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LONGIPINENE DERIVATIVES FROM *STEVIA SERRATA*

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Key Word Index—*Stevia serrata*; Eupatorieae; Compositae; sesquiterpenes; longipinene derivatives.

Abstract—Five new longipinene derivatives, together with three known substances, were isolated from the roots of *Stevia serrata*. The new structures were established by spectroscopic and chemical methods.

INTRODUCTION

Chemical studies on *Stevia* species have revealed that many of them contain highly oxygenated longipinene derivatives [1–4]. Such is the case for *Stevia serrata* Cav. which yielded rastevione (**1**) [3] and diangelate (**2**) [4], from specimens collected in Mexico, and tiglate-methacrylate (**7**) as well as mixtures of **8** and **9**, and **10** and **11**, from a sample collected in Guatemala [5]. The present paper reports an exhaustive investigation of the minor constituents of this species, which further allowed the isolation of stigmasterol, eupha-8,24-dien-3β-yl acetate, the known longipinene derivative **12** previously isolated from *Eupatorium hyssopifolium* [6], and five new longipinene derivatives (**3**, **4**, **5**, **13** and **14**).

RESULTS AND DISCUSSION

Compound **3** showed IR bands for a hydroxyl group, a ketone and α,β-unsaturated ester groups. The ^{1}H NMR spectrum showed vinylic signals corresponding to angelate groups at δ6.19 and 6.10. The signals for the protons geminal to the oxygen atoms appeared as a doublet at δ5.46 (J = 3.4 Hz, H-9), a doublet at 5.20 (J = 11.1 Hz, H-7) and a double double doublet at 4.14 (J = 11.1, 8.5 and 3.4 Hz, H-8), which upon addition of D_2O became a double doublet. The multiplicity and chemical shifts of the three signals allowed the positional assignment of both angelate groups as was previously done for other longipinene derivatives [7, 8]. The remaining ^{1}H NMR and ^{13}C NMR spectral data (see Experimental and Table 1, respectively) revealed the presence of the longipinene moiety [3, 8] in agreement with structure **3**.

Compound **4** also showed IR absorptions for a hydroxyl group, a ketone and α,β-unsaturated ester groups. The ^{1}H NMR spectrum of **4** clearly indicated that this derivative was a positional isomer of **3**. The presence of a doublet at δ5.49 (J = 3.4 Hz) and a double doublet at 5.32 (J = 11.1 and 3.4 Hz) showed that the angelate groups were located at C-8 and C-9, while the double doublet at δ3.91 located the hydroxyl group at C-7. The remaining ^{1}H and ^{13}C NMR signals corroborate structure **4**.

Compound **5** was isolated by HPLC. Its IR spectrum indicated the presence of a saturated ester group, a ketone and α,β-unsaturated ester groups. The ^{1}H NMR spectrum showed at δ5.49 a doublet (J = 12.0 Hz), at 5.40 a double doublet (J = 3.1 and 12.0 Hz) and at 5.38 a doublet (J = 3.1 Hz). The comparison of the ^{1}H and ^{13}C NMR spectral data with those of **3** and **4** indicated that **5** could be the acetyl derivative of one of them. In order to determine its structure, we prepared the acetyl derivatives of both substances (**3** and **4**). Acetylation of **4** afforded **6**, whose spectral data were different from those of the natural product **5**, while acetylation of **3** afforded a substance identical in all respects to the natural product **5**. Therefore in **5** the acetate group was located at C-8 and the angelate groups at C-7 and C-9.

Compound **13** was also isolated by HPLC. Its IR spectrum showed bands for an acetate group, α,β-unsaturated ester groups and an α,β-unsaturated ketone. The ^{1}H NMR spectrum showed characteristic vinyl signals for angelate groups at δ6.13 and 6.07 and a singlet at 1.90 for the acetate group. The comparison of the signals for the protons geminal to the ester groups H-7, H-8 and H-9 with those of known compounds [8, 9] revealed that the acetate group was located at C-8 and the angelate groups at C-7 and C-9. The ^{13}C NMR spectrum (Table 1) showed the corresponding signals for the longipinene skeleton.

