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# SESQUITERPENE LACTONES FROM *ROLANDRA FRUTICOSA*

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**Key Word Index**—*Rolandra fruticosa*; Compositae; sesquiterpene lactones; glaucolides; bourbonenolides.

**Abstract**—A reinvestigation of the aerial parts of *Rolandra fruticosa* afforded in addition to rolandriolide reported previously, some new lactones. The structures of the so-called isorolandrolides have been revised. Structures were elucidated by high field NMR techniques and some chemical transformations.

## INTRODUCTION

The monotypic genera *Rolandra* and *Spiracantha* have been separated from the large subtribe Vernoniinae and placed in the new subtribe Rolandrinae [1]. The results on the chemistry of *R. fruticosa* (L.) Kuntze collected in Panama seem to support this treatment as from this species a new type of sesquiterpene lactone, the rolandrolides, were reported [2]. However, the precursor of rolandrolide (**4c**) and of acetoxy rolandrolide is closely related to cistiglaucolide-8-*O*-methacrylate, the 14-acetoxy derivative from *Vernonia cistifolia* which is present in the enantiomeric form [3]. The absolute configuration of all glaucolides most likely has to be changed to the 8α-acyloxy series [4, 5].

The unique isorolandrolides [2] were formulated as conjugated trienes. As this type of sesquiterpene lactone was biogenetically not very likely we have reinvestigated a sample from French Guayana.

## RESULTS AND DISCUSSION

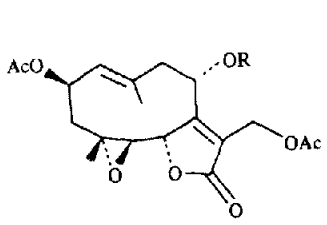
An extract of the aerial parts of *R. fruticosa* afforded in addition to acetoxyrolandrolide (**4a**) [2], three glaucolides, with the main constituent being **1a** as well as **1b** and **2**, a further rolandrolide (**4b**), three bourbonenolides (**6a**–**6c**) and the isomer **5a** while rolandrolide (**4c**) [2], isorolandrolide (**7b**) [2] and ethoxyisorolandrolide (**7a**) [2] were not isolated. However, short treatment of **1a** with potassium carbonate afforded the lactone **3**, its $^1$H and $^{13}$C NMR data being identical with those reported for **7b** [2] (Tables 1 and 2).

The structure of **1a** followed from its $^1$H NMR spectrum (Table 1) which was similar to that of the corresponding triacetate [6, 7]. Spin decoupling allowed the assignment of all signals. Configuration and conformation followed from the observed NOE's. Irradiation of H-14 caused effects on H-2 (10%), H-5 (8%) and H-9 (6%) while with H-15 NOE's with H-1 (8%), H-3β (5%), H-6 (14%) and H-8 (5%) were observed. The $^{13}$C NMR spectrum (Table 2) also agreed well with the structure. The $^1$H NMR data of **1b** clearly showed that this lactone was the corresponding 8α-tigloyloxy derivative. As shown previously [4], 4α,5β-epoxyglaucolides undergo a transformation to the isomeric 4α-hydroxy-5*Z*-enolether. Accordingly, the structure of isorolandrolide has to be revised to **3**. As could be shown by the $^1$H NMR data and the observed NOE's lactone **3** is present in solution in one preferred conformation. Thus, NOE's were observed between H-14, H-3α (3%) and H-3β (4%), as well as between H-15, H-2 (12%), H-5 (8%) and H-9α (4%). This must be the result of the 2β-acetoxy group, as in the case of the desacetoxy derivative two conformations in different concentrations depending on solvents used were observed [4]. Accordingly, the subsequent 2 + 2-addition gave in the case of **3** only the cyclobutane derivative **5b**, while in the case of the 2-desacetoxy derivative due to the presence of two conformers in addition to a compound of type **5**, a second one of type **6** was obtained [4].

