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ACANTHOSPERMOLIDES AND OTHER CONSTITUENTS FROM *BLAINVILLEA ACMELLA*

P. SINGH, A. K. SHARMA, K. C. JOSHI, J. JAKUPOVIC* and F. BOHLMANN*

Department of Chemistry, University of Rajasthan, Jaipur 302004, India; *Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany

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Key Word Index—*Blainvillea acmella*; Compositae; sesquiterpene lactones; germacranolides; ovatifolin derivatives; melampolides; acanthospermolides.

Abstract—The aerial parts of *Blainvillea acmella* afforded, in addition to widespread triterpenes, desacetyl ovatifolin, desacyl grazielic acid tiglate, 8β-[2-methylbutyryloxy]-9β-hydroxy-14-oxo-acanthospermolide, four new germacranolides and seven acanthospermolides. The roots gave ovatifolin, two widespread thiophenacetylenes and two daucane derivatives. Comparison of the data with those of cyclochaenin required a revision of its structure. The structures were elucidated by high field ^{1}H NMR spectroscopy. Biogenetic relationships and taxonomic aspects are discussed briefly.

INTRODUCTION

The genus *Blainvillea* (tribe Heliantheae) is placed in the subtribe Ecliptinae [1, 2]. So far the chemistry of only one species has been studied [3]. The isolation of acanthospermolides was of taxonomic interest as this type of sesquiterpene lactone had not been observed previously in any genus of the subtribe Ecliptinae. We have now investigated a further species, *Blainvillea acmella* L.

RESULTS AND DISCUSSION

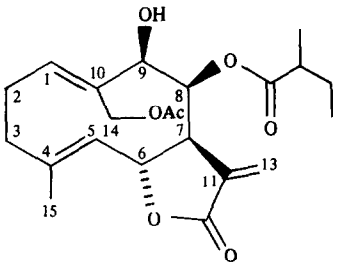
The aerial parts gave some widely distributed compounds (see Experimental), desacetylovatifolin (**19**) [4], desacylgrazielic acid tiglate (**20**) [5], four new lactones related to ovatifolin (**1–4**), 8β-[2-methylbutyryloxy]-9β-hydroxy-14-oxo-acanthospermolide (**5**), which was already known to be present in *B. dichotoma* [3], and seven additional acanthospermolides (**6–12**). The structure of **1** was deduced from its ^{1}H NMR spectrum (Table 1) which was close to that of ovatifolin (**18**) [6]. However, the presence of an additional oxygen function was obvious as the pair of double doublets (H-9) were replaced by a doublet at δ4.40. Furthermore, the H-8 signal was shifted downfield if compared with the corresponding shift in the spectrum of ovatifolin. Typical signals of a 2-methylbutyrate indicated that this was the ester at C-8. The configurations at C-8 and C-9 followed from the small couplings which only agreed with a β-orientated oxygen function.

The molecular formula of **2** ($C_{15}H_{22}O_4$) together with its IR spectrum indicated the presence of a dihydroxy lactone. The ^{1}H NMR spectrum (Table 1) showed some similarities to that of desacetylovatifolin. However, the absence of the exomethylene double bond was obvious. The characteristic signals of these protons were replaced by a methyl doublet and a double quartet which could be assigned by spin decoupling to H-11. The coupling of the latter clearly showed an α-orientated C-11 methyl group. The ^{1}H NMR spectrum of **3** (Table 1) was close to that of **2**. The presence of the corresponding tiglate followed from the typical ^{1}H NMR signals and the observed downfield shift of the H-8 signal. Thus **3** was the 8-*O*-tiglate of **2**.

The ^{1}H NMR spectrum of **4** (Table 1) differed somewhat from that of **2** though many signals were similar. That it was a derivative of **2** followed from the results of spin decoupling. The absence of an H-8 signal together with a new pair of doublets below δ3 clearly indicated a carbonyl group at C-8. All this agreed with the presence of desacetoxy-11β,13-dihydroovatifolin-8-one.