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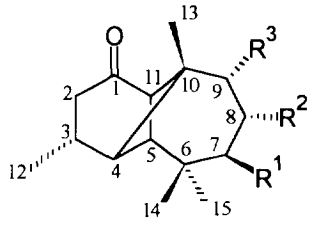

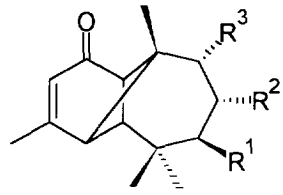

	R^1	R^2	R^3
1	OAng	OAng	OH
2	OAng	OAng	H
3	OAng	OH	OAng
4	OH	OAng	OAng
5	OAng	OAc	OAng
6	OAc	OAng	OAng

	R^1	R^2	R^3
7*	OTigl	H	OMeacr
8*	OAng	OAng	OH
9*	OAng	OMeBu	OH
10*	OAng	OAng	H
11*	OAng	OMebu	H
12*	OAng	H	H
13	OAng	OAc	OAng
14	OAng	O*i*-Bu	H

*The position and stereochemistry of the ester gropus were revised. See refs [3 and 12].

Table 1. ^{13}C NMR data of longipinene derivatives **3–6**, **10**, **13** and **14**

C	**3***	**4†**	**5‡**	**6§**	**10‖**	**13¶**	**14****
1	211.3	211.6	211.1	211.1	202.9	202.2	202.9
2	41.9	41.8	41.9	41.8	122.6	122.8	122.6
3	26.8	26.8	26.8	26.8	170.8	170.0	170.1
4	44.5	44.4	44.4	44.5	49.1	48.0	49.0
5	46.4	46.3	46.2	46.2	65.2	65.4	65.2
6	35.0	35.6	35.1	35.1	36.7	36.4	36.7
7	75.0	71.6	71.0	71.8	75.9	70.5	77.2
8	69.7	71.6	69.5	68.7	68.2	69.5	68.5
9	77.2	74.4	74.0	74.0	43.9	73.7	43.7
10	45.7	45.5	45.5	45.6	57.8	54.8	57.7
11	52.8	52.8	52.9	52.9	52.4	53.5	52.3
12	19.7	19.9	19.6	19.7	23.3	23.3	23.3
13	20.3	19.6	20.1	19.9	24.0	21.0	24.0
14	19.9	18.6	19.9	19.8	20.5	20.1	20.6
15	27.4	27.32	27.1	27.1	26.8	26.5	26.8

*Ang: 168.9, 167.6, 140.2, 138.7, 127.7, 127.5, 20.7, 20.6, 16.0 and 15.8 ppm.

†Ang: 167.0, 166.9, 140.3, 139.1, 127.5, 127.0, 20.7, 20.2, 15.8 and 15.8 ppm.

‡Ang: 167.4, 166.5, 138.7, 138.1, 127.8, 127.7, 20.6, 20.6, 15.8 and 15.7 ppm. Ac: 169.9 and 20.0 ppm.

§Ang: 166.8, 166.1, 140.8, 139.9, 127.5, 126.8, 20.5, 20.1, 15.9 and 15.8 ppm. Ac: 169.8 and 20.7 pm.

‖Ang: 166.8, 166.5, 139.4, 139.3, 127.5, 127.4, 15.8, 15.7, 20.3 and 20.2 ppm.

¶Ang: 167.2, 166.5, 138.9, 138.1, 127.8, 127.7, 20.6, 20.5, 15.8 and 15.7 ppm. Ac: 169.8 and 21.0 ppm.

