stereochemistry in which the C-3 acetate is in a $\beta$-position. $^1$H NMR signals indicate the presence of one acetate and one angelate moiety in this molecule.

$^1$H NMR spectra of compounds **5–10** partially resemble spectra of 4α,5β-epoxy-*trans*-germacra-12,6α-olides such as 8α-acetoxyparthenolide (**11**) [6] (Table 2). However, compounds **5–10** are typified by $J_{7,13}$ values less than 1 Hz, while **11** exhibits characteristic $J_{7,13}$ > 3 Hz. Other coupling constants for **5–10** are consistent with germacrolide structures indicating that, like **1–3**, the small $J_{7,13}$ of **5–10** must be due to $\beta$-orientation of the lactone oxygen at C-6.

8α-Angeloyloxy-4β,5α-epoxy-*trans*-germacra-1(10)-en-12,6β-olide (**5**), $C_{20}H_{26}O_5$ and its 8α-senecionyl isomer (**6**) were isolated as a mixture. The $^1$H NMR spectrum of **5** and **6** displayed the characterisitic broad singlets at δ 5.67 (H-13a) and 6.29 (H-13b) and a broadened doublet of a doublet at δ 3.22 (H-7). Irradiation of the signal at δ 3.22 collapsed two downfield one-proton signals at δ 4.07 and 5.27. The doublet of a doublet at δ 4.07 was assigned to H-

Table 2. $^1$H NMR signals for compounds **5**–**10** (200 MHz, TMS as internal standard, $CDCl_3$) at 300°K and $C_6D_6$ at 348°K

| | **5** | **6** | **7** | **8** ($CDCl_3$) | **9** ($CDCl_3$) | **9** ($C_6D_6$) | **10** ($CDCl_3$) |
|---|---|---|---|---|---|---|---|
| H-1 | 5.44 *t* (7.5) | 5.45 *m* | 5.44 *m* | 5.62 *m* | 5.57 | 5.31 *m** | 5.58 *m** |
| H-2 | 2.1–2.4 | 2.1–2.4 | 2.1–2.4 | * | 2.20–3.50 | * | * |
| H-3 | 2.0–2.4 | 2.0–2.4 | 2.0–2.4 | * | | * | * |
| H-5 | 3.05 *br d* (10.0) | 3.04 *br d* (10.0) | 3.05 *br d* (10.0) | 2.99 (9.5) | 2.98 *d* (9.5) | 2.73 *d* (9.5) | 3.00 *d* (9.5) |
| H-6 | 4.07 *dd* (10.0, 5.0) | 4.06 *dd* (10.0, 5.5) | 4.07 *dd* (10.0, 5.0) | 4.05 *dd* (9.5, 6.0) | 4.05 *dd* (9.5, 6.0) | 3.67 *dd* (9.5, 5.0) | 4.05 *dd* (9.5, 6.0) |
| H-7 | 3.22 *br dd* (5.0, 8.0) | 3.18 *br dd* (5.5, 10.0) | 3.22 *br dd* (5.0, 8.0) | 3.09 *ddt* (6.0, 6.0, 1.0) | 3.07 *br dd* (6.0, 6.5) | 2.62 *ddt* (6.0, 6.5, 1.0) | 3.08 *br dd* (6.0, 6.5) |
| H-8 | 5.27 *m* | 5.27 *m* | 5.27 *m* | 4.25 *m*† | 4.25 *dd*† | 3.94 *dd* (7.0, 9.5) | 4.27 *dd*† (7.0, 9.0) |
| H-9 | | | | 4.66 *br d*† (9.0) | 4.65 *d* (9.0) | 4.70 *d* (9.0) | 4.65 *br d*† (9.0) |
| H-13a | 5.67 *d* (1.0) | 5.62 *br s* | 5.67 *d* (1.0) | 5.73 *d* (1.0) | 5.73 *br s* | 5.26 *br s* | 5.47 *d* (1.5) |
| H-13b | 6.29 *d* (1.0) | 6.16 *d* (1.0) | 6.29 *d* (1.0) | 6.38 *d* (1.0) | 6.38 *br s* | 6.27 *br s* | 6.38 *d* (1.5) |
| H-14 (3H) | 1.83 *br s* | 1.83 *br s* (1.0) | 1.83 *br s* | 1.99 *br s*† | 1.98 *br s* | 1.63 *d* (1.0) | 1.97 *br s*† |
| H-15 (3H) | 1.31 *s* | 1.31 *s* | 1.31 *s* | 1.30 *s* | 1.30 *s* | 0.83 *s* | 1.29 *s* |
| H-2′ | | 5.56 *m* | 2.0–2.5 | 5.71 *m** | 2.42 *hex* (7.0) | 2.29 *hex* (7.0) | 2.55 *hep* (7.0) |
| H-2′ Me | 1.88 *d* (1.0) | | 1.0–1.1 | | 1.14 *d* (7.0) | 1.08 *d* (7.0) | 1.16 *d* (7.0) |
| H-3a′ | 5.96 *qq* (1.0, 7.0) | | 1.0–1.5 | | 1.47 *pent* (7.0) | * | 1.17 (3H) *d* (7.0) |
| H-3b′ | | | 1.0–1.5 | | 1.68 *pent* (7.0) | * | |
| C-3′-Me | 1.96 *dq* (1.0, 7.0) | 2.13 *d* (1.0) 1.89 *d* (1.5) | 0.8–1.0 | 2.16 *d* (1.0) 1.90 *d* (1.5) | 0.89 *t* (7.0) | 0.83 *t* (7.0) | |