Though lactone **6** gave no molecular ion the molecular formula could be deduced from the presence of the $[M-RCO_2H]^+$ and the acyl (*m/z* 85) ions in the mass spectrum and the presence of a 2-methylbutyrate group according to the ^{1}H NMR spectrum. The other ^{1}H NMR spectral data (Table 2) strongly indicated that **6** was an isomer of **5** [3]. As could be deduced from the chemical shifts of H-8 and H-9, **5** and **6** differed only in the position of the ester residue. NOE difference spectroscopy indicated that the preferred conformation had both C-14 and C-15 above the plane. Clear NOEs were observed between H-15 and H-6 (15%), between H-7, H-8 (6%) and H-9α (8%), between H-5 and H-7 (6%), between H-9, H-7 (15%) and H-2 (10%) as well as between H-14 and H-1 (15%).

The ^{1}H NMR spectra of **7–10** (Table 2) were in part very similar. Obviously **8–10** differed from each other only in the nature of the ester residue, which had to be placed at C-8 on the basis of spin decoupling. The typical ester signals showed that **8** was the acetate, **9** the tiglate and **10** the 2-methylbutyrate of **7**. The signals of **7** were in part very close to those of **6**. However, the absence of an oxygen function at C-9 led to the appearance of a pair of threefold doublets at δ2.62 and 2.00. On the other basis of models it was obvious that the first signal was that of H-9α, as in **6** a *W*-coupling was observed between that proton (H-9α) and H-14. Of course the absence of an ester group in **7** caused a considerable upfield shift of the signal of H-8.



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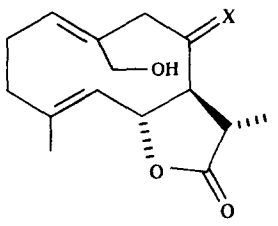
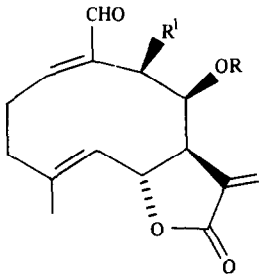
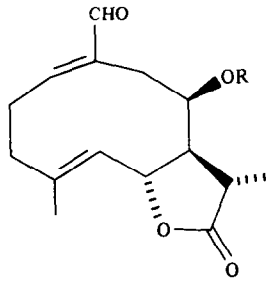


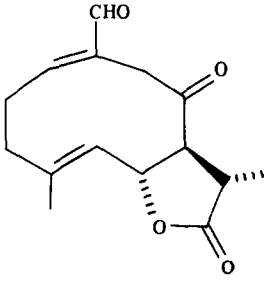
	2	**3**	**4**
X	βOH, H	βOTigl, H	O



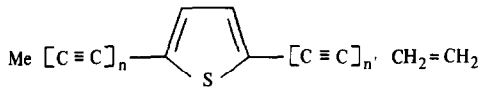
	5	**6**
R	βMebu	H
R^1	OH	OMebu



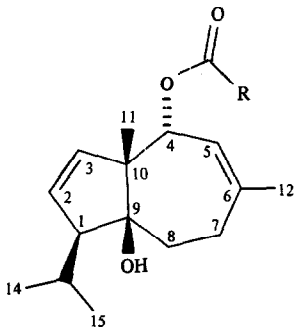
	7	**8**	**9**	**10**
R	H	Ac	Tigl	Mebu



11 **12** $\Delta^{7(11)}$



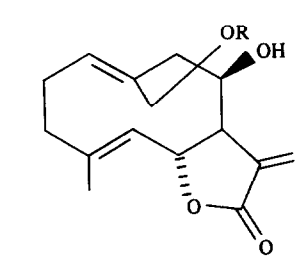
13 n = 1, n′ = 2 **14** n = 2, n′ = 1



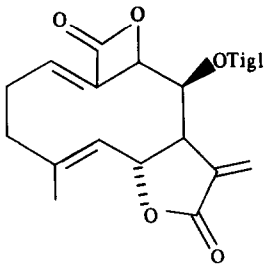
15 R = CH=CHPh (*trans*)
16 R = CH=CHPh (*trans*) 2, 3H
17 R = CH=CHC$_6$H$_4$OMe (*trans*, *p*) 2, 3H