**Ang: 166.5, 139.9, 127.4, 15.9 and 20.3. *i*-Bu: 176.2, 34.1, 18.8, and 18.6 ppm.

Compound **14** was purified by HPLC. Its IR showed bands for saturated ester group, α,β-unsaturated ester group and α,β-unsaturated ketone. The ^{1}H NMR spectrum showed vinylic signals for an angelate group at δ6.15 and for H-2 at 5.80. The presence of the *iso*-butyrate ester residue was clear from the signals at δ2.44 (*quint*, 1H), 1.10 (*d*, 3H) and 1.07 (*d*, 3H). Two signals for the protons geminal to ester groups H-7 and H-8 ap-

peared at δ5.13 and 5.32, respectively. The multiplicity of H-8 (*ddd*) indicated the presence of a methylene group at C-9. The comparison of the chemical shifts of H-7 and H-8 with the corresponding signals of diangelate **10**, located the *iso*-butyrate group at C-8 in **14**. The ^{13}C NMR data of **10** and **14** are listed in Table 1.

EXPERIMENTAL

General. IR spectra were obtained in $CHCl_3$. UV spectra were measured in EtOH. Specific rotations were determined in $CHCl_3$. NMR measurements were performed at 300 MHz for ^{1}H and 75.4 MHz for ^{13}C from $CDCl_3$ solns containing TMS as int. standard. CC was carried out on Merck silica gel 60 (70–230 mesh ASTM) and silica gel 60 (230–400 mesh ASTM). HPLC sepns were done by using a reverse-phase Micropack MCH-5-N-CAP column, i.d. 4 mm, length 150 mm + 40 mm (pre-column) or a Micropack Si-10, i.d. 8 mm, length 300 mm + 40 mm (pre-column). UV detection at 254 nm was employed. Mass spectra were recorded at 70 eV. Mp: uncorrected.

Plant material. Specimens of *Stevia serrata* Cav. were collected in La Galera, State of Michoacán, México in October 1991 and identified by Dr Jerzy Rzedowski (Herbarium of the Instituto de Ecología A. C., Pátzcuaro, Mich).

Extraction and isolation. Air-dried roots (3 kg) of *S. serrata* were extracted with hexane to afford a yellow viscous oil (17 g). Crystallization from $CHCl_3$–hexane gave rastevione (**1**) (8 g). The mother liquors were evapd to dryness and a portion (4.5 g) was CC on silica gel (70–230 mesh). Elution with hexane afforded eupha-8,24-dien-3β-yl acetate (10 mg) [10] and stigmasterol (20 mg) [11]. Elution with hexane–EtOAc (19:1) yielded 3 frs containing **3**, **4** and **5**, respectively. Elution with hexane–EtOAc (9:1) afforded pure **2** (10 mg), and 4 frs containing **14**, **13**, **10** and **12**, and **8**, respectively. Compound **3** was purified by CC on silica gel (230–400 mesh). Frs eluted with CH_2Cl_2–acetone (9:1) yielded a yellow solid (8 mg) which was recrystallized from CH_2Cl_2–hexane to give pure **3**. Compound **4** was purified by CC on silica gel (230–400 mesh). Frs eluted with hexane–EtOAc (9:1) yielded needles (70 mg) which were recrystallized from Me_2CO–hexane to give pure **4**. Compound **5** was purified by HPLC using the Si-10 column. injecting samples containing *ca* 1 mg of the compound in MeOH and eluting with hexane–MeOH (99.7:0.3) with a flow rate of 1 ml min^{-1}. Each run afforded *ca* 0.5 mg of pure **5** (R_t = 39.2 min). Compound **14** was purified by HPLC using the reverse-phase column injecting samples containing *ca* 1 mg of the compound in MeOH and eluting with MeOH–H_2O (7:3), with a flow rate of 1 ml min^{-1}. Each run afforded *ca* 0.5 mg of pure **14** (R_t = 10.8 min). Compound **13** was purified by HPLC using the reverse-phase column injecting samples containing *ca* 1 mg of the compound in MeOH and eluting with MeOH–H_2O (7:3), with a flow rate of 1 ml min^{-1}. Each run afforded *ca* 0.5 mg of pure **13** (R_t = 12.8 min). Compounds **12** and **10** were purified by HPLC using the reverse-phase column injecting samples containing *ca* 1 mg of the mixt. in MeOH and eluting with MeOH–H_2O (4:1), with a flow rate of 1 ml min^{-1}. Each run afforded *ca* 0.5 mg of pure **12** (R_t = 11.6 min) and *ca* 0.3 mg of pure **10** (R_t = 16.8 min). Compound **8** was purified by HPLC using the reverse-phase column injecting samples containing *ca* 1 mg of the compound in MeOH and eluting with MeOH–H_2O (3:2) with a flow rate of 1 ml min^{-1}. Each run afforded *ca* 0.6 mg of pure **8** R_t = 24.0 min.

