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GUAIANOLIDES AND OTHER CONSTITUENTS FROM *LIABUM FLORIBUNDUM*

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Key Word Index—*Liabum floribundum*; Compositae; sesquiterpene lactones; guaianolides; eudesmanolide; sesquiterpenes; monoterpenes; dihydroxysabinanes.

Abstract—The reinvestigation of the aerial parts of *Liabum floribundum* afforded seven new guaianolides, all with a 9β-hydroxy group, a related eudesmanolide, two epimeric dihydroxysabinanes, two guaiane endoperoxides and a seco-sesquiterpene. The structures were elucidated by high field ^{1}H NMR spectroscopy and a few chemical transformations. The C-4 configuration of a guaianolide from *Arctotis grandis* has been revised.

INTRODUCTION

So far only a few species from the Central and South American genus *Liabum* have been investigated chemically. In addition to tridecapentaynene and tridecaenetetraynene, a few simple sesquiterpene lactones of different types have been isolated [1–3]. We have now re-investigated in more detail *L. floribundum* collected in Peru. The results are discussed in this paper.

RESULTS AND DISCUSSION

Previous investigations of small samples of *L. floribundum* Less. from Peru [1] and Ecuador [2] gave different, not very characteristic constituents. We have, therefore, re-investigated a larger sample which was collected in Peru. The polar fractions afforded a complex mixture which was separated with difficulty to give the guaianolides **1**–**7**, the eudesmanolide **10**, the epimeric sabinane diols **11a** and **b**, the seco-diketone **13** and the endoperoxides **14** and **15**.

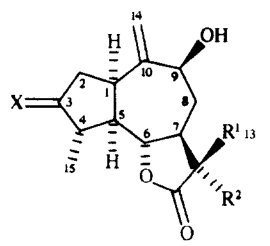
The ^{1}H NMR spectrum of **7** (Table 1) was close to that of the corresponding 3-keto derivative which had been reported from a *Vernonia* species [4]. However, the replacement of the keto group by a hydroxy group caused some shift differences and a broadened double doublet at δ4.64 indicated the presence of an allylic hydroxy group. The position of the latter followed from the allylic coupling with H-15. The β-configuration of the hydroxy group at C-3 was deduced from the couplings and from comparison with the spectrum of zaluzanin C [5]. The stereochemistry at C-9 also followed from the couplings which agreed with those of 9β-hydroxydehydrozaluzanin [4]. As lactone **7** was not completely free from **5** it was purified as its pyrazoline derivative **8** and also via the pyrrolidine adduct **9** which was transformed to **7** by reaction with methyl iodide and hydrogen carbonate [6]. The ^{1}H NMR spectra of **8** and **9** (Table 1) and the ^{13}C NMR spectrum of **7** (see Experimental) also supported the structure.

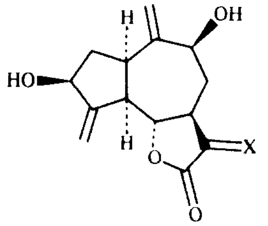
The ^{1}H NMR spectra of **5** and **6** (Table 1) clearly indicated that they were the corresponding 11,13-dihydro derivatives of **7**. The couplings of H-11 and its chemical shift indicated the configurations at C-11. The ^{1}H NMR spectrum of the diacetate of **6** also supported the structure (see Experimental).

The ^{1}H NMR spectra of **1** and **2** (Table 1) showed some similarities with the spectrum of 4β,15-dihydro-3-dehydrozaluzanin C [7]. However, additional methyl doublets at δ1.30 and 1.22 as well as double quartets at δ2.25 and 2.75, respectively and H-9 double doublets indicated that 9β-hydroxy derivatives of the corresponding epimeric 11,13-dihydrolactones were present. Again, from the couplings and the chemical shifts the configuration at C-11 could be deduced. Furthermore, the stereochemistry of **1** was established by the observed NOEs (H-15 with H-5, H-1 with H-9, H-5 and H-7, H-6 with H-4, H-8β and H-11 as well as H-14′ with H-2β and H-4). Accordingly, lactone **1** is identical with a guaianolide isolated from *Arctotis grandis* [8].