The ^{1}H NMR spectrum of **11** (Table 2) showed similarities to that of **7**. However, in addition to some shift differences the absence of an H-8 signal and the downfield shifts of the signals of H-7 and H-9 showed that the corresponding 8-keto derivative was present. The changed situation at this centre also led to a different conformation as indicated by the absence of *W*-coupling between H-9 and H-14.

The ^{1}H NMR spectrum of **12**, whose molecular formula had two hydrogens less than **11**, showed the presence of an olefinic methyl (1.96 *d*) while no signals for H-7, H-8 and H-11 were observed. As, however, the



18 R=Ac **19** R=H



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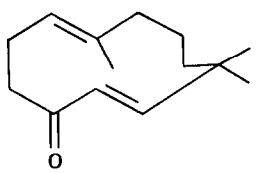

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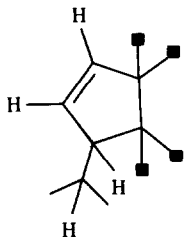
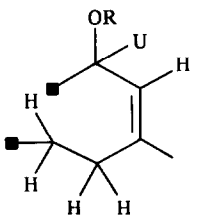


A



B

Table 1. ^{1}H NMR spectral data of **1–4** (400 MHz, $CDCl_3$, TMS as internal standard)

H	1*	2	3†	4‡
1	5.30 *dd(br)*	5.05 *dd(br)*	5.06 *dd(br)*	5.32 *dd(br)*
5	4.78 *d(br)*	4.77 *d(br)*	4.75 *d(br)*	5.04 *d(br)*
6	4.95 *dd*	5.00 *t*	5.02 *t*	4.70 *t*
7	2.94 *ddd*	1.85 *dd(br)*	2.01 *dd(br)*	3.11 *m*
8	5.99 *d(br)*	4.09 *d(br)*	5.48 *dd(br)*	—
9	4.40 *d*	2.86 *dd(br)*	3.30 *dd(br)*	3.43 *d(br)*
9′		2.34 *dd*	2.37 *dd*	3.24 *d*
11	—	2.79 *dq*	2.40 *dq*	3.11 *m*
13	6.37 *d* 5.87 *d*	1.25 *d*	1.28 *d*	1.20 *d*
14	4.66 *d*	4.17 *d(br)*	4.20 *d(br)*	4.22 *d*
14′	4.45 *dd*	3.85 *d(br)*	3.80 *d(br)*	3.88 *d(br)*
15	1.80 *d*	1.64 *d*	1.65 *d*	1.50 *s(br)*

*OAc: 2.03 *s*; OMebu: 2.37 *tq*, 1.67 *ddq*, 1.45 *ddq*, 0.88 *t*, 1.13 *d* [*J* (Hz): 2, 3 = 3, 4 = 2, 5 = 7; 3, 3′ = 14].

†OTigl: 6.88 *qq*, 1.88 *dq*, 1.85 *dq* [*J* (Hz): 3, 4 = 7; 3, 5 = 4, 5 = 1].

‡C_6D_6: H-7, 2.46 *dd*, H-11, 2.95 *dq*.

J (Hz): Compound **1**: 1, 2 = 12; 1, 2′ = 4; 1, 14′ = 1; 5, 6 = 10; 6, 7 = 9; 7, 8 ~ 0.5; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 1.5; 14, 14′ = 12; compounds **2–4**: 1, 2 = 1, 2′ = 4; 5, 6 = 6, 7 = 10; 7, 11 = 12; 8, 9 = 5; 8, 9′ = 1.5; 9, 9′ = 14; 11, 13 = 7; 14, 14′ = 12 (compound **4**: 1, 2 = 12; 1, 2′ = 3; 9, 9′ = 10.5)

remaining signals were close to those of **11**, the presence of the 7,11-dehydro derivative of the latter could be deduced. As in similar cases, it could not be excluded that **12** might have been formed by isomerization of the 11,13-dehydro derivative of **11**, whose presence, however, was not detected.