7β,9α-Diangeloyloxy-8α-hydroxylongipinan-1-one (**3**). Needles, mp 155–158°. CIMS (CH_4) *m/z* (rel. int.): 433 $[M + H]^+$ (6), 418 (85), 361 (30), 333 (60), 315 (32), 233 (100), 215 (31), 101 (32); UV λ_{max} (EtOH) nm (log ε): 225 (4.01); IR ν_{max} ($CHCl_3$) cm^{-1}: 3600 (OH), 1718 (O=C, ketone), 1704, 1645 (O=C – C=C, angelate);

$[\alpha]$ =	589	578	546	436	365 nm
	+ 24.8	+ 27.3	+ 30.5	+ 43.6	+ 32.7

($CHCl_3$; c = 0.9).

^{1}H NMR: δ6.19 (1H *qq*, J = 7.5 and 1.5 Hz, H3, angelate), 6.10 (1H, *qq*, J = 7.5 and 1.5 Hz, H-3, angelate), 5.46 (1H, *d*, $J_{8,9}$ = 3.4 Hz, H-9), 5.20 (1H, *d*, $J_{7,8}$ = 11.1 Hz, H-7), 4.14 (1H, *ddd*, $J_{7,8}$ = 11.1, $J_{8,9}$ = 3.4 and $J_{8,OH}$ = 8.5 Hz, H-8), 2.97 (1H, *d*, $J_{4,11}$ = 5.6 Hz, H-11), 2.57 (1H, *dd*, $J_{2\alpha,2\beta}$ = 19 and $J_{2\beta,3}$ = 8.5 Hz, H-2β), 2.37 (1H, *m*, H-3), 2.27 (^{1}H, *d*, $J_{8,OH}$ = 8.5 Hz, OH), 2.19 (1H, *d*, $J_{4,11}$ = 5.6 Hz, H-4), 2.15 (1H, *dd*, $J_{2\alpha,2\beta}$ = 19 and $J_{2\alpha,3}$ = 6.1 Hz, H-2α), 2.06 (3H, *dq*, J = 7.5 and 1.5 Hz, Me-4 angelate), 1.99 (3H, *dq*, J = 7.5 and 1.5 Hz, Me-4 angelate), 2.05 (3H, *quint*, J = 1.5 Hz, Me-5 angelate), 1.94 (3H, *quint*, J = 1.5 Hz, Me-5 angelate), 1.85 (1H, *s*, H-5), 1.11 (3H, *d*, $J_{3,12}$ = 6.7 Hz, Me-12), 1.09 (3H, *s*, Me-15), 0.98 (3H, *s*, Me-14), 0.93 (3H, Me-13); ^{13}C NMR: see Table 1.

8β,9α-Diangeloyloxy-9α-hydroxylonpipinan-1-one (**4**). Needles, mp 137–139°. CIMS (CH_4) *m/z* (rel. int.): 433 $[M + H]^+$ (5), 415 (35), 361 (10), 333 (47), 315 (33), 233 (100), 215 (20), 101 (15); UV λ_{max}^{EtOH} nm (log ε): 225 (3.9); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3570 (OH), 1720 (O=C, ketone), 1708, 1646 (O= C–C=C, angelate);

$[\alpha]$ =	589	578	546	436	365 nm
	+ 25.3	+ 26.7	+ 30.0	+ 46.7	+ 50.7

($CHCl_3$; c = 1.5).