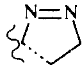
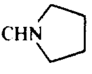
The ^{1}H NMR spectra of **3** and **4** (Table 1) were close to those of **5** and **6**, respectively, but also in part to those of **1** and **2**. The differences clearly showed that these lactones were epimeric at C-11. The stereochemistry was established by NOE difference spectroscopy. As the lactones **3** and **4** both showed clear effects between H-15 and H-3 the former should be identical with a diol from *Arctotis grandis* [9]. Comparison of the ^{1}H NMR spectra, however, showed that they must be isomers. This was deduced from the observed clear NOEs of 4 *epi*-**4** [9] between H-15 and H-6 as well as between H-4 and H-3. Thus the stereochemistry of the *Arctotis* lactone has to be revised from 4α- to 4β-methyl.

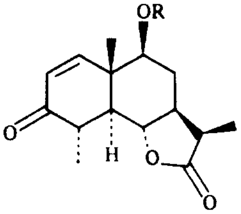
The structure of **10a** followed from the ^{1}H NMR spectrum of its acetate **10b** (Table 1) which differed markedly from those of **1**–**7**. A pair of doublets at δ6.80 and 5.96 (J = 10 Hz) clearly indicated the presence of a conjugated cyclohexenone derivative. These results suggested an eudesmanolide was present. Spin decoupling established this assumption. Though the H-11 signal was overlapped



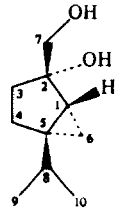


	1	2	3	4
X	O	O	βOH,H	βOH,H
R¹	H	Me	H	Me
R²	Me	H	Me	H

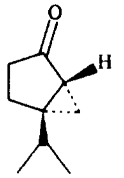
	5	6	7	8	9
X	αMe,H	βMe,H	CH₂		αCHN  ,H



10a R = H
10b R = Ac



11a
11b 2*epi*



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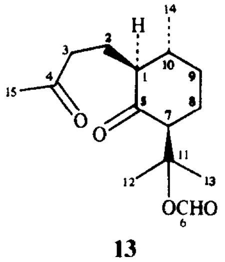

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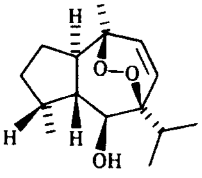

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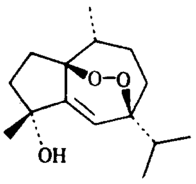

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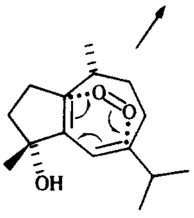

the chemical shift indicated the presence of a 11β-methyl derivative. The ^1H NMR spectrum was in part close to that of tuberiferin [10] which is the corresponding 9-desacetoxy derivative with an 11(13)-double bond.

The structure and the stereochemistry of **11a/b** followed from ^1H NMR data (Table 2) and the periodate degradation to (+) sabina ketone. Therefore the diols were epimeric at C-2. The relative configuration in the case of **11b** was determined by a NOE between H-6α and H-7. The absolute configuration followed from the positive Cotton-effect of the sabina ketone (**12**) obtained by degradation. Application of the inverse rule for cyclopropyl ketones [11, 12] led to the shown configuration.