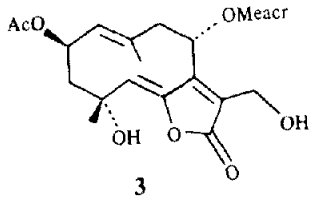
As the isorolandrolides showed a bathochromic shift of the UV maximum when compared to that of **4a**, a conjugated trienone was proposed. Inspection of models indicated that the most likely reason for this is the strain in compound **4a** while in **3a** complete planar orientation of the chromophore is possible. Furthermore, homoconjugation with the 1(10)-double bond is probably present in **3**. As pointed out previously [4, 5], the absolute configurations of glaucolides and related compounds are most likely enantiomeric to that proposed for rolandrolide.

The structure of **2** also followed from its $^1$H NMR spectrum (Table 1). All signals could be assigned by spin decoupling and the observed couplings fitted the proposed configurations. Furthermore, this lactone is the obvious precursor of **4a**, its structure being established by X-ray analysis [2]. The $^1$H NMR data of **4b** (Table 1) only differed from that of **4a** in the expected way due to the different ester groups.

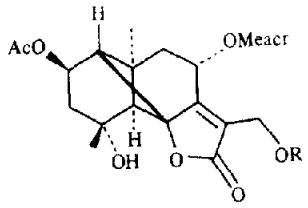
The $^1$H and $^{13}$C NMR spectra of **6a** (Tables 1 and 2) clearly indicated that a bourbonenolide was present. Accordingly, the spectrum was similar to that of the corresponding 2-desacetoxy derivative [4]. However, the couplings of H-1 differed. The configuration was established by the observed NOE's. Saturation of H-14 gave clear effects with H-1 (12%), H-5 (2%) and H-9α (6%), of H-15 with H-5 (5%), H-3β (3%) and H-8 (3%), H-5 with H-1 (6%) as well as of H-8 with H-2 (5%), H-3β (8%) and H-15 (2%).



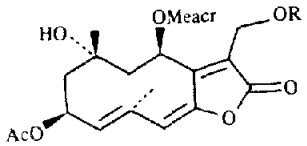
**1a** **1b**
R Meacr Tigl



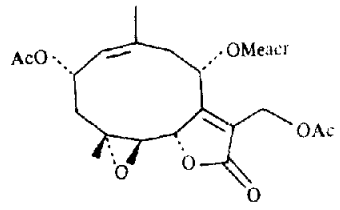
**3**



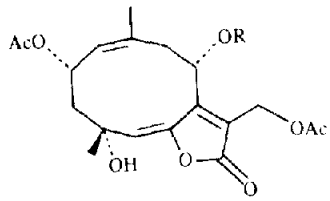
**5a** **5b**
R Me H



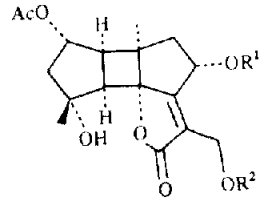
**7a** **7b**
R Et H



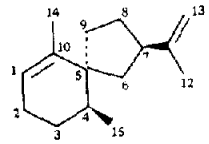
**2**



**4a** **4b** **4c**
R Meacr Tigl Meacr
13-OH



**6a** **6b** **6c**
$R^1$ Meacr Meacr Tigl
$R^2$ Ac Me Ac



**8**

The $^1$H NMR data of **6b** (Table 1) indicated that this lactone was derived from **6a** by replacement of the 13-acetoxy by a methoxy group. Accordingly, the H-13 signal was shifted up field and a methoxy singlet was visible at $\delta$3.26. The $^1$H NMR spectrum of **6c** (Table 1) was very similar to that of **6a**, only the ester signals being replaced by those of a tiglate.