^{1}H NMR: δ6.12 (1H, *qq*, J = 7.5 and 1.5 Hz, H3, angelate), 6.11 (1H, *qq*, J = 7.5 and 1.5 Hz, angelate), 5.49 (1H, *d*, $J_{8,9}$ = 3.4 Hz, H-9), 5.32 (1H, *dd*, $J_{7,8}$ = 11.1 and $J_{8,9}$ = 3.4 Hz, H-8), 3.91 (1H, *dd*, $J_{7,8}$ = 11.1, $J_{7,OH}$ = 4.5 Hz, H-7), 2.91 (1H, *d*, $J_{4,11}$ = 5.8 Hz, H-11), 2.56 (1H, *dd*, $J_{2\alpha,2\beta}$ = 18.9 and $J_{2\beta,3}$ = 8.4 Hz, H-2β), 2.36 (1H, *m*, H-3), 2.31 (1H, *d*, $J_{4,11}$ = 5.8 Hz, H-4), 2.16 (1H, *dd*, $J_{2\alpha,2\beta}$ = 18.9 and $J_{2\alpha,3}$ = 6 Hz, H-2α), 2.06 (1H, *d*, $J_{7,OH}$ = 4.5 Hz, OH), 2.00 (3H, *dq*, J = 7.5 and 1.5 Hz, Me-4 angelate), 1.90 (3H, *dq*, J = 7.5 and 1.5 Hz, Me-4 angelate), 1.93 (3H, *quint*, J = 1.5 Hz, Me-5 angelate), 1.87 (1H, *s*, H-5), 1.80 (3H, *quint*, J = 1.5 Hz, Me-5 angelate), 1.12 (3H, *d*, $J_{3,12}$ = 6.8 Hz, Me-12), 1.11 (3H, *s*,

Me-15), 1.04 (3H, *s*, Me-14), 0.89 (3H, Me-13); ^{13}C NMR: see Table 1.

7β,9α-*Diangeloyloxy*-8α-*acetyloxylongipinan*-1-*one* (**5**). Oil. CIMS (CH_4) *m/z* (rel. int.): 475 $[M + H]^+$ (10), 461 (15), 415 (20), 375 (20), 316 (31), 315 (100), 233 (80), 215 (92); UV λ_{max}^{EtOH} nm (log ε): 220 (3.9); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1737 (O=C, OAc), 1718 (O=C, ketone), 1709, 1643 (O=C–C=C, angelate);

	589	578	546	436	365 nm
[α] =	+ 10.0	+ 11.1	+ 13.3	+ 15.6	− 5.5

($CHCl_3$; *c* = 0.9).

^{1}H NMR: δ6.11 (1H, *qq*, *J* = 7.5 and 1.5 Hz, H-3, angelate), 6.06 (1H, *qq*, *J* = 7.5 and 1.5 Hz, H-3 angelate), 5.49 (1H, *d*, $J_{7,8}$ = 12 Hz, H-7), 5.40 (1H, *dd*, $J_{7,8}$ = 12 and $J_{8,9}$ = 3.1 Hz, H-8). 5.38 (1H, *dd*, $J_{8,9}$ = 12 Hz, H-9), 3.03, (1H, *d*, $J_{4,11}$ = 5.6 Hz, H-11), 2.58 (1H, *dd*, $J_{2\alpha,2\beta}$ = 19 and $J_{2\beta,3}$ = 8.5 Hz, H-2β), 2.38 (1H, *m*, H-3), 2.33 (1H, *d*, $J_{4,11}$ = 5.6 Hz, H-4), 2.16 (1H, *dd*, $J_{2\alpha,2\beta}$ = 19 and $J_{2\alpha,3}$ = 6 Hz, H-2α), 2.01 (3H, *dq*, *J* = 7.5 and 1.5 Hz, Me-4 angelate), 1.95 (3H, *dq*, *J* = 7.5 and 1.5 Hz, Me-4 angelate), 2.03 (3H, *quint*, *J* = 1.5 Hz, Me-5 angelate), 2.02 (1H, *s*, H-5), 1.88 (3H, Me, OAc), 1.87 (3H, *quint*, *J* = 1.5 Hz, Me-5 angelate), 1.12 (3H, *d*, $J_{3,12}$ = 6.2 Hz, Me-12), 1.09 (3H, *s*, Me-15), 0.91 (3H, *s*, Me-14), 0.97 (3H, Me-13); ^{13}C NMR: see Table 1.