The extract of the roots gave stigmasterol, sitosterol, the germacranolide ovatifolin [6], the thiopheneacetylenes **13** and **14** [7], rudbeckianone (**21**) [8], 1-hydroxy-α-curcumene and two carotol derivatives, the cinnamates **15** and **16**. The presence of cinnamate esters was deduced easily from the ^{1}H NMR spectra of **15** and **16** (see Table 3) which were in part very much broadened. The molecular formulae agreed with those of hydroxylated sesquiterpene cinnamates differing in the number of hydrogens. As followed from the ^{1}H NMR data at elevated temperature, **15** had two double bonds, one, according to the observed vicinal couplings, in a five

Table 2. ^{1}H NMR spectral data of **6–12** (400 MHz, $CDCl_3$, TMS as internal standard)

H	6*	7	8†	9‡	10§	11	12
1	6.87 *dd*	6.55 *ddd*	6.59 *ddd*	6.59 *ddd*	6.59 *ddd*	6.80 *ddd*	6.66 *ddd*
2α	2.80 *m*	2.30 *dddd*	2.28 *dddd*	2.30 *dddd*	2.30 *dddd*	2.35 *dddd*	2.33 *ddd*
2β		2.47 *dddd*	2.50 *dddd*	2.50 *dddd*	2.50 *dddd*	2.61 *dddd*	2.60 *dddd*
3α	2.36 *m*	2.06 *dd(br)*	2.06 *ddd*	2.08 *ddd*	2.08 *ddd*	2.17 *ddd*	2.12 *ddd*
3β		2.35 *ddd*	2.37 *ddd*	2.38 *ddd*	2.37 *ddd*	2.42 *ddd*	2.43 *ddd*
5	5.44 *d(br)*	4.90 *d(br)*	4.90 *d(br)*	4.90 *d(br)*	4.91 *d(br)*	5.14 *d(br)*	4.68 *d(br)*
6	5.10 *t*	5.05 *t*	4.98 *t*	5.02 *t*	4.99 *t*	4.59 *t*	5.56 *dq*
7	2.97 *d(br)*	1.37 *ddd*	1.50 *ddd*	1.52 *ddd*	1.52 *ddd*	2.61 *dd*	—
8	4.56 *s(br)*	4.87 *ddd*	6.02 *ddd*	6.07 *ddd*	6.00 *ddd*	—	—
9α	5.61 *s(br)*	2.62 *ddd*	2.75 *ddd*	2.78 *ddd*	2.77 *ddd*	3.20 *d(br)*	3.34 *d(br)*
9β		2.00 *ddd*	1.91 *ddd*	1.95 *ddd*	1.92 *ddd*	2.77 *d*	2.97 *d*
11	—	2.72 *dq*	2.32 *dq*	2.33 *dq*	2.30 *dq*	3.10 *dq*	—
13	6.29 *d*	1.12 *d*	1.18 *d*	1.20 *d*	1.20 *d*	1.14 *d*	1.96 *d*
	5.56 *d*						
14	9.43 *d*	9.40 *d*	9.43 *d*	9.44 *d*	9.44 *d*	9.55 *s*	9.40 *s*
15	1.59 *s(br)*	1.89 *s(br)*	1.89 *d*	1.91 *d*	1.91 *d*	1.80 *d*	1.89 *d*

*OMebu: 2.35 *tq*, 0.80 *t*, 1.08 *d*.
†OAc: 2.11 *s*.
‡OTigl: 6.88 *qq*, 1.86 *dq*, 1.83 *dq* [*J* (Hz): see Table 1].
§OMebu: 2.43 *tq*, 1.68 *ddq*, 1.50 *ddq*, 0.91 *t*, 1.17 *d* [*J* (Hz): see Table 1].