The structure of **5a** also followed from its $^1$H NMR spectrum (Table 1) which was similar to that of the corresponding desacetoxy derivative [4]. The configuration again was established by the observed NOE's between H-14, H-1 (3%), H-2 (12%), H-5 (3%), H-9$\alpha$ (4%) and H-9$\beta$ (4%), between H-15, H-5 (8%) and H-3$\beta$ (6%) as well as between H-1, H-2 (4%) and H-8 (2%). The $^{13}$C NMR spectrum (Table 2) also supported the structure. On standing of compound **3** for two days in deuteriobenzene, lactone **5b** was obtained. All data were nearly identical with those of **5a** except for the chemical shift of H-13 and the absence of the methoxy singlet.

The most likely biogenetic precursors of all lactones are **1a** and **2**, respectively, where the isomer **1a** due to the preferred conformation gives **3** and subsequently **5b** while the 1 (10)-*Z*-isomer **2** leads to **4a** and then to **6a**. Due to the conformation of **4a** the bourbonenolide **6a** is formed and not the corresponding *anti* isomer obtained from lactones with a 1(10)-*E*-configurated double bond [4].

The roots of *R. fruticosa* gave in addition to **1a**, lupeyl acetate, caryophyllene and cyperene, the hydrocarbon **8**. The structure followed from its $^1$H NMR spectrum (see Experimental) which was very similar to that of hinesol. Spin decoupling allowed the assignment of all signals which established the sequences and the couplings were identical with those of hinesol. The structure was further supported by the $^{13}$C NMR spectrum which clearly required a *spiro* system ($\delta$48.75). The sign of the optical rotation was the same as that for hinesol [8]. Therefore, the proposed absolute configuration is very likely.

The chemistry of *Rolandra* differs from that of most *Vernonia* species only by the presence of glaucolides with a 1(10)-double bond. This bond usually is further transformed in *Vernonia* species in different ways, probably always first starting with epoxidation of the double bond. Surely, it will be of interest to study the chemistry of *Spiracantha*, the second genus, placed in the same subtribe. However, further species should be studied to see whether the observed structural differences are of chemo-

Table 1. $^1$H NMR spectral data of **1a**, **1b**, **2**, **3**, **4b**, **5a**, **5b** and **6a–6c** (400 MHz, $CDCl_3$, $\delta$-values)