Acetylation of **4**. A soln of **4** (20 mg) in pyridine (1 ml) was treated with Ac_2O (0.5 ml). The reaction mixt. was heated on a steam bath for 4 hr, poured on ice and extracted with EtOAc. The organic layer was washed with HCl (10%) and H_2O, dried over Na_2SO_4, filtered and evapd to dryness. The residue was chromatographed on silica gel. The frs eluted with hexane–AcOEt (19:1) gave 15 mg of 8β,9α-diangeloyloxy-7α-acetyloxylongipinan-1-one (**6**) as an oil. CIMS (CH_4) *m/z* (rel. int.): 457 $[M + H]^+$ (5), 461 (40), 415 (75), 375 (25), 315 (25), 275 (68), 233 (100), 215 (84); UV λ_{max}^{EtOH} nm (log ε): 220 (3.9); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1738 (O=C, OAc), 1720 (O=C, ketone) 1710, 1645 (O=C-C=C, angelate);

	589	578	546	436	365 nm
[α] =	+ 29.0	+ 30.4	+ 34.3	+ 52.9	+ 57.0

($CHCl_3$; *c* = 3.6).

^{1}H NMR: δ6.26 (1H, *qq*, *J* = 7.5 and 1.5 Hz, H-3, angelate), 6.23 (1H, *qq*, *J* = 7.5 and 1.5 Hz, H-3, angelate), 5.55 (1H, *d*, $J_{7,8}$ = 11.3 Hz, H-7), 5.62 (1H, *dd*, $J_{8,9}$ = 2.9 Hz, H-8), 5.56 (1H, *dd*, $J_{8,9}$ = 11.3 Hz, H-9), 3.13 (1H, *d*, $J_{4,11}$ = 5.6 Hz, H-11), 2.69 (1H, *dd*, $J_{2\alpha,2\beta}$ = 19 and $J_{2\beta,3}$ = 8.5 Hz, H-2β), 2.50 (1H, *m*, H-3), 2.47 (1H, *d*, $J_{4,11}$ = 5.6 Hz, H-4), 2.27 (1H, *dd*, $J_{2\alpha,2\beta}$ = 19 and $J_{2\alpha,3}$ = 6 Hz, H-2α), 2.14 (3H, *dq*, *J* = 7.5 and 1.5 Hz, Me-4 angelate), 2.10 (3H, *dq*, *J* = 7.5 and 1.5 Hz, Me-4 angelate), 2.11 (3H, Me OAc), 2.13 (3H, *quint*, *J* = 1.5 Hz, Me-5 angelate), 1.99 (1H, *s*, H-5), 1.82 (3H, *quint*, *J* = 1.5 Hz, Me-5 angelate), 1.24 (3H, *d*, $J_{3,12}$ = 6.6 Hz, Me-12), 1.21 (3H, *s*, Me-15), 1.07 (3H, *s*, Me-14), 1.02 (3H, Me-13); ^{13}C NMR: see Table 1.

Acetylation of **3**. A soln of **3** (8 mg) in pyridine (0.2 ml) was treated with Ac_2O (1.0 ml). The reaction mixt. was stored at room temp. for 6 hr, poured on ice and extracted with CH_2Cl_2. The organic layer was washed with HCl (10%) and H_2O, dried over Na_2SO_4, filtered and evapd to dryness to give a product identical in all respects to naturally occurring **5**.