*Obscured by other signals.

†Broadening due to presence of configurational differences evident at 300 K.

6 by reciprocal irradiation at $\delta$4.07 and an affected doublet at $\delta$ 3.05 (H-5, $J_{5,6}$ = 10 Hz), a pair of signals that together with a sharp three-proton singlet at $\delta$ 1.31 (H-15) are characteristic of a 4,5-epoxy-germacra-6,12-olide. Upon irradiation at $\delta$ 3.22, the multiplet at $\delta$ 5.27 simplifies to a doublet of a doublet ($J_{8,9a}$ = 11 Hz, $J_{8,9b}$ = *ca* 3 Hz) and is assigned to H-8. Aside from signals characteristic of angelate (**5**) and senecionate (**6**) moieties, the only remaining downfield signal, a multiplet at $\delta$ 5.44, upon irradiation, sharpened the three-proton broad singlet at $\delta$ 1.83 (H-14) indicating that the signal at $\delta$ 5.44 must be due to H-1. Low resolution EIMS of **5** and **6** did not yield a molecular ion but produced a strong $[M - C_5H_8O_2]^+$ (*m/z* 246) corresponding to the loss of angelic acid (**5**) and senecionic acid (**6**). Ions at *m/z* 83 $[C_5H_7O]^+$ and *m/z* 55 $[C_4H_7]^+$ are characteristic of both angelates and senecionates. CIMS (M + 1 = 347.2) and high resolution mass spectrometry confirmed the molecular formulae for **5** and **6** ($C_{20}H_{26}O_5$). $^1$H NMR, EIMS and CIMS indicated that **7** only differed from **5** and **6** by the presence of a 2-methylbutyrate at C-8 (Table 2).

$^1$H NMR spectra of compounds **8**, **9** and **10** indicated that they were also 4β,5α-epoxy germacra-1(10)-en-12,6β-olides (Table 2). Differences in the $^1$H NMR spectra of **2** and **9** were limited to the chemical shifts of H-5, H-6 and H-15, indicating that the two structures were identical except for the presence of the 4,5-*trans* double bond in **2** and the 4,5-epoxide in **9**. Complete decoupling experiments ($C_6D_6$, 348 K) confirmed the location of the C-8 hydroxy and C-9 ester function of **9**. $^1$H NMR (Table 2) and EIMS results for **8** and **10** indicated that they differed from **9** in the ester functions at C-9, with **8** displaying signals corresponding to a senecionate and **10** exhibiting signals for an isobutyrate moiety (see Experimental).

The stereochemistry of the 4,5-epoxide function in compounds **5**–**10** is tentatively assigned on biogenetic grounds. It is a reasonable assumption that germacrolides of structural type **1** have [$^1D_{14,15}D^5$]-conformation [7] as do their analogs with established X-ray structure [2]. If the above conformational representatives also represent the biogenetic precursors for the epoxides **5**–**10**, bio-epoxidation should only occur from the outer face of the medium ring resulting in a stereochemistry of the 4,5-epoxide group as shown for the lactones **5**–**10**.