| H | 1a | 1b | 2 | 3 | 4b | 5a | 5b | 6a | 6b | 6c |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 5.58 *br d* | 5.59 *br d* | 5.20 *br d* | 4.76 *br d* | 5.11 *br d* | 2.42 *dd* | 2.41 *dd* | 2.71 *br d* | 2.71 *br d* | 2.72 *br d* |
| 2 | 5.69 *br ddd* | 5.69 *br ddd* | 5.30 *br ddd* | 5.92 *ddd* | 5.52 *ddd* | 5.45 *ddd* | 5.45 *ddd* | 5.39 *br d* | 5.40 *br d* | 5.39 *br d* |
| 3α | 1.82 *dd* | 1.83 *dd* | 1.49 *dd* | 2.06 *dd* | 2.17 *dd* | 2.50 *dd* | 2.44 *dd* | 2.23 *br d* | 2.23 *br d* | 2.24 *br d* |
| 3β | 2.26 *dd* | 2.27 *dd* | 2.33 *dd* | 2.30 *dd* | 2.12 *dd* | 2.15 *dd* | 2.14 *dd* | 2.55 *dd* | 2.60 *dd* | 2.57 *dd* |
| 5 | 2.32 *d* | 2.32 *d* | 2.72 *d* | 5.74 *s* | 6.16 *s* | 2.47 *d* | 2.51 *d* | 3.44 *dd* | 3.44 *dd* | 3.44 *dd* |
| 6 | 4.93 *br d* | 4.95 *br d* | 4.94 *br d* | — | — | — | — | — | — | — |
| 8 | 5.17 *dd* | 5.18 *dd* | 5.41 *dd* | 6.49 *dd* | 6.15 *dd* | 6.17 *dd* | 6.14 *dd* | 6.34 *br dd* | 6.33 *br dd* | 6.34 *br dd* |
| 9α | 2.52 *dd* | 2.51 *dd* | 2.53 *dd* | 2.84 *dd* | 2.26 *dd* | 1.89 *dd* | 1.94 *dd* | 1.84 *dd* | 1.86 *dd* | * |
| 9β | 3.03 *br dd* | 3.02 *br dd* | 3.33 *br dd* | 2.32 *dd* | 3.48 *br dd* | 2.47 *dd* | 2.52 *dd* | 2.88 *dd* | 2.84 *dd* | 2.87 *dd* |
| 13 | 4.98 *br d* | 4.99 *br d* | 4.97 *br d* | 4.59 *d* | 5.02 *d* | | 4.47 *d* | 4.87 *dd* | 4.19 *dd* | 4.86 *dd* |
| | | | | | | 4.15 *br s* | | | | |
| 13′ | 4.85 *br d* | 4.87 *br d* | 4.91 *br d* | 4.54 *d* | 4.92 *d* | | 4.42 *d* | 4.73 *br d* | 4.11 *br d* | 4.73 *br d* |
| 14 | 1.68 *br s* | 1.68 *br s* | 1.73 *d* | 2.04 *br s* | 1.58 *br s* | 1.30 *s* | 1.31 *s* | 1.32 *s* | 1.32 *s* | 1.32 *s* |
| 15 | 1.57 *s* | 1.58 *s* | 1.70 *s* | 1.70 *s* | 1.96 *s* | 1.44 *s* | 1.44 *s* | 1.24 *s* | 1.29 *s* | 1.26 *s* |
| OAc | 2.07 *s* | 2.08 *s* | 2.04 *s* | 1.99 *s* | 2.04 *s* | 2.01 *s* | 2.02 *s* | 2.06 *s* | 2.07 *s* | 2.07 *s* |
| OMe | 2.06 *s* | 2.06 *s* | 2.04 *s* | | 2.04 *s* | 3.32 *s* | | 2.00 *s* | 3.26 *s* | 2.01 *s* |
| OCOR | 6.13 *br s* | 6.89 *br q* | 6.13 *br s* | 6.24 *br s* | 6.93 *br q* | 6.14 *br s* | 6.16 *br s* | 6.13 *br s* | 6.19 *br s* | 6.89 *br q* |
| | 5.67 *br s* | 1.83 *br d* | 5.68 *br s* | 5.79 *br s* | 1.84 *br s* | 5.65 *br s* | 5.68 *br s* | 5.69 *br s* | 5.69 *br s* | 1.85 *br s* |
| | 1.91 *br s* | 1.81 *br s* | 1.92 *br s* | 1.96 *br s* | 1.83 *br d* | 1.98 *br s* | 1.97 *br s* | 1.96 *br s* | 1.99 *br s* | 1.83 *br d* |

*Overlapped by the signals of the tiglate.

$J$[Hz]: Compounds **1a** and **1b**: 1,2 = 2,3α = 8; 2,3β = 2.5; 3α, 3β = 15; 5,6 = 9; 8,9α = 12; 8,9β = 5.5; 9α,9β = 13; 13,13′ = 12; compound **2**: 1,2 = 10; 2,3α = 12; 2,3β = 2; 3α,3β = 13; 5,6 = 9.5; 8,9α = 10; 8,9β = 9; 9α,9β = 14; 13,13′ = 13; compound **4b**: 1,2 = 2,3α = 10; 1,2β = 3; 3α,3β = 14; 8,9α = 11; 8,9β = 8.5; 9α,9β = 13; 13,13′ = 12; compound **5**: 1,2 = 2; 1,5 = 6; 2,3α = 9; 2,3β = 7; 3α,3β = 15.5; 8,9α = 3.5; 8,9β = 9.5; 9α,9β = 16; compounds **6a–6c**: 1,5 = 10; 2,3β = 7; 3α,3β = 16.5; 3β,5 = 2; 8,9α = 9.5; 8,9β = 8; 9α,9β = 14; 8,13′ = 1.5; 13,13′ = 13.