7β,9α-*Diangeloyloxy*-8α-*acetyloxylongipin*-2-*en*-1-*one* (**13**). Oil. UV λ_{max}^{EtOH} nm (log ε): 227 (3.89), 250 (3.45); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1736 (O=C, OAc), 1712, 1649 (O=C–C=C, angelate), 1678, 1618 (O=C–C=C, ketone); ^{1}H NMR: δ6.13 (1H, *qq*, *J* = 7.5 and 1.5 Hz, H-3 angelate), 6.07 (1H, *qq*, *J* = 7.5 and 1.5 Hz, H-3, angelate), 5.82 (1H, *dq*, $J_{2,11}$ = 1.2 and $J_{2,12}$ = 1.5 Hz, H-2), 5.51 (1H, *d*, $J_{7,8}$ = 11.2 Hz, H-7), 5.40 (1H, *dd*, $J_{7,8}$ = 11.2 and $J_{8,9}$ = 2.7 Hz, H-8), 5.48 (1H, *dd*, $J_{8,9}$ = 2.7 Hz, H-9), 3.14 (1H, *dd*, $J_{2,11}$ = 1.2 and $J_{4,11}$ = 6.9 Hz, H-11), 2.83 (1H, *d*, $J_{4,11}$ = 6.9 Hz, H-4), 2.39 (1H, *s*, H-5), 2.08 (3H, *d*, $J_{2,12}$ = 1.5 Hz, Me-12), 2.01 (3H, *dq*, *J* = 7.5 and 1.5 Hz, Me-4 angelate), 2.04 (3H, *quint*, *J* = 1.5 Hz, Me-5 angelate), 1.96 (3H, *dq*, *J* = 7.5 and 1.5 Hz, Me-4 angelate), 1.90 (3H, Me OAc), 1.87 (3H, *quint*, *J* = 1.5 Hz, Me-5 angelate), 1.30 (3H, *s*, Me-13), 1.01 (3H, *s*, Me-15), 0.94 (3H, Me-14); ^{13}C NMR: see Table 1.

7β-*Angeloyloxy*-8α-*isobutyryloxylongipin*-2-*en*-1-*one* (**14**). Oil. UV λ_{max}^{EtOH} nm (log ε): 225 (3.93); 250 (3.72); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740 (O=C, Oi-Bu), 1710, 1649 (O=C–C=C, angelate), 1670, 1614 (O=C–C=C, ketone);

	589	578	546	436	365 nm
[α] =	+ 35	+ 40	+ 50	+ 110	+ 375

($CHCl_3$; *c* = 0.2).

^{1}H NMR: δ6.15 (1H, *qq*, *J* = 7.5 and 1.5 Hz, H-3, angelate), 5.80 (1H, *dq*, $J_{2,11}$ = 1.5 and $J_{2,12}$ = 1.6 Hz, H-2), 5.32 (1H, *ddd*, $J_{7,8}$ = 11, $J_{8,9\alpha}$ = 11 Hz and $J_{8,9\beta}$ = 5 Hz, H-8), 5.13 (1H, *d*, $J_{7,8}$ = 11 Hz, H-7), 2.87 (1H, *dd*, $J_{2,11}$ = 1.5 and $J_{4,11}$ = 7.0 Hz, H-11), 2.75 (1H, *d*, $J_{4,11}$ = 7 Hz, H-4), 2.44 (1H, *quint*, *J* = 7 Hz, H-2 Oi-Bu), 2.30 (1H, *s*, H-5), 2.14 (1H, *dd*, $J_{8,9\beta}$ = 5 and $J_{9\alpha,9\beta}$ = 14 Hz, H-9β), 2.05 (3H, *d*, $J_{2,12}$ = 1.6 Hz, Me-12), 2.02 (3H, *dq*, *J* = 7.5 and 1.5 Hz, Me-4 angelate), 1.88 (3H, *quint*, *J* = 1.5 Hz, Me-5 angelate), 1.14 (3H, *s*, Me-13), 1.10 (3H, *d*, *J* = 7 Hz Me Oi-Bu), 1.07 (3H, *d*, *J* = 7 Hz Me Oi-Bu), 1.02 (3H, *s*, Me-15), 0.91 (3H, *s*, Me-14); ^{13}C NMR: See Table 1.

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