The diketone **13** gave no molecular ion in the EIMS, but by CIMS an $[M+1]^+$ ion was obtained which agreed with $C_{15}H_{24}O_4$. Also in the ^{13}C NMR spectrum (see Experimental) 15 signals were visible. As, in addition to the carbonyl signals at δ208.9 and 210.6, only one further low field signal at δ160.5 was present the latter must be due to an additional carbonyl carbon. The chemical shift of the latter only agreed with a formate. This was supported by a singlet at δ7.69 in the ^1H NMR spectrum. Spin decoupling in C_6D_6 led to a sequence which required a tri-substituted cyclohexanone, one being methyl, one 3-oxo-butyl and the last an isopropyl group with a formate residue. The arrangement and the configurations were established by NOE difference spectroscopy. Clear NOEs were obtained between H-14, H-1 and H-2, between H-12 and H-6, between H-13, H-6 and H-7 as well as between H-7, H-1 and H-6. All data,

Table 1. ^{1}H NMR spectral data of compounds **1–9** and **10b** (400 MHz, $CDCl_3$)

H	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8***	**9†**	**10b‡**
1	2.96 *br ddd*	2.99 *br ddd*	2.74 *br ddd*	2.77 *br ddd*	2.82 *br ddd*	2.84 *br ddd*	2.85 *m*	2.87 *br ddd*	2.85 *m*	6.80 *d*
2	2.60 *dd*	2.60 *dd*	2.20 *m*	2.19 *ddd*	2.42 *m*	2.40 *m*	2.47 *ddd*	2.45 *m*	2.39 *ddd*	5.96 *d*
2′	2.49 *ddd*	2.49 *ddd*	1.80 *m*	1.80 *m*	1.80 *ddd*	1.81 *ddd*	1.85 *ddd*	1.88 *ddd*	1.81 *ddd*	
3	—	—	3.71 *ddd*	3.72 *ddd*	4.59 *br t*	4.58 *br t*	4.64 *br t*	4.64 *br t*	4.61 *br t*	—
4	2.31 *ddq*	2.30 *ddq*	1.80 *m*	1.80 *m*	—	—	—	—	—	2.67 *m*
5	2.16 *ddd*	2.17 *ddd*	1.80 *m*	1.80*m*	2.76 *br dd*	2.78 *br dd*	2.85 *m*	2.92 *dddd*	2.78 *br dd*	2.08 *dd*
6	3.94 *dd*	4.07 *dd*	3.86 *dd*	4.00 *dd*	3.96 *dd*	4.09 *dd*	4.01 *dd*	4.90 *dd*	3.97 *dd*	4.22 *dd*
7	2.05 *dddd*	2.56 *dddd*	1.80 *m*	2.29 *dddd*	1.92 *dddd*	2.42 *m*	2.85 *m*	2.25 *ddd*	2.30 *dddd*	2.25 *m*
8	2.53 *ddd*	2.33 *ddd*	2.36 *ddd*	2.16 *ddd*	2.43 *m*	2.21 *ddd*	2.61 *ddd*	1.80 *ddd*	2.66 *ddd*	2.15 *m*
8′	1.35 *ddd*	1.41 *ddd*	1.33 *ddd*	1.43 *ddd*	1.32 *ddd*	1.41 *ddd*	1.42 *ddd*	1.50 *m*	1.34 *ddd*	1.70 *ddd*
9	4.22 *br dd*	4.23 *br dd*	4.04 *br dd*	4.07 *br dd*	4.12 *br dd*	4.13 *br dd*	4.22 *br dd*	4.09 *br dd*	4.16 *br dd*	4.81 *dd*
11	2.25 *dq*	2.75 *dq*	2.20 *m*	2.67 *dq*	2.24 *dq*	2.70 *dq*	—	—	2.88 *ddd*	2.67 *m*
13	1.30 *d*	1.22 *d*	1.23 *d*	1.16 *d*	1.26 *d*	1.19 *d*	6.27 *d* 5.55 *d*	2.45 *m* 1.50 *m*	2.45 *m*	1.23 *d*
14	5.43 *d*	5.42 *d*	5.46 *br s*	5.42 *br s*	5.43 *t*	5.43 *t*	5.44 *t*	5.46 *t*	5.42 *t*	1.27 *s*
14′	4.82 *br s*	4.82 *br s*	5.13 *d*	5.12 *d*	5.20 *t*	5.19 *t*	5.25 *t*	5.26 *t*	5.19 *t*	
15	1.25 *d*	1.25 *d*	1.19 *d*	1.20 *d*	5.33 *dd* 5.29 *dd*	5.34 *dd* 5.30 *dd*	5.40 *dd* 5.32 *dd*	5.48 *dd* 5.39 *dd*	5.33 *dd* 5.29 *dd*	1.40 *d*