Table 2. $^{13}C$ NMR signals of **1a**, **3**, **5a** and **6a** ($CDCl_3$, $\delta$-values)

| C | 1a | 3 | 5a | 6a |
|---|---|---|---|---|
| 1 | 129.2 *d* | 129.0 | 58.8 *d* | 51.0 *d* |
| 2 | 71.7 *d* | 68.6 | 62.7 *d* | 77.2 *d* |
| 3 | 42.7 *t* | 51.2 | 43.8 *t* | 49.2 *t* |
| 4 | 59.1 *s* | 72.8 | 72.2 *s* | 80.6 *s* |
| 5 | 63.2 *d* | 133.3 | 59.1 *d* | 59.5 *d* |
| 6 | 82.3 *d* | 143.7 | 83.3 *s* | 92.0 *s* |
| 7 | 163.8 *s* | 150.3 | 165.1 *s* | 169.0 *s* |
| 8 | 68.5 *d* | 69.8 | 69.4 *d* | 70.8 *d* |
| 9 | 40.5 *t* | 44.3 | 40.1 *t* | 45.2 *t* |
| 10 | 131.0 *s* | 135.4 | 36.6 *s* | 47.8 *s* |
| 11 | 128.2 *s* | 125.6 | 123.9 *s* | 123.5 *s* |
| 12 | 170.7 *s* | 169.0 | 170.8 *s* | 170.3 *s* |
| 13 | 55.2 *t* | 54.7 | 64.2 *t* | 55.3 *t* |
| 14 | 19.5 *q* | 21.2 | 21.3 *q* | 22.6 *q* |
| 15 | 21.1 *q* | 28.8 | 33.0 *q* | 23.3 *q* |
| OAc | 170.2 *s* | 170.3 | 171.4 *s* | 170.2 *s* |
| (OMe) | 170.0 *s* | 20.1 | 21.2 *q* | 170.1 *s* |
| | 20.9 *q* | | 51.9 *q* | 21.2 *q* |
| | 20.7 *q* | | | 20.5 *q* |
| OR | 166.2 *s* | 166.4 | 165.9 *s* | 166.2 *s* |
| | 135.0 *s* | 135.3 | 135.7 *s* | 135.1 *s* |
| | 127.4 *t* | 127.4 | 126.6 *t* | 127.3 *t* |
| | 18.0 *q* | 18.4 | 18.3 *q* | 18.2 *q* |

taxonomic relevance. The proposed relationship of *Rolandra* to *Elephantopus* [1] is not supported by the chemistry as no glaucolides are present in the latter genus.

## EXPERIMENTAL

Aerial parts of *R. fruticosa* (360 g, collected near the road S of Cayenne, French Guajana, in June 1988, voucher deposited in the US National Herbarium, Washington, U.S.A.) were extracted with MeOH–$Et_2O$–petrol (1:1:1) and the extract obtained was first sepd as reported previously [8] by CC affording 36 mg lupeol and 48 mg of its acetate. The next fr. ($Et_2O$–petrol, 3:1 and $Et_2O$) gave after crystallization from $Et_2O$ 280 mg **1a** and the mother liquor in MeOH 40 mg of a mixt. of stigmasterol and sitosterol. HPLC (RP 8, *ca* 100 bar, flow rate 12 ml/min, MeOH–$H_2O$, 3:2) gave 10 mg vanillin ($R_t$ 5.0 min), 20 mg **1a** ($R_t$ 15.5 min) and 4 mixts ($R_t$ 13.4, 17.5, 18.7 and 21.9 min). The first gave by TLC ($Et_2O$–petrol, 6:1, two developments) 34 mg **4a** ($R_f$ 0.6) and 15 mg **6a** ($R_f$ 0.4) while the second gave by TLC ($Et_2O$–petrol, 3:1, two developments) 4 mg **6b** ($R_f$ 0.2) and 3 mg **2** ($R_f$ 0.4). The third fr. gave by TLC ($Et_2O$–petrol, 3:1) 4 mg **4b** ($R_f$ 0.8) and 7 mg **6c** ($R_f$ 0.6) and the last gave by TLC ($Et_2O$–petrol, 3:1) 5 mg **1b** ($R_f$ 0.5). The most polar CC fraction ($Et_2O$–MeOH, 9:1) gave by HPLC (see above) 5 mg **5a** ($R_t$ 25.8 min).