## EXPERIMENTAL

For general procedures, see ref. [8]. NMR spectra were

Table 1. $^1$H NMR spectral data of compounds **3–6** (400 MHz, $CDCl_3$, TMS as internal standard)

| | 3 | 4 | $CDCl_3/C_6D_6$ | 5 | 6 |
|---|---|---|---|---|---|
| H-1 | 4.93 *dd br* | 3.18 *m* | 2.84 *ddd br* | 3.18 *m* | 3.60 *ddd* |
| H-2 | 2.52 *ddd br* | 2.51 *dddq* | 2.33 *dddq* | 2.50 *dd br* | 5.80 *dd* |
| H-2′ | 2.33 *ddd* | 2.42 *dddq* | 2.26 *dddq* | 2.41 *d br* | |
| H-3 | 4.36 *dd* | 5.57 *dddq* | 5.41 *dddq* | 5.57 *dddq* | 6.01 *dd* |
| H-5 | 4.84 *d br* | 2.85 *dd br* | 2.57 *dd br* | 2.84 *dd br* | 2.96 *dd* |
| H-6 | 5.21 *dd* | 4.51 *dd* | 4.37 *dd* | 4.47 *dd* | 4.71 *dd* |
| H-7 | 2.92 *ddd br* | 3.18 *m* | 2.75 *dddd* | 3.18 *m* | 3.12 *dddd* |
| H-8 | 5.81 *ddd* | 5.67 *ddd* | 5.44 *ddd* | 5.66 *ddd* | 5.75 *ddd* |
| H-9 | 2.85 *dd br* | 2.59 *dd* | 2.41 *dd* | 2.59 *dd* | 2.81 *dd* |
| H-9′ | 2.33 *dd* | 2.54 *dd* | 2.22 *dd* | 2.54 *dd* | 2.42 *dd br* |
| H-13 | 6.33 *d* | 6.24 *d* | 6.12 *d* | 6.25 *d* | 6.29 *d* |
| H-13′ | 5.63 *d* | 5.55 *d* | 5.34 *d* | 5.54 *d* | 5.65 *d* |
| H-14 | 1.52 *s br* | 5.01 *s br* | 4.85 *s br* | 5.00 *s br* | 4.92 *s* |
| H-14′ | | 4.87 *s br* | 4.71 *s br* | 4.85 *s br* | |
| H-15 | 1.81 *d* | 1.87 *s br* | 1.80 *s br* | 1.87 *s br* | 1.45 *s* |
| H-3′ | 6.72 *t* | 7.02 *t* | 6.88 *t* | 6.90 *t* | 7.05 *t* |
| H-4′ | 4.85 *dd* | 4.50 *dd* | 4.20 *dd* | 4.88 *d* | 5.01 *d* |
| | | 4.45 *dd* | 4.15 *dd* | | 4.89 *d* |
| H-5′ | 4.38 *s br* | 4.97 *d* | 4.78 *d* | 4.89 *d* | 4.53 *dd* |
| | | 4.91 *d* | 4.73 *d* | 4.85 *d* | 4.48 *dd* |
| H-8′ | — | 6.89 *q* | 6.75 *q* | 7.04 *q* | 6.89 *q* |
| H-9′ | — | 1.90 *d* | 1.69 *d* | 1.93 *d* | 1.92 *d* |
| H-10′ | — | 4.30 *s* | 4.16 *s* | 4.80 *s* | 4.32 *s* |
| OAc | 2.10 *s* | — | — | | |

*J* [Hz]: compounds **4–6**: 1, 2 = 8.5; 1, 2′ = 5; 1, 5 = 8.5; 2, 2′ = 17; 2, 3 = 2, 3′ = 3, 5 = 3, 15 ~ 1.5; 5, 6 = 10.5; 6, 7 = 9; 7, 8 = 2.5; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 5; 8, 9′ = 5; 9, 9′ = 14; 3′, 4′ = 6; $4_1$′, $4_2$′ = 16; $5_1$′, $5_2$′ = 12; 8′, 9′ = 7.5 (compound **6**: 1, 2 = 2.5; 1, 3 = 1.5; 1, 5 = 10; 2, 3 = 6; 5, 6 = 11; 6, 7 = 9). Compound **3**: 1, 2 = 3.5; 1, 2′ = 11.5; 2, 2′ = 14; 2, 3 = 6; 2′, 3 = 10; 5, 6 = 10; 5, 15 = 1.5; 6, 7 = 9; 7, 8 ~ 1; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 5; 8, 9′ = 2; 9, 9′ = 14; 3′, 4′ = 6.5; 4′, 5′ = 1.5.