J (Hz): Compound **6**: 1, 2β = 6; 1, 2α = 11; 5, 6 = 6, 7 = 10; 7, 8 ~ 1; 7, 13 = 3.5; 7, 13′ = 3; 8, 9α ~ 1.5; 9α, 14 = 1.5; compounds **7–10**: 1, 2β = 7.5; 1, 2α = 9; 1, 9α = 1.5; 2α, 2β = 13; 2β, 3β = 6.5; 2β, 3α ~ 2; 2α, 3β = 2; 2α, 3α = 11; 3α, 3β = 12; 5, 6 = 6, 7 = 10; 5, 15 = 1; 7, 8 = 1.5; 7, 11 = 12.5; 8, 9α = 7.5; 8, 9β = 10; 9, 9β = 14; 9α, 14 = 1.5; 11, 13 = 7; compounds **11** and **12**: 1, 2β = 7; 1, 2α = 10; 1, 9α = 1.5; 2α, 2β = 13; 2β, 3β ~ 7; 2β, 3α = 2α, 3β ~ 2; 2α, 3α = 11; 3β, 3α = 12; 5, 6 = 6, 7 = 10; (compound **11**: 7, 11 = 12; 9α, 9β = 18; compound **12**: 9α, 9β = 17).

Table 3. ^{1}H NMR spectral data of **15–17** (400 MHz, $CDCl_3$, TMS as internal standard)

H	15	15 60°	16	17
1	2.50 *m*	2.50 *dd*	2.05 *m*	2.05 *m*
2	5.71 *d(br)*	5.71 *dd*	1.68 *m*	1.60–1.80 m
3	5.37 *m*	5.37 *dd*		
4	5.33 *m*	5.33 *d*	5.21 *d*	5.31 *d*
5	5.48 *m*	5.48 *dq*	5.46 *d(br)*	5.52 *d(br)*
7	2.55 *m*	2.55 *dd(br)*	2.40 *m*	2.42 *m*
7′	2.38 *m*	2.42 *dd(br)*	2.25 *m*	2.32 *m*
8	2.18 *m*	2.18 *m*	2.05 *m*	2.05 *m*
8′	2.05 *m*	2.04 *m*		
11	1.12 *s*	1.12 *s*	1.05 *s*	1.08 *s*
12	1.75 *s(br)*	1.75 *s(br)*	1.70 *s(br)*	1.70 *s(br)*
13	1.84 *dqq*	1.85 *dqq*	1.85 *dqq*	1.87 *dqq*
14	1.09 *d*	1.09 *d*	1.06 *d*	1.06 *d*
OCOR	7.62 *d*	7.62 *d*	7.67 *d*	8.01 *d*
	6.33 *d*	6.35 *d*	6.43 *d*	6.94 *d*
	7.50 *m*	7.50 *m*	7.53 *m*	
	7.38 *m*	7.38 *m*	7.40 *m*	
OMe	—	—	—	3.88 *s*

J (Hz): 4, 5 = 7; 5, 12 = 1; 7, 7′ = 13; 7, 8′ ~ 7; 7′, 8 ~ 10; 1, 13 = 13, 14 = 13, 15 = 7; compound **15**: 1, 2 = 3; 1, 3 = 2; 2, 3 = 6; OCinn: 7′, 8′ = 16; COC_6H_4OMe: 2′, 3′ = 8.

membered ring and the other a trisubstituted double bond bearing a methyl group. The signal of the olefinic proton was allylically coupled to the methyl group and vicinally coupled to a proton under the oxygen function which itself showed no further coupling. All signals could be assigned by spin decoupling which led to two sequences (A and B) which could be combined best to give **15**. The stereochemistry was deduced by NOE difference spectroscopy, which also established the proposed mode of connection of A and B. Thus the hydroxy proton showed NOEs with H-11 (3%) and H-13 (10%), H-2 with H-1 (10%) and H-14 (5%), H-4 with H-11 (3%) and H-11 with H-3 (10%), H-4 (12%), H-5 (8%) and H-7 (7%).

