

## 6 $\beta$ -LACTONIZED XANTHANOLIDES FROM *RATIBIDA* SPECIES

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**Key Word Index:**—*Ratibida columnifera*; *R. peduncularis*; Compositae; sesquiterpene lactones; xanthanolides; nerolidol derivative; phenylpropane derivative.

**Abstract**—The aerial parts of two *Ratibida* species gave, in addition to two known ones, eight new xanthanolides, a nerolidol and a phenylpropane derivative as well as a tetrayne thioenol ether. The structures and the stereochemistry were elucidated by high-field NMR spectroscopy. The chemotaxonomy of the genus *Ratibida* is discussed briefly.

### INTRODUCTION

The small genus *Ratibida* (tribe Heliantheae) was previously placed as a section of *Rudbeckia* in the subtribe Verbesinae. But recently the re-erected genus was transferred to Helianthinae [1] and then to the new, exclusively North American, subtribe Rudbeckiinae [2]. It differs from the Helianthinae by the striate achenes, the radial or vertical arrangement of the thickenings in the endothelial cells, the distinctive cluster of short, cylindrical glands on the anther appendages, and the common occurrence of a prominent reddish resin in the ducts of the disk corolla throat. The chemistry of the main genus *Rudbeckia* is not very characteristic. In addition to acetylenic compounds, especially thiophene acetylenes [3], different types of natural products are reported [4-7]. From the genus *Ratibida* so far only one species, *R. columnifera* (Nutt.) Woot. et Standl., has been investigated chemically and shown to contain unusual sesquiterpene lactones, the ratibidanolides and several xanthanolides [8]. We have now studied a further species and have re-investigated *R. columnifera* from a different location. The results are discussed in this paper.

### RESULTS AND DISCUSSION

The aerial parts of *R. columnifera*, collected in Colorado, gave eight xanthanolides (1-7 and 10), the tetrayne 13 [9], xanthanodiene (11) [10], pinocembrin, the nerolidol derivative 12 and the phenyl propanoid 14.

The main compound was the diketone 1. The  $^1\text{H}$  NMR spectrum of 1 (Table 1) showed the presence of a methylbutyrate residue (2.36 *td*, 1.64 and 1.45 *ddq*, 0.89 *t* and 1.10 *d*). Furthermore, a propenyl ketone followed from the typical signals. A quartet at  $\delta$  3.44 was attributed to H-10 as it was coupled with a secondary methyl group. This, together with a pair of double doublets at  $\delta$  2.75 and 2.69, which were coupled with H-7, made the presence of a keto group at C-9 very likely. Spin decoupling allowed the assignment of the remaining signals (H-5, H-6, H-7 and H-13). Thus the presence of a further xanthanolide was very likely. This assumption was supported by the