*H-16 4.79 *ddd*; H-16′ 4.68 *ddd*.

†Pyrrolidine 2.55 *m*, 2.50 m, 1.76 m.

‡OAc 2.15 s.

J [Hz]: Compounds **1** and **2**: 1, 2 = 1, 5 = 5, 6 = 8.5; 1, 2′ = 2′, 4 = 9, 14 = 1.5; 2, 2′ = 19; 4, 15 = 11, 13 = 7; 4, 5 = 8, 9′ = 10.5; 6, 7 = 10.5; 7, 8 = 2.5; 7, 8′ = 7, 11 = 11.5; 8, 8′ = 13; 8, 9 = 5.5 (compound **2**: 7, 11 = 7); compound **3**: 1, 2 = 1, 2′ = 1, 5 ~ 8.5; 2, 2′ = 13; 2, 3 = 6.5; 2′, 3 = 3, 4 = 9; 5, 6 = 6, 7 = 9.5; 7, 8 = 3.5; 7, 8′ ~ 8; 7, 11 ~ 10; 8, 8′ = 12; 8, 9 = 3.5; 8, 9′ = 10; 11, 13 = 7; compound **4**: 1, 2 = 2, 3 = 6.5; 1, 2′ = 1, 5 = 5, 6 = 6, 7 ~ 9; 2, 2′ = 12.5; 7, 8 = 3; 7, 8′ = 11; 7, 11 = 11, 13 = 7.5; 8, 9 = 3; 8′, 9 = 11; 8, 8′ = 12; compound **5**: 1, 2 = 2, 3 ~ 5; 1, 2′ = 1, 5 = 5, 6 = 6, 7 ~ 9; 2′, 3 = 8; 7, 8 = 2.5; 3.15 = 5, 15 ~ 1.5; 7.8′ = 10; 7, 11 = 12; 8, 8′ = 12; 8, 9 = 4; 8′, 9 = 11; 11, 15 = 7; compound **6**: 1, 2 = 2, 3 ~ = 6; 1, 2′ = 1.5 = 5, 6 = 6, 7 = 2′, 3 ~ 9; 2, 2′ = 13; 3, 15 = 5, 15 ~ 1.5; 7, 11 = 7; 7, 8 = 3; 7,8′ = 10; 8, 8′ = 13; 8, 9 = 4; 8′, 9 = 10; 11, 13 = 7; compound **7–9**: 1, 2 = 2, 3 = 6; 1, 2′ = 5; 2, 2′ = 14; 3, 15 = 5, 15 = 1; 5, 6 = 6, 7 = 9; 7, 8 = 8; 7, 8′ = 10; 7, 13 = 3.5; 7, 13′ = 3; 8′, 8′ = 14; 8, 9 = 5; 8′, 9 = 10 (compound **8**: 3, 15 = 5, 15 ~ 1.5; 7, 8 = 5; 7, 8′ = 12; 13, 16 = 4; 13, 16′ = 9.5; 13′, 16 = 9; 13′, 16′ = 7; 16, 16′ = 17; compound **9**: 3, 15 = 5, 15 = 1.5; 7, 8 = 2.5; 7, 8′ = 11′; 7, 11 = 12; 11, 13 = 4) compound **10b**: 1, 2 = 10; 4, 5 = 10; 4, 15 = 11, 13 = 7; 5, 6 = 6, 7 = 10.5; 7, 8′ = 10.5; 8, 8′ = 12; 8, 9 = 4; 8′, 9 = 10.5.