The ^{1}H NMR spectrum of **16** was in part very similar to tht of carotol [9] and **15**, but showed only one olefinic signal. All data agreed with the presence of the 8,9-dihydro derivative of **15**. Cyclachaenin, which has been isolated previously from *Iva xanthifolia* [10], is the corresponding *p*-methoxybenzoate and therefore its structure has to be revised to **17**. The ^{1}H NMR data are given in Table 3.

The isolation of several acanthospermolides from *B. acmella* again indicates that these compounds may be characteristic for the genus. So far such sesquiterpene lactones with an aldehyde group at C-10 and a 8β-oxygen function have been reported from *Acanthospermum* [11, 12], *Smallanthus* [13], *Siegesbeckia* [14] and *Ichthyothere* [15], while from *Melampodium* [16], *Tetragonotheca* [17] and *Enhydra* [18] similar lactones with an ester group at C-10 have been isolated. Acanthospermolides with an aldehyde group at C-10 are reported from two genera belonging to the tribe Mutisieae [19, 20], however, these have a 8α-oxygen function, a difference which may be significant also in other types of sesquiterpene lactones. Most likely therefore the acanthospermolides of Mutisieae are not closely related to those of the Heliantheae. The co-occurrence of acanthospermolides and ovatifolin derivatives in *Blainvillea* is an indication that enzymatic oxidation of the hydroxy group at C-14 may be accompanied by isomerization of the 1(10)-double bond. If this is true *Blainvillea* may be related to *Podanthus*, which is also placed in the subtribe Ecliptinae and where lactones like **1** are present.

EXPERIMENTAL

The air dried plant material, collected in September 1984 in Ramgarh, Rajasthan, India (voucher No. RUBL 18371, Jaipur) was extracted with Et_2O–petrol (1:2) at room temp. CC (silica gel) fractions of the extract of the aerial parts (250 g) were as follows: 1 (Et_2O–petrol, 1:4), 2 (Et_2O) and 3 (Et_2O–MeOH, 9:1). TLC of fraction 1 (silica gel, PF 254, Et_2O–petrol, 1:4) gave 5 mg lupenone, 35 mg lupeyl acetate, 15 mg phytol and 30 mg lupeol. TLC of fraction 2 (Et_2O–petrol, 9:1, detection by UV light and spraying with $KMnO_4$) gave five bands (2/1–2/5). Repeated TLC of 2/1 (CH_2Cl_2–C_6H_6, 1:1) gave 1 mg **6** (R_f 0.35). TLC of 2/2 (CH_2Cl_2–C_6H_6–Et_2O, 9:9:2, several developments) gave 0.6 mg **10** (R_f 0.38), 0.5 mg **9** (R_f 0.36) and 0.5 mg **6** (R_f 0.25). TLC of 2/3 (same solvent as for 2/2) gave 2.8 mg **8** (R_f 0.40) and 2 mg **4** (R_f 0.20). TLC of 2/4 (same solvent as for 2/2, several developments) afforded 1 mg **12** (R_f 0.30), 0.5 mg **11** (R_f 0.29) and 3.5 mg **7** (R_f 0.15). TLC of 2/5 (CH_2Cl_2–C_6H_6–Et_2O, 2:2:1) gave 1 mg **1** (R_f 0.25) and 1.6 mg **4** (R_f 0.20). TLC of fraction 3 (Et_2O) gave 2 mg desacyl grazielic acid tiglate (R_f 0.50), 3 mg **2** (R_f 0.15) and 7 mg desacetylovatifolin (R_f 0.10). CC (silica gel) of the extract from the roots (50 g) gave three fractions. TLC of the petrol fraction gave 5 mg **13** and 1 mg **14**. TLC of the fraction with Et_2O–petrol (1:3) gave 5 mg stigmasterol, 2 mg sitosterol, and a mixture which by repeated TLC (Et_2O–petrol, 1:10) gave 5 mg 1-hydroxy-α-curcumene (R_f 0.3), 2 mg rudbeckianone (R_f 0.28), 1 mg **15** (R_f 0.24) and 1 mg **16** (R_f 0.22), while TLC of the polar fraction (Et_2O–petrol, 9:1) afforded 3 mg ovatifolin. Known compounds were identified by comparing their 400 MHz ^{1}H NMR spectra with those of authentic materials. The purity of all compounds was tested by TLC in different solvent mixtures and by their ^{1}H NMR spectra.