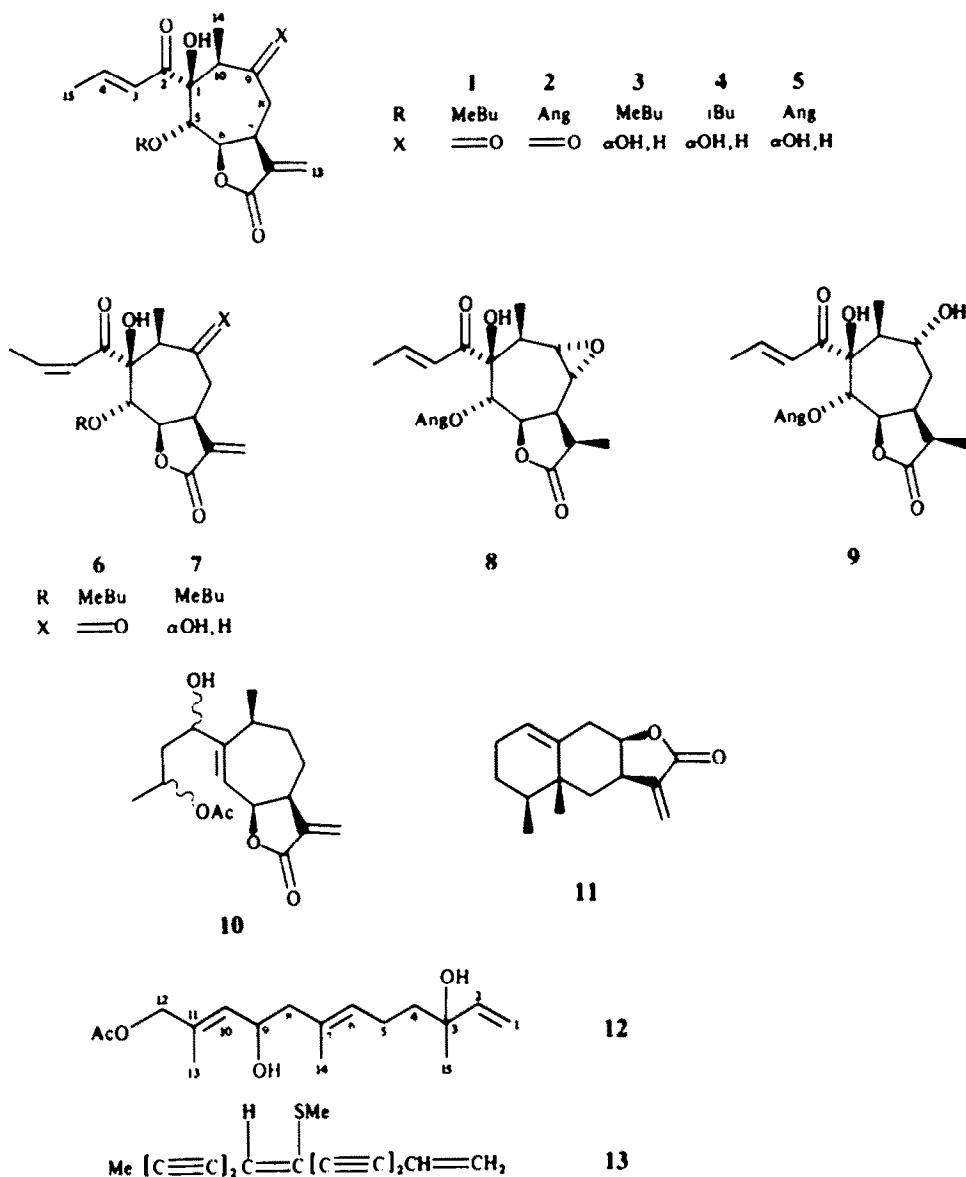
$^{13}\text{C}$  NMR spectrum and by the mass spectrum (see Experimental), where the loss of the propenylketone side chain gave rise to a pronounced fragment ( $m/z$  309). The stereochemistry was deduced by NOE difference spectroscopy. Clear effects were obtained between H-10, H-6, H-7 and H-3; between H-7, H-6, H-10 and H-13; between OH, H-3 and H-5; and between H-6, H-7, H-10 and H-3 (always irradiation of the first proton). We have named compound 1 with a free C-5 hydroxyl group and no function at C-9 *seco*-ratiferolide.

The  $^1\text{H}$  NMR spectrum of 2 (Table 1) was very similar to that of 1; only the signals of the ester residue were different. The presence of an angelate was deduced from the typical signals. The  $^1\text{H}$  NMR spectral data of 6 (Table 1) indicated, by the chemical shifts and couplings of H-3, H-4 and H-15, that this lactone was the 3*Z*-isomer of 1.

The  $^1\text{H}$  NMR data of 3-5 (Table 1) showed that these *seco* compounds were close to 1. The typical signals of the ester residue showed that we were dealing with a methyl butyrate (3), an isobutyrate (4) and an angelate (5). The additional three-fold doublet around  $\delta$  3.8 indicated that the 9-keto group was replaced by a hydroxyl group. Spin decoupling verified this assumption and allowed the assignment of all signals. The couplings observed agreed with those reported for 9 [8], and the  $^{13}\text{C}$  NMR spectrum of 5 also supported the proposed structures (see Experimental). Thus 5 was the 11,13-dehydro derivative of the angelate isolated from the same species collected in the city limits of Austin [8].

The  $^1\text{H}$  NMR spectrum of 7 (Table 1) showed that this lactone was a 3*Z*-isomer of 3.