*newberryi*, especially the lactones, which are close to those of some genera of the tribe Eupatorieae, makes it a strong candidate as a likely primitive species in this 'core-group'.

## EXPERIMENTAL

The air-dried aerial parts (480 g) (collected in south central Colorado, U.S.A.; voucher Turner *s.n.* TEX) were extracted at room temp. with $Et_2O$–petrol–MeOH, 1:1:1, for 12 hr. The extract obtained was treated with MeOH to remove saturated long-chain hydrocarbons and was first separated by CC ($SiO_2$) into five fractions (each 100 ml): 1 (petrol), 2 ($Et_2O$–petrol, 1:10), 3 ($Et_2O$–petrol, 1:1), 4 ($Et_2O$) and 5 ($Et_2O$–MeOH, 10:1). TLC ($SiO_2$ PF 254) of fractions 1 and 2 gave no characteristic compounds. TLC of fraction 3 ($Et_2O$–petrol, 1:3, detection by UV light) afforded 4 mg **7** and 3 mg **8** [$R_f$ 0.46 and 0.49 respectively: identical with authentic material (400 MHz $^1$H NMR)], while TLC of fraction 4 gave no characteristic compounds. Repeated TLC of fraction 5 ($Et_2O$, followed by $CHCl_3$–MeOH, 10:1, detection by UV light) gave 200 mg **2** ($R_f$ 0.07), a mixture of **3** and **4** and **6** ($R_f$ 0.23), as well as 10 mg **1** ($R_f$ 0.7). **1** and **2** were identified by comparing the 400 MHz $^1$H NMR spectra with those of authentic material, and by systematic spin decoupling. The mixture of **2–4**, **6** and **9** was separated by HPLC (RP 8, MeOH–$H_2O$, 3:2). The main fraction ($R_t$ 8.1 min) gave 28 mg **4**, while the others ($R_t$ 2.0 and 3.8 min) were still impure. HPLC (RP 8, MeOH–$H_2O$, 11:9) of these fractions gave 10 mg of a mixture of **4** and **9**, 5 mg **3** ($R_t$ 2.7 min) and 2 mg **6** ($R_t$ 1.8 min). The mixture of **4** and **9** was separated after acetylation ($Ac_2O$, 1 hr, 70°). TLC ($Et_2O$) afforded 3 mg **5** and 5 mg **10** ($R_f$ 0.52). **3–6** could not be induced to crystallize, but their $^1$H NMR spectra showed no apparent impurities and they were homogeneous by TLC ($CHCl_3$–MeOH, 30:1 and $CHCl_3$–$C_6H_6$–$Et_2O$, 1:1:1).

*3β-Hydroxy-8β-(4′-acetoxy-5′-hydroxytigloyloxy)-costunolide* (**3**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 3620, 3420 (OH), 1770 (γ-lactone), 1745, 1240 (OAc), 1715 (C=$CCO_2R$); MS *m/z* (rel. int.): 246.125 [M − $RCO_2H$]$^+$ (8) (calc. for $C_{15}H_{18}O_3$: 246.125), 228 [246 − $H_2O$]$^+$ (7), 115 [RCO − ketene]$^+$ (40), 97 [115 − $H_2O$]$^+$ (54), 69 [97 − CO]$^+$ (100); CI (isobutane): 421 [M + 1]$^+$ (80), 247 [M − $RCO_2H$]$^+$ (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{+64 \quad +68 \quad +79 \quad +156} \ (CHCl_3;\ c\ 0.4).$$

*Ligustrin-[4′-hydroxy-5′-(5′-hydroxytigloyloxy)-tiglate]* (**4**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 3590, 3430 (OH), 1765 (γ-lactone), 1710 (C=$CCO_2R$); MS *m/z* (rel. int.): 458.194 [M]$^+$ (2) (calc. for $C_{25}H_{30}O_8$: 458.194), 440 [M − $H_2O$]$^+$ (1), 422 [440 − $H_2O$]$^+$ (0.6), 360 [M − $C_5H_6O_2$]$^+$ (3), 342 [M − $RCO_2H$]$^+$ (3), 246 [M − $C_{10}H_{12}O_5$]$^+$ (5), 228 [M − $RCO_2H$]$^+$ (41), 213 [RCO]$^+$ (10), 99 [RCO]$^+$ (67), 69 [99 − CHO]$^+$ (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{+18 \quad +19 \quad +22 \quad +71} \ (CHCl_3;\ c\ 2.6).$$