9β-Hydroxyovatifolin-8-O-[*2-methylbutyrate*] (**1**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1785 (γ-lactone), 1740 (OAc); MS *m/z* (rel. int.): 346 $[M-HOAc]^+$ (1), 328 $[346-H_2O]^+$ (0.5), 244.109 $[346-RCO_2H]^+$ (10) (calc. for $C_{15}H_{16}O_3$: 244.109), 226 $[244-H_2O]^+$ (12), 211 $[226-Me]^+$ (3), 198 $[226-CO]^+$ (4), 85 $[C_4H_9CO]^+$ (38), 57 $[85-CO]^+$ (100); $[\alpha]_D = -35$ ($CHCl_3$; $c = 0.1$).

Desacetyl-11β,13-dihydroovatifolin (**2**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1760 (γ-lactone); MS *m/z* (rel. int.): 266.152 $[M]^+$ (1) (calc. for $C_{15}H_{22}O_4$: 266.152), 248 $[M-H_2O]^+$ (4), 230 $[248-H_2O]^+$ (2), 220 $[248-CO]^+$ (6), 205 $[220-Me]^+$ (6), 59 (100); $[\alpha]_D = -18$ ($CHCl_3$; $c = 0.2$).

Desacetyl-11β,13-dihydroovatifolin-8-O-*tiglate* (**3**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1785 (γ-lactone), 1720, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 330.183 $[M-H_2O]^+$ (0.5) (calc. for $C_{20}H_{26}O_4$: 330.183), 248 $[M-RCO_2H]^+$ (6), 230 $[248-H_2O]^+$ (12), 217 $[248-CH_2OH]^+$ (5), 202 $[217-Me]^+$ (5), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (65).

Desacetyl-11β,13-dihydroovatifolin-8-*one* (**4**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1700 (C=O); MS *m/z* (rel. int.): 264.136 $[M]^+$ (7) (calc. for $C_{15}H_{20}O_4$: 264.133), 246 $[M-H_2O]^+$ (20), 220 $[M-CO_2]^+$ (7), 219 $[M-CO_2H]^+$ (30), 205 $[220-Me]^+$ (10), 190 $[205-Me]^+$ (7), 69 (100); $[\alpha]_D = -466$ ($CHCl_3$; $c = 0.06$).

8β-Hydroxy-9β-[*2-methylbutyryloxy*]-*14-oxo-acanthospermolide* (**6**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1740 (CO$_2$R), 1690 (C=CCHO); MS *m/z* (rel. int.): 260.102 $[M-RCO_2H]^+$ (4) (calc. for $C_{15}H_{16}O_4$: 260.102), 242 $[260-H_2O]^+$ (4), 213 $[242-CHO]^+$ (4), 185 $[213-CO]^+$ (2), 85 $[C_4H_9CO]^+$ (34), 57 $[85-CO]^+$ (100); $[\alpha]_D = +26$ ($CHCl_3$; $c = 0.07$).

8β-Hydroxy-14-oxo-11β,13-dihydroacanthospermolide (**7**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1760 (γ-lactone), 2750, 1680 (C=CCHO); MS *m/z* (rel. int.): 264.131 $[M]^+$ (10) (calc. for $C_{15}H_{20}O_4$: 264.131), 246 $[M-H_2O]^+$ (10), 218 $[246-CO]^+$ (9), 217 $[246-CHO]^+$ (6), 203 $[218-Me]^+$ (5), 84 (100); $[\alpha]_D = -140$ ($CHCl_3$; $c = 0.33$).