The  $^1\text{H}$  NMR spectrum of 10 (Table 1) indicated that a xanthanolide with a saturated side chain was present. Spin decoupling showed the presence of oxygen functions at C-2 and C-4. The chemical shifts of the corresponding signals showed that a 2-hydroxy-4-acetoxy compound was present. Spin decoupling indicated homoallylic coupling of H-2 with a broadened doublet at  $\delta$  5.42 (H-6) which was further coupled with an olefinic signal (H-5). Although some signals were overlapped multiplets, the structure 7 was very likely. The configurations at C-2 and C-4 could not be determined.



The  $^1\text{H}$  NMR spectrum of 12 (see Experimental) was close to those of related nerolidol derivatives. Spin decoupling showed that the oxygen functions were at C-3, C-5 and C-12 while the chemical shifts indicated the position of the acetoxy group; in particular the shift of H-10 excluded a 13-acetoxy group. The configuration of the double bonds was deduced by comparison of the chemical shifts with those of similar nerolidol derivatives [11].

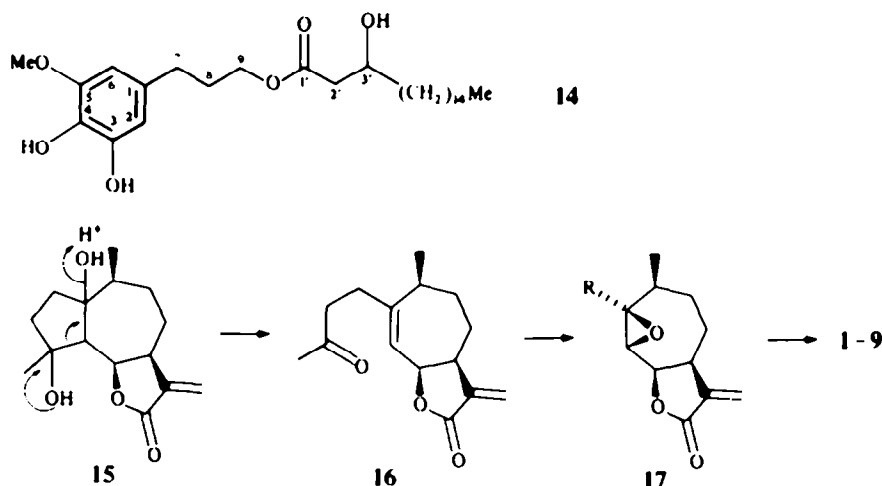
The structure of 14 followed from the spectral data, which were close to those of schkuhrianol, the corresponding 4-O-methyl derivative. The relative position of the remaining methoxyl group was deduced from the fact that the aromatic signals showed different chemical shifts. Furthermore, elimination of methanol was not observed in the mass spectrum which is typical for 4-methoxy derivatives [12]. All fragments agreed with those obtained with schkuhrianol [12].

The aerial parts of *R. peduncularis* Barnh., collected near Monterrey, Mexico, also gave the *seco*-ratiferolides

3-5, the 11,13-dihydro derivative 9 [8] and the epoxide 8 [8]. The structures and the stereochemistry of the last two compounds (8 and 9) were determined by  $^1\text{H}$  NMR and their NOEs. The data agreed nicely with those in the literature [8].

The constituents of *R. columnifera* from the two locations show clear differences. The *seco*-lactones from the Colorado collection were always methylene lactones, and no traces of any ratibidanolides, the main lactones from the Austin collection, were detected. Only 11, which is also a rearranged lactone, is formed via the common precursor proposed for the ratibidanolides (see ref. [8]). From both locations a nerolidol derivative was isolated but these also were structurally different.

The isolation of xanthanolides from the genus *Ratibida* is remarkable. So far, similar lactones with 6 $\beta$ ,12-lactone rings and a 10 $\beta$ -methyl group have only been reported from the genera *Parthenium*, *Parthenice*, *Iva* and *Dicoria* [13-16] while xanthan-8,12-olides are typical of the genus