Table 2. ^{1}H NMR spectral data of compounds **11a** and **11b** (400 MHz, $CDCl_3$)

H	**11a**	**11b**	multiplicity	*J* [Hz]
1	1.19	1.13	*dd*	8.5, 3.5
3	1.59	1.23	*ddd*	13, 13, 8
3′	1.72	1.67	*dd*	13, 8
4	1.90	1.56	*ddd*	13, 13, 8
4′	1.20	1.64	*dd*	13, 8
6α	0.73	0.25	*dd*	5, 3.5
6β		0.42	*dd*	8.5, 5
7	3.55	3.58	*d*	11
7′	3.50	3.54	*d*	11
8	1.33	1.47	*qq*	7, 7
9	0.88	0.91	*d*	7
10	0.91	1.00	*d*	7

therefore, agreed with the proposed structure of this diketone which we have named secofloribundione. It is probable that **13** is biogenetically derived from the guaiane derivative **15** (see below) which is transformed first to the corresponding bis-epoxide. The latter could give a diketone by proton attack of the 1,5-epoxide followed by rearrangement with ring contraction and oxidative cleavage of a hemi-acetal.

The structure of **14** was also deduced by its ^{1}H and ^{13}C NMR spectra (see Experimental). Spin decoupling in C_6D_6 led to sequences which only agreed with the presence of the endoperoxide **14** and the observed NOEs led to the proposed stereochemistry. Thus clear NOEs were observed between H-15, H-1 and H-6, between H-14, H-1, H-2β and H-9, between H-13 and H-6 as well as between H-4, H-3α and H-5. The structure of the second endoperoxide was deduced from its ^{1}H NMR spectrum. The stereochemistry followed from NOEs between H-12 and H-6, H-13 and H-6, H-15 and H-6 as well as between H-6, H-11, H-12, H-13 and H-15. **14** and **15** are probably formed by reaction of the corresponding guaiadienes with singlet oxygen. Similarly, in the lactones **1–7** and **10a** the 9-hydroxy group is probably formed as a result of reactions with singlet oxygen followed by reduction of the corresponding hydroperoxides. This type of enzymatic reactions seems to be typical for the tribe Liabeae as similar oxidation steps have been observed in other members [1, 13, 14].

EXPERIMENTAL

The air-dried aerial parts (350 g, collected in Spring 1986 in Peru, Prof. Ferenhafe, 15 km SW of Incahuasi, slop of Rio de la Leche, 2000 m, voucher Dillon et Skillman 4184 deposited in the National Field Museum, Chicago, U.S.A.) were extracted with

MeOH–Et_2O–petrol (1:1:1) at room temp. The extract obtained was first separated by CC (silica gel) into three crude fractions (1: petrol and Et_2O–petrol, 1:3; 2: Et_2O–petrol, 1:1; 3: Et_2O and Et_2O–MeOH, 9:1). Fraction 1 gave by TLC (silica gel, PF 254) triglycerides and 400 mg squalene. HPLC of fraction 2 (MeOH–H_2O, 7:3, always RP 18, *ca* 100 bar) gave 5 mg **13** (R_t 3.4 min), 7 mg **14** (R_t 4.4 min) and a mixture which gave by TLC (Et_2O–petrol, 1:1) 3 mg **15** (R_f 0.34). Fraction 3 was defatted by treatment with MeOH and separated by flash chromatography (silica gel, ϕ 30–60 μ) affording four crude fractions (3/1–3/4). TLC of 3/1 (CH_2Cl_2–Et_2O, 4:1) gave 15 mg **11a**/**11b**. 20% of 3/2 gave by HPLC (MeOH–H_2O, 9:11) 10 mg **5** (R_t 1.6 min), 1.5 mg **3** (R_t 2.4 min.) and 17 mg **1** (R_t 2.8 min). HPLC of 3/3 (MeOH–H_2O, 9:11) afforded 40 mg of a mixture of **5** and **7** (R_t 2.0 min) which by addition of pyrrolidine and TLC gave pure **5** and **9** (see below) and a mixture, which was treated with Ac_2O (1 hr, 70°). HPLC (MeOH–H_2O, 7:3) gave 3 mg **10b** (R_t 1.4 min). HPLC of 20% of 3/4 (MeOH–H_2O, 2:3) afforded 7 mg **6** (R_t 0.9 min), 6 mg **2** (R_t 1.5 min), 7 mg **4** (R_t 1.9 min) and a mixture of **4** and **7**, which was treated with CH_2N_2 (see below). Probably due to the minute amounts, the lactones could not be induced to crystallize.