The roots of the plant (45 g) gave an extract which afforded 10 mg lupeyl acetate, 100 mg **1a**, 5 mg **8** (TLC, $AgNO_3$-coated silica gel, $Et_2O$–petrol, 1:20, $R_f$ 0.5), 3 mg caryophyllene and 5 mg cyperene. Known compounds were identified by comparing their $^1H$ NMR spectral data with those of authentic materials.

2-epi-*Glaucolide E* (**1a**). Colourless crystals, mp 159°; IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 1770 ($\gamma$-lactone), 1730 ($CO_2R$); MS *m/z* (rel. int.): 448 $[M]^+$ (0.2), 388.152 $[M-HOAc]^+$ (1) (calc. for $C_{21}H_{24}O_7$: 388.152), 362 $[M-RCO_2H]^+$ (2), 302 $[362-HOAc]^+$ (2), 260 (8), 242 $[302-HOAc]^+$ (14), 69 $[RCO]^+$ (100); $[\alpha]_D^{24°}$ −25 ($CHCl_3$; *c* 0.86).

8-*Desacyl*-2-epi-*glaucolide E tiglate* (**1b**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 1770 ($\gamma$-lactone), 1735, 1720 ($CO_2R$); MS *m/z* (rel. int.): 462 $[M]^+$ (0.1), 402.168 $[M-HOAc]^+$ (0.5) (calc. for $C_{22}H_{26}O_7$: 402.168), 362 $[M-RCO_2H]^+$ (2.5), 302 $[362-HOAc]^+$ (1.3), 242 $[302-HOAc]^+$ (6), 83 $[RCO]^+$ (100).

14-*Desacetoxycistiglaucolide*-8-O-*methacrylate* (**2**). Colourless, very unstable gum; MS *m/z* (rel. int.): 388.152 $[M-HOAc]^+$ (1) (calc. for $C_{21}H_{24}O_7$: 388.152), 362 $[M-RCO_2H]^+$ (2), 69 $[RCO]^+$ (100).

2*β*-*Acetoxy*-4*α*,13-*dihydroxy*-8*α*-*methacryloyloxygermacra*-1(10)E,5Z,7(11)-*trien*-12,6-*olide* ("isorolandrolide") (**3**). **1a** (100 mg) in 5 ml dioxane were stirred for 1 hr with 7 ml 0.1 M $K_2CO_3$ soln. TLC ($Et_2O$) gave the lactone **3** as a colourless gum ($R_f$ 0.6). $^1H$ NMR see Table 1. $^{13}C$ NMR see Table 2. On standing in $C_6D_6$ the lactone **5b** was obtained (see below).

8-*Desacyl*-*acetoxyrolandrolide*-8-O-*tiglate* (**4b**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 1770 ($\gamma$-lactone), 1725 ($CO_2R$); MS *m/z* (rel. int.): 362 $[M-RCO_2H]^+$ (0.1), 302.115 $[362-HOAc]^+$ (1) (calc. for $C_{17}H_{18}O_5$: 302.115), 242 $[302-HOAc]^+$ (16), 83 $[RCO]^+$ (100).

2*β*-*Acetoxy*-4*α*-*hydroxy*-13-*methoxy*-8*α*-*methacryloyloxycopa*-7(11)-*en*-12,6*α*-*olide* (**5a**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3580 (OH), 1765 ($\gamma$-lactone), 1736 ($CO_2R$); MS *m/z* (rel. int.): 274.121 $[M-HOAc, RCO_2H]^+$ (10) (calc. for $C_{16}H_{18}O_4$: 274.121), 242 (16), 147 (42), 69 $[RCO]^+$ (100).