*Xanthium* [17]. All these genera are placed in the subtribe Ambrosiinae, where pseudoguaianolides with the same configuration at C-6 and C-10 are common [17]. It may be of interest that *Rudbeckia mollis* contains an ambrosanolide [7]. Most likely the precursor of the ratiferolides is derived from a corresponding guaianolide. Thus 15 could be transformed to 16, which would then lead to the epoxide 17, the common precursor of 1-9, and 10 could be formed directly from 16 by allylic oxidation and reduction of the 4-keto group. Further investigations may show whether these findings are of chemotaxonomic

relevance, especially as xanthan-6 $\beta$ ,12-olides are rare and even 6 $\beta$ ,12-lactones, in general, are restricted to a few genera [17]. Compounds like 12-14 are probably not very characteristic since they have been reported from very different genera of the Heliantheae. However, the separation of the Rudbeckiinae from the subtribe Helianthinae is strongly supported by the chemistry. A connection to *Gaillardia*, as pointed out by Cronquist [18], is indicated only by the co-occurrence of pentacyclic-derived sulphur compounds like 13. However, the sesquiterpene lactones in this genus are

Table 1.  $^1\text{H}$ NMR spectral data of compounds 1-7 and 10 (400 MHz,  $\text{CDCl}_3$ , TMS as internal standard)

H	1	2	3 (57°)	4 (57°)	5 (57°)	6	7 (57°)	10*
3	6.76 dq	6.71 dq	6.48 br d	6.49 br d	6.49 br d	6.62 dq	6.39 br d	1.58 m 1.39 m
4	7.09 dq	7.10 dq	7.11 dq	7.12 dq	7.07 dq	6.49 dq	6.48 dq	5.20 ddq
5	5.28 d	5.30 d	5.21 br d	5.21 br d	5.30 br d	5.25 d	5.25 d	5.74 br s
6	5.08 dd	5.14 dd	4.93 br dd	4.94 br dd	4.97 br dd	5.12 dd	4.92 br dd	5.42 br d
7	3.81 dddd	3.84 m	3.64 dddd	3.65 dddd	3.66 dddd	3.82 m	3.64 dddd	2.98 dddd
8	2.75 dd		2.33 ddd	2.36 ddd	2.35 ddd		2.36 ddd	†
8'	2.69 dd	2.75 m	2.05 m	2.05 m	2.05 m	2.76 m	2.05 m	†
9		—	3.81 ddd	3.84 ddd	3.83 ddd		3.82 ddd	†
10	3.44 q	3.44 q	1.95 m	1.95 m	1.97 m	3.39 q	1.96 m	2.49 m
13	6.34 d	6.36 q	6.31 d	6.34 d	6.32 d	6.37 d	6.33 d	6.28 d
13'	5.71 d	5.70 d	5.64 d	5.65 d	5.65 d	5.72 d	5.64 d	5.54 d
14	0.91 d	0.93 d	0.88 d	0.90 d	0.88 d	0.91 d	0.88 d	1.00 d
15	1.94 dd	1.93 dd	1.94 dd	1.95 dd	1.90 dd	2.28 dd	2.17 d	1.15 d
OH	3.92 s	†	4.39 br s	4.40 br s	4.47 br s	3.87 br s	4.44 br s	†
OCOR	2.36 ddq	6.19 qq	2.33 m	2.47 qq	6.07 qq	2.38 ddq	2.29 ddq	1.96 s
	1.64 ddq	1.98 dq	1.60 ddq	1.11 d	1.92 dq	1.66 ddq	1.62 ddq	
	1.45 ddq	1.82 dq	1.40 ddq	1.08 d	1.76 br s	1.45 ddq	1.42 ddq	
	0.89 t		0.87 t			0.89 t	0.88 t	
	1.10 d		1.04 d			1.10 d	1.07 d	

\*H-2 = 4.16 br d.

†Obscured signals.

J(Hz): 3,4 = 15; 3,15 ~ 2; 4,15 = 7; 5,6 = 10; 6,7 = 7.5; 7,13 = 3.3; 7,13' = 2.7; 10,14 = 7; (compounds 1 and 2: 7,8 = 11; 7,8' = 5; 8,8' = 18; compounds 3-5 and 7: 7,8 = 12; 7,8' = 4; 8,8' = 15; 8,9 = 4; 8',9 = 9; 9,10 = 3; compounds 6 and 7: 3,4 = 11.5; compound 10: 2,3 = 10; 2,3' = 2.5 = 2.6 ~ 1.5; 3,4 = 10; 3',4 = 2.5; 4,15 = 7; 6,7 = 9; 7,8 ~ 10; 7,8' = 7,13 ~ 3; 10,14 = 7).

markedly different due to the presence of pseudoguainolides with a 10 $\alpha$ -methyl group [17]. Furthermore, no relationship to *Echinacea* is visible.