9β-Hydroxy-4β,15,11α,13-tetrahydro-dehydrozaluzanin C **2**). Colourless oil; IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3600 (OH), 1765 (γ-lactone), 1735 (C=O); MS *m/z* (rel. int.): 264.136 $[M]^+$ (51) (calcd for $C_{15}H_{20}O_4$: 264.136), 246 (8), 109 (66), 107 (62), 95 (76), 93 (66), 81 (77), 69 (82), 55 (100).

9β-Hydroxy-4β,15,11β,13-tetrahydrozaluzanin C (**3**). Colourless oil; IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3600 (OH), 1770 (γ-lactone); MS *m/z* (rel. int.): 266.152 $[M]^+$ (7) (calcd for $C_{15}H_{22}O_4$: 266.152), 248 (59), 230 (34), 220 (30), 175 (94), 121 (56), 81 (100), 55 (93).

9β-Hydroxy-4β,15,11α,13-tetrahydrozaluzanin C (**4**). Colourless oil; IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3600 (OH), 1770 (γ-lactone); MS *m/z* (rel. int.): 266 $[M]^+$ (3), 248.141 $[M-H_2O]^+$ (12) (calcd for $C_{15}H_{20}O_3$: 248.141), 230 (17), 220 (18), 175 (83), 121 (52), 109 (76), 81 (92), 55 (100); $[\alpha]_D^{29°}$ +27 ($CHCl_3$; *c*0.57).

9β-Hydroxy-11β,13-dihydrozaluzanin C (**5**). Colourless oil; IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3600 (OH), 1770 (γ-lactone); *MS m/z* (rel. int.): 264.136 $[M]^+$ (19) (calcd for $C_{15}H_{20}O_4$: 264.136), 246 (32), 228 (12), 218 (14), 173 (80), 91 (76), 55 (100); ^{13}C NMR ($CDCl_3$, C-1–C-15): δ40.6 *d*, 38.7 *t*, 73.1 *d*, 153.1 *s*, 49.4 *d*, 83.8 *d*, 48.6 *d*, 40.4 *t*, 74.5 *d*, 153.2 *s*, 41.6 *d*, 178.0 *s*, 13.1 *q*, 110.3 *t*, 110.0 *t* (assigned by ^1H–^{13}C correlated spectrum).