2*β*-*Acetoxy*-4*α*,13-*dihydroxy*-8*α*-*methacryloyloxy*-*copa*-7(11)-*en*-12,6*α*-*olide* (**5b**). Colourless gum, purified by TLC ($Et_2O$, $R_f$ 0.55); IR $\nu_{max}^{CCl_4}$ $cm^{-1}$: 3600 (OH), 1765 ($\gamma$-lactone), 1730 ($CO_2R$); MS *m/z* (rel. int.): 260.105 $[M-HOAc, RCO_2H]^+$ (22) (calc. for $C_{15}H_{16}O_4$: 260.105), 216 (28), 149 (50), 97 (74), 69 $[RCO]^+$ (100).

2*α*,13-*Diacetoxy*-4*α*-*hydroxy*-8*α*-*methacryloyloxybourbonen*-12,6*α*-*olide* (**6a**). Colourless crystals, mp 58°; IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3580 (OH), 1760 ($\gamma$-lactone), 1730 ($CO_2R$); MS *m/z* (rel. int.): 388 $[M-HOAc]^+$ (0.02), 302.115 $[388-RCO_2H]^+$ (3) (calc. for $C_{17}H_{18}O_5$: 302.115), 242 $[302-HOAc]^+$ (28), 69 $[RCO]^+$; $[\alpha]_D$ −70 ($CHCl_3$; *c* 1.0).

2*α*-*Acetoxy*-4*α*-*hydroxy*-13-*methoxy*-8*α*-*methacryloyloxybourbonen*-12,6*α*-*olide* (**6b**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3580 (OH), 1760 ($\gamma$-lactone), 1730 ($CO_2R$); MS *m/z* (rel. int.): 274.120 $[M-AcOH, RCO_2H]^+$ (9) (calc. for $C_{16}H_{18}O_4$: 274.120), 69 $[RCO]^+$ (100).

2*α*,13-*Diacetoxy*-4-*hydroxy*-8*α*-*tigloyloxybourbonen*-12,6*α*-*olide* (**6c**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3580 (OH), 1765 ($\gamma$-lactone), 1740 ($CO_2R$); MS *m/z* (rel. int.): 302.115 $[M-HOAc, RCO_2H]^+$ (2) (calc. for $C_{17}H_{18}O_5$: 302.115), 242 $[302-HOAc]^+$ (18), 83 $[RCO]^+$ (100).

*Hinesene* (**8**). Colourless oil; IR $\nu_{max}^{CCl_4}$ $cm^{-1}$: 1645, 900 (C=$CH_2$); MS *m/z* (rel. int.): 204.188 $[M]^+$ (46) (calc. for $C_{15}H_{24}$: 204.188), 189 (28), 175 (21), 161 (80), 147 (50), 133 (61), 107 (100), 93 (95); $[\alpha]_D^{24°}$ −44 ($CHCl_3$; *c* 0.1); $^1H$ NMR ($CDCl_3$): 5.31 (*ddq*, H-1, $J$ = 3, 4, 1.5 Hz), 1.93 (*m*, H-2), 1.31 (*m*, H-3), 1.55 (*m*, H-3', H-4), 1.72 (*ddd*, H-6, $J$ = 1.5, 6.5, 13), 1.37 (*dd*, H-6', $J$ = 12, 13), 2.44 (*br dddd*, H-7, $J$ = 6.5, 6.5, 12, 12), 1.85 (*ttd*, H-8, $J$ = 1.5, 6.5, 12), 1.65–1.5 (*m*, H-8', H-9), 1.74 (*br s*, H-12), 4.71 and 4.67 (*br s*, H-13), 1.68 (*q*, H-13, $J$ = 1.5), 0.94 (*d*, H-15, $J$ = 6.5); $^{13}C$ NMR ($CDCl_3$, C-1–C-15): 121.6, 24.5, 28.2, 47.6, 48.7, 37.2, 37.5, 32.2, 35.8, 140.3, 148.7, 19.8, 108.0, 21.3, 16.4.

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