### EXPERIMENTAL

The air-dried plant material was extracted with MeOH-Et<sub>2</sub>O-petrol (1:1:1) and the extracts obtained were separated as reported previously [19]. The extract of the aerial parts (600 g) of *R. columnifera* (voucher RMK 9491, collected in Colorado) gave on CC (silica gel) four fractions (Et<sub>2</sub>O-petrol, 3:7; Et<sub>2</sub>O petrol, 1:1; Et<sub>2</sub>O-MeOH, 9:1 and MeOH). Prep. TLC of fraction 1 (Et<sub>2</sub>O petrol, 1:9; 3 developments) gave 25 mg 13 and 10 mg lupeyl acetate. Prep. TLC fraction 2 (same solvent) gave 24 mg 11. Fraction 3 gave, on standing at -20° in Et<sub>2</sub>O, 300 mg 1. The mother liquor afforded, on prep. TLC (Et<sub>2</sub>O-petrol, 4:1), 16 mg 11, 10 mg pinocembrin, 5 mg stigmasterol, 5 mg sitosterol and 30 mg 14 (Et<sub>2</sub>O petrol, 1:1, *R<sub>f</sub>* 0.6). Fraction 4 gave, on standing at -20° in Et<sub>2</sub>O, 500 mg 1. Prep. TLC of the mother liquor (Et<sub>2</sub>O-petrol, 4:1) gave 31 mg 14 and two mixtures (4/2 and 4/3). Fraction 4/2 gave on repeated prep. TLC and HPLC (always RP 8, MeOH-H<sub>2</sub>O, 3:2, flow rate ca 3 ml/min, 100 bar) 3 mg 10 (*R<sub>f</sub>* 5.9 min), 1 mg 12 (*R<sub>f</sub>* 8.1 min), 3.5 mg 2 (*R<sub>f</sub>* 8.6 min) and a crude fraction which afforded on TLC (CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O-toluene, 1:1:1; 2 developments) 7 mg 6 (*R<sub>f</sub>* 0.5). HPLC of fraction 4/3 gave 15 mg 4 (*R<sub>f</sub>* 7.5 min), 65 mg 5 (*R<sub>f</sub>* 8.5 min), 80 mg 3 (*R<sub>f</sub>* 9.8 min), 35 mg 7 (*R<sub>f</sub>* 11.2 min) and 80 mg 1 (*R<sub>f</sub>* 12.7 min).

The extract of the aerial parts (300 g) of *R. peduncularis* (voucher 7974, deposited at the Herbarium of the Inst. Tecnológico, Monterrey, Mexico) gave by CC, prep. TLC and HPLC (see above) 40 mg 7-hydroxy-5,6E-dehydro-6,7-dihydrolinalol, 3 mg 3, 2.5 mg 4, 5.5 mg 5, 4.5 mg 8 and 3.8 mg 9. Known compounds were identified by comparing the 400 MHz <sup>1</sup>H NMR spectra with those of authentic material.

**9-Oxo-seco-ratiferolide-5 $\alpha$ -O-[2-methylbutyrate]** (1). Colourless crystals, mp 131°; IR  $\nu_{\text{max}}^{\text{CHCl}_3}$  cm<sup>-1</sup>: 3540 (OH), 1780 ( $\gamma$ -lactone), 1730 (CO<sub>2</sub>R), 1690 (C=CC=O); MS *m/z* (rel. int.): 378.167 [M]<sup>+</sup> (0.7) (calc. for C<sub>20</sub>H<sub>24</sub>O<sub>6</sub>: 378.168), 309 [M - MeCH=CHCO]<sup>+</sup> (27), 276 [M - RCO<sub>2</sub>H]<sup>+</sup> (2), 207 [309 - RCO<sub>2</sub>H]<sup>+</sup> (3), 85 [C<sub>4</sub>H<sub>8</sub>CO]<sup>+</sup> (92), 69 [MeCH=CHCO]<sup>+</sup> (60), 57 [85 - CO]<sup>+</sup> (100); <sup>13</sup>C NMR (CDCl<sub>3</sub>, C-1 to C-15): 81.5 s, 199.0 s, 125.6 d, 148.8 d, 77.6 d, 76.5 d, 41.0 d, 44.0 t, 206.4 s, 49.3 d, 137.0 s, 167.8 s, 124.2 t, 8.6 q, 18.6 q; OCOR: 176.8 s, 36.2 d, 26.3 t, 11.4 q, 16.1 q; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -245° (CHCl<sub>3</sub>; c 1.05).