9β-Hydroxy-11α,13-dihydrozaluzanin C (**6**). Colourless gum; IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3600 (OH) , 1765 (γ-lactone); MS *m/z* (rel. int.): 264.136 $[M]^+$ (10) (calcd for $C_{15}H_{20}O_4$: 264.136), 246 (23), 231 (7), 228 (8), 218 (15), 173 (82), 95 (68), 91 (76), 79 (86), 55 (100); $[\alpha]_D^{24°}$ +83 ($CHCl_3$; *c*0.24). Acetylation (Ac_2O, 1 hr, 70°) gave the diacetate; ^1H NMR ($CDCl_3$): δ2.98 (*ddd*, H-1, *J* = 9, 8.5, 5.5 Hz), 2.34 (*dt*, H-2, *J* = 14, 8.5), 1.85 (*dt*, H-2′, *J* = 14, 5.5), 5.58 (*br dd*, H-3, *J* = 5.5, 8.5), 2.85 (*tt*, H-5, *J* = 9, 2), 4.08 (*t*, H-6, *J* = 9.5), 2.47 (*dddd*, H-7, *J* = 2.5, 9.5, 7, 11), 2.20 (*dt*, H-8, *J* = 12, 4), 1.55 (*t*, H-8′, *J* = 12, 11), 5.05 (*dd*, H-9, *J* = 11, 4), 2.24 (*dq*, H-11, *J* = 7, 7), 1.21 (*d*, H-13, *J* = 7), 5.28 and 5.08 (*br s*, H-14), 5.42 and 5.31 (*t*, H-15, *J* = 2).

9β-Hydroxyzaluzanin C (**7**). To 27 mg of a crude fraction containing **7** in 2 ml MeOH 30 mg pyrrolidin was added. After 48 hr at room temp., TLC (Et_2O–MeOH, 9:1) afforded 15 mg **9** (R_f 0.3) (^1H NMR see Table 1). To15 mg **9** in 2 ml THF excess of MeI was added. After 1 hr the soln was stirred with $NaHCO_3$ solution. Usual work-up afforded 8 mg **7**; colourless gum, IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3600 (OH), 1770 (γ-lactone); MS *m/z* (rel. int): 262.121 $[M]^+$ (6) (calcd for $C_{15}H_{18}O_4$: 262.121), 244 (17), 226 (12), 135 (38), 95 (56), 91 (57), 55 (100); ^{13}C NMR ($CDCl_3$, C-1–C-15): δ40.7 *d*, 39.1 *t*, 73.2 *d*, 152.6 *s*, 49.5 *d*, 84.3 *d*, 42.1 *d*, 40.7 *t*, 74.5 *d*, 153.0 *s*, 138.3 *s*, 169.8 *s*, 120.8 *t*, 110.9 *t*, 109.9 *t*.

To 10 mg crude **7** containing **3** excess of CH_2N_2 in Et_2O was added. TLC (Et_2O–MeOH, 20:1) afforded 4 mg **3** and 2 mg **8**; IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3600 (OH), 1780 (γ-lactone); MS *m/z* (rel. int.): 276.136 $[M-N_2]^+$ (13) (calcd for $C_{16}H_{20}O_4$: 276.136), 258 (30), 240 (17), 105 (72), 91 (100).

9β-Acetoxy-11α,13-dihydrotuberiferin (**10b**). Colourless gum; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1790 (γ-lactone), 1745 (OAc), 1680 (C=CC=O); MS *m/z* (rel. int.): 306.147 $[M]^+$ (19) (calcd for $C_{17}H_{22}O_5$: 306.147), 264 (30), 246 (38), 123 (94), 69 (100).

2α,7- and 2β,7-Dihydroxysabinane (**11a**/**b**). Colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 139 $[M-CH_2OH]^+$ (100), 121 (66), 109 (91), 81 (71).

10 mg **11a**/**b** in 2 ml MeOH was stirred for 30 min with 20 mg $NaIO_4$ in 0.5 ml H_2O. TLC (Et_2O–petrol, 1:9) gave 5 mg **12**; ^1H NMR ($CDCl_3$): δ1.67 (*br dd*, H-1, *J* = 8.5, 3.5 Hz), 2.15 (*m*, H-3), 1.98 (*m*, H-4), 1.20 (*br dd*, H-6, *J* = 8.5, 4.5), 1.10 (*dd* H-6′, *J* = 4.5, 3), 1.59 (*qq*, H-8, *J* = 7, 7), 1.01 (*d*, H-9, *J* = 7), 0.97 (*d*, H-10, *J* = 7); CD (MeCN): $\Delta\varepsilon_{285}$ +2.1.