8β-Acetoxy-14-oxo-11β,13-dihydroacanthospermolide (**8**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1785 (γ-lactone), 1750 (OAc), 2750, 1695 (C=CCHO); MS *m/z* (rel. int.): 246.126 $[M-HOAc]^+$ (30) (calc. for $C_{15}H_{18}O_3$: 246.126), 218 $[246-CO]^+$ (6), 217 $[246-CHO]^+$ (8), 190 $[218-CO]^+$ (12), 57 (100); $[\alpha]_D = -92$ ($CHCl_3$; $c = 0.27$).

8β-Tigloyloxy-14-oxo-11β,13-dihydroacanthospermolide (**9**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1785 (γ-lactone), 2750, 1690 (C=CCHO); MS *m/z* (rel. int.): 246.125 $[M-RCO_2H]^+$ (38) (calc. for $C_{15}H_{18}O_3$: 246.125), 218 $[246-CO]^+$ (4), 217 $[246-CHO]^+$ (5), 203 $[218-Me]^+$ (2), 189 $[217-CO]^+$ (5), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (60).

8β-[*2-Methylbutyryloxy*]-*14-oxo-11β,13-dihydroacanthospermolide* (**10**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1785 (γ-lactone), 1740 (CO$_2$R), 2750, 1690 (C=CCHO); MS *m/z* (rel. int.): 348 $[M]^+$ (0.5), 246.126 $[M-RCO_2H]^+$ (38) (calc. for $C_{15}H_{18}O_3$: 246.126), 218 $[246-CO]^+$ (6), 217 $[246-CHO]^+$ (8), 189 $[217-CO]^+$ (5), 85 $[C_4H_9CO]^+$ (30), 57 $[85-CO]^+$ (100); $[\alpha]_D = -121$ ($CHCl_3$; $c = 0.06$).

8,14-*Dioxo*-11β,13-*dihydroacanthospermolide* (**11**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1785 (γ-lactone), 1710 (C=O), 1690 (C=CCHO); MS *m/z* (rel. int.): 262.119 $[M]^+$ (5) (calc. for $C_{15}H_{18}O_4$: 262.119), 234 $[M-CO]^+$ (1), 205 $[234-CHO]^+$ (1), 178 $[M-C_5H_8O]^+$ (12), 69 (100).

8,14-*Dioxo*-7,11-*dehydro*-11,13-*dihydroacanthospermolide* (**12**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1710 (C=O), 1695 (C=CCHO); MS *m/z* (rel. int.): 260.104 $[M]^+$ (14) (calc. for $C_{15}H_{16}O_4$: 260.104), 232 $[M-CO]^+$ (7), 231 $[M-CHO]^+$ (8), 203 $[231-CO]^+$ (9), 69 (100).

4α-*Cinnamoyloxy*-2,3-*dehydrocarotol* (**15**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1710, 1640 (C=CCO$_2$R); MS *m/z* (rel. int.): 366.219 $[M]^+$ (1) (calc. for $C_{24}H_{30}O_3$: 366.219), 218 $[M-RCO_2H]^+$ (10), 200 $[218-H_2O]^+$ (9), 185 $[200-Me]^+$ (4), 175 $[218-C_3H_7]^+$ (12), 131 $[PhCH{=}CHCO]^+$ (100), 103 $[131-CO]^+$ (26), 77 $[103-C_2H_2]^+$ (18); $[\alpha]_D = -198$ ($CHCl_3$; $c = 0.05$).

4α-*Cinnamoyloxycarotol* (**16**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1710, 1640 (C=CCO$_2$R); MS *m/z* (rel. int.): 368.235 $[M]^+$ (3) (calc. for $C_{24}H_{32}O_3$: 368.235), 220 $[M-RCO_2H]^+$ (8), 202 $[220-H_2O]^+$ (7), 187 $[202-Me]^+$ (5), 148 $[PhCH{=}CHCO_2H]^+$ (100); $[\alpha]_D = -77$ ($CHCl_3$; $c = 0.07$).

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