**9-Oxo-seco-ratiferolide-5 $\alpha$ -O-angelate** (2). Colourless oil; IR  $\nu_{\text{max}}^{\text{CHCl}_3}$  cm<sup>-1</sup>: 3620 (OH), 1780 ( $\gamma$ -lactone), 1720 (C=O, CO<sub>2</sub>R); MS *m/z* (rel. int.): 376.152 [M]<sup>+</sup> (2) (calc. for C<sub>20</sub>H<sub>24</sub>O<sub>6</sub>: 376.152), 307 [M - MeCH=CHCO]<sup>+</sup> (11), 83 [C<sub>4</sub>H<sub>8</sub>CO]<sup>+</sup> (100), 69 (48), 55 [83 - CO]<sup>+</sup> (32).

**9 $\alpha$ -Hydroxy-seco-ratiferolide-5 $\alpha$ -O-[2-methylbutyrate]** (3). Colourless oil; IR  $\nu_{\text{max}}^{\text{CHCl}_3}$  cm<sup>-1</sup>: 3620 (OH), 1780 ( $\gamma$ -lactone), 1750 (CO<sub>2</sub>R), 1690 (C=CC=O); MS *m/z* (rel. int.): 311.150 [M - MeCH=CHCO]<sup>+</sup> (5) (calc. for C<sub>18</sub>H<sub>22</sub>O<sub>6</sub>: 311.150), 209 [311 - RCO<sub>2</sub>H]<sup>+</sup> (15), 85 [C<sub>4</sub>H<sub>8</sub>CO]<sup>+</sup> (58), 69 (61), 57 [85 - CO]<sup>+</sup> (100); [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -147° (CHCl<sub>3</sub>; c 0.95).

**9 $\alpha$ -Hydroxy-seco-ratiferolide-5 $\alpha$ -O-isobutyrate** (4). Colourless oil; IR  $\nu_{\text{max}}^{\text{CHCl}_3}$  cm<sup>-1</sup>: 3620 (OH), 1780 ( $\gamma$ -lactone), 1750 (CO<sub>2</sub>R); MS *m/z* (rel. int.): 297.134 [M - MeCH=CHCO]<sup>+</sup> (47) (calc. for C<sub>17</sub>H<sub>20</sub>O<sub>6</sub>: 297.134), 209 [297 - RCO<sub>2</sub>H]<sup>+</sup> (32), 71 [C<sub>3</sub>H<sub>6</sub>CO]<sup>+</sup> (100); [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -87° (CHCl<sub>3</sub>; c 0.7).

**9 $\alpha$ -Hydroxy-seco-ratiferolide-5 $\alpha$ -O-angelate** (5). Colourless oil; IR  $\nu_{\text{max}}^{\text{CHCl}_3}$  cm<sup>-1</sup>: 3620 (OH), 1780 ( $\gamma$ -lactone), 1740 (CO<sub>2</sub>R), 1690 (C=CC=O); MS *m/z* (rel. int.): 378.167 [M]<sup>+</sup> (1.4) (calc. for C<sub>20</sub>H<sub>24</sub>O<sub>6</sub>: 378.168), 309 (12), 209 [309 - RCO<sub>2</sub>H]<sup>+</sup> (3), 83

[C<sub>4</sub>H<sub>8</sub>CO]<sup>+</sup> (100), 69 (26), 55 (41); <sup>13</sup>C NMR (CDCl<sub>3</sub>, C-1 to C-15): 82.4 s, 197.7 s, 125.5 d, 145.6 d, 78.5 d, 77.5 d, 41.7 d, 37.0 t, 70.9 d, 34.7 d, 138.0 s, 166.8 s, 123.0 t, 12.7 q, 18.5 q; OAc: 168.8 s, 126.7 s, 140.5 d, 18.3 q, 15.6 q; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -118° (CHCl<sub>3</sub>; c 0.92).