Seco-floribundione (**13**). Colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1720 (C=O); CIMS *m/z* (rel. int.): 269 $[M+1]^+$ (3), 223 (100); ^{13}C NMR ($CDCl_3$, C-1–C-15): δ57.4 *d*, 28.7 *t*, 41.3 *t*, 208.9 *s*, 210.6 *s*, 160.5 *s*, 57.6 *d*, 20.5 *t*, 34.4 *t*, 40.8 *d*, 84.5 *s*, 24.9 *q*, 23.5 *q*, 20.1 *q*, 29.9 *q*; ^1H NMR (C_6D_6): δ1.62 (*br dt*, H-1, *J* = 10, 6 Hz), 1.78 (*dt*, H-2, *J* = 6, 7.5), 2.09 and 2.29 (*dt*, H-3, *J* = 17, 7.5), 7.69 (*s*, H-6), 3.16 (*br dd*, H-7, *J* = 13, 5), 1.81 (*m*, H-8), 1.08 (*dddd*, H-8′, *J* = 13, 13, 13, 3.5), 1.43 (*dddd*, H-9, *J* = 13, 3, 3, 3), 1.23 (*m*, H-9′), 1.18 (*m*, H-10), 1.74 (*s*, H-12), 1.52 (*s*, H-13), 0.83 (*d*, H-14, *J* = 6), 1.73 (*s*, H-15).

6β-Hydroxyguai-8-ene-7β,10β-endoperoxide (**14**). Colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH); CIMS *m/z* (rel. int.): 253 $[M+1]^+$ (4), 235 (100); ^{13}C NMR (C_6D_6, C-1–C-15): δ52.3 *d*, 28.2 *t*, 31.1 *t*, 31.2 *d*, 32.9 *d*, 71.6 *d*, 83.8 *s*, 129.4 *d*, 135.9 *d*, 79.9 *s*, 43.0 *d*, 18.7 *q*, 17.2 *q*, 21.2 *q*, 15.8 *q*; ^1H NMR (C_6D_6): δ2.06 (*ddd*, H-1, *J* = 16.5, 12.5, 12.5 Hz), 0.77 (*dddd*, H-2β, *J* = 12.5, 12.5, 10.5, 9), 1.51 (*dddd*, H-2α, *J* = 12.5, 7.5, 6.5, 2), 1.05 (*m*, H-3β), 1.81 (*dddd*, H-3α, *J* = 13, 10.5, 8.5, 2), 2.16 (*dddq*, H-4, *J* = 3.5, 7, 8.5, 7), 0.99 (*m*, H-5), 3.75 (*d*, H-6, *J* = 9), 5.76 (*d*, H-8, *J* = 10), 5.97 (*d*, H-9, *J* = 10), 2.19 (*qq*, H-11, *J* = 7, 7), 1.20 (*d*, H-12, *J* = 7), 1.15 (*d*, H-13, *J* = 7), 1.10 (*s*, H-14), 0.93 (*d*, H-15, *J* = 7).

4α-Hydroxyguai-5-ene-1β,7β-endoperoxide (**15**). Colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 220 $[M-O_2]^+$ (100), 205 (66), 202 (22) 187 (20), 149 (64), 125 (58); CIMS: 253 $[M+1]^+$ (21), 234 (100), 217 (34): ^1H NMR ($CDCl_3$): δ2.27 and 1.80 (*m*, H-2), 1.80 (*m*, H-3), 6.11 (*s*, H-6), 1.75 (*t*, H-8, *J* = 6 Hz), 2.19 and 1.23 (*m*, H-9), 2.11 (*m*, H-10), 1.86 (*qq*, H-11, *J* = 7, 7), 0.99 (*d*, H-12, *J* = 7), 0.96 (*d*, H-13, *J* = 7), 1.02 (*d*, *J* = 7), 1.54 (*s*, H-15).

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