**9-Oxo-3Z-seco-ratiferolide-5 $\alpha$ -O-[2-methylbutyrate]** (6). Colourless oil; IR  $\nu_{\text{max}}^{\text{CHCl}_3}$  cm<sup>-1</sup>: 3420 (OH), 1780 ( $\gamma$ -lactone), 1720 (CO, CO<sub>2</sub>R), 1690 (C=CC=O); MS *m/z* (rel. int.): 378.167 [M]<sup>+</sup> (1) (calc. for C<sub>20</sub>H<sub>24</sub>O<sub>6</sub>: 378.168), 309 (40), 207 (3), 85 (86), 69 (44), 57 (100).

**9 $\alpha$ -Hydroxy-3Z-seco-ratiferolide-5 $\alpha$ -O-[2-methylbutyrate]** (7). Colourless oil; IR  $\nu_{\text{max}}^{\text{CHCl}_3}$  cm<sup>-1</sup>: 3620 (OH), 1785 ( $\gamma$ -lactone), 1745 (CO<sub>2</sub>R), 1675 (C=CC=O); MS *m/z* (rel. int.): 380.184 [M]<sup>+</sup> (0.2) (calc. for C<sub>20</sub>H<sub>24</sub>O<sub>6</sub>: 380.184), 311 (31), 209 (20), 85 (100), 69 (44); [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -93° (CHCl<sub>3</sub>; c 1.1).

**2-Hydroxy-4-acetoxyxanthan-1(5)-en-6 $\beta$ ,12-olide** (10). Colourless oil; IR  $\nu_{\text{max}}^{\text{CHCl}_3}$  cm<sup>-1</sup>: 3620 (OH), 1780 ( $\gamma$ -lactone), 1745 (OAc); MS *m/z* (rel. int.): 248 [M - HOAc]<sup>+</sup> (28), 230 [248 - H<sub>2</sub>O]<sup>+</sup> (22), 204 [248 - CO<sub>2</sub>]<sup>+</sup> (35), 43 (100); [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -41° (CHCl<sub>3</sub>; c 0.3).

**9-Hydroxy-12-acetoxynerylolide** (12). Colourless oil; IR  $\nu_{\text{max}}^{\text{CHCl}_3}$  cm<sup>-1</sup>: 3600 (OH), 1750 (OAc); MS *m/z* (rel. int.): 296 [M]<sup>+</sup> (0.2) (C<sub>17</sub>H<sub>22</sub>O<sub>4</sub>), 236 [M - HOAc]<sup>+</sup> (0.3), 225 [M - C<sub>4</sub>H<sub>8</sub>O]<sup>+</sup> (0.5), 183 [225 - ketene]<sup>+</sup> (2), 85 (100); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.06 (dd, H-1c), 5.20 (dd, H-1t), 5.90 (dd, H-2), 5.27 (t (br), H-6), 2.14 (d (br), H-8), 4.47 (dt (br), H-9), 5.44 (d (br), H-10), 4.46 (s (br), H-12), 1.71 (s (br), H-13), 1.65 (s (br), H-14), 1.26 (s, H-15) [J (Hz): 1c, 2 = 10; 1t, 2 = 17; 5, 6 = 8, 9 = 9, 10 ~ 7].

**4-O-Desmethylichukrianol** (14). Colourless oil; MS *m/z* (rel. int.): 480.345 [M]<sup>+</sup> (12) (calc. for C<sub>28</sub>H<sub>44</sub>O<sub>6</sub>: 480.345), 269 [M - C<sub>15</sub>H<sub>11</sub>]<sup>+</sup> (19), 198 [M - R-CH=C=O]<sup>+</sup> (24), 180 [198 - H<sub>2</sub>O]<sup>+</sup> (73), 57 (100); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.27 (d, H-2), 6.41 (d, H-6), 2.56 (t (br), H-7), 1.93 (tt, H-8), 4.11 (t (br), H-9), 2.50 (dd, H-2), 2.38 (dd, H-2), 3.99 (m, H-3), (1.27 m, H-5, H-17), 0.85 (t, H-18), 3.84 (s, OMe) [J (Hz): 2, 6 = 1.5; 7, 8 = 8, 9 = 7; 2, 2' = 16; 2, 3 = 3; 2, 3' = 10, 17, 18' = 7].

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