

LABDANE DERIVATIVES AND ALICYCLIC DITERPENES FROM *GUTIERREZIA ESPINOSAE*

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Key Word Index—*Gutierrezia espinosae*; Compositae; diterpenes; labdanes; alicyclic diterpenes.

Abstract—The extract of the aerial parts of *Gutierrezia espinosae* gave 11 new and two known labdanes as well as five new nerylgeraniol derivatives. The structures were elucidated by high field ^1H NMR spectroscopy. The chemotaxonomic aspects are discussed briefly.

INTRODUCTION

The American genus *Gutierrezia* (Compositae, tribe Astereae) with about 20 species is closely related to *Grindelia* and *Xanthocephalum* all placed in the subtribe Solidagininae. So far 14 species have been studied chemically, especially for flavanoids [1-14] and labdanes [14-22]. However, from one species [23] clerodanes, as well as alicyclic diterpenes [16] and some bisabolones [15, 16], are reported. We have studied a further species, *G. espinosae* Acev. and the results are discussed in this paper.

RESULTS AND DISCUSSION

The extract of the aerial parts of *G. espinosae* afforded as the main constituent the methylbutyrate **1**, the corresponding isobutyrate **2**, the propionate **3**, the 3-phenylpropionate **4**, the acetate **5**, the free alcohol **6** and the angelate **7**, all isolated as their methyl esters (**1a-7a**). The esters **1a** and **2a** were isolated previously from *G. mandonii* as a mixture [18] which could not be separated. The acetate **5a**, as well as the free alcohol **6a**, were prepared from the mixture of the esters of **6a** [18]. The ^1H NMR spectra of **1a-7a**, the latter not being free from **1a** (Table 1), clearly showed that the labdanes only differed in the oxygen function at C-6 and its nature was easily deduced from the characteristic NMR signals.

The ^1H NMR spectrum of **8** (Table 2) was in part similar to that of **1a**. However, the methoxy group was missing and an additional low field four-fold doublet at δ 5.61 was present. Spin decoupling indicated that it was due to H-12 as allylic couplings with H-14 and H-16 were visible. The molecular formula ($\text{C}_{25}\text{H}_{34}\text{O}_5$) and the chemical shift of H-12 required a lactone ring. Further spin decoupling indicated the presence of a 12,17-lactone with a 6 α -2-methylbutyryloxy group. The configuration at C-12 could not be deduced with certainty from the NMR spectrum. Inspection of models showed that the relatively small couplings of H-12 with H-11 required a conformation with an axial furane group. This was established by the observed NOE's. Thus saturation of H-14 gave clear effects with H-9 (3%), H-11 α (3%) and H-15

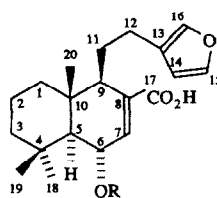
(10%). Further effects between H-18, H-5 (10%) and H-6 (10%), between H-19, H-6 (11%), H-2 β (6%) and H-3 β (5%) as well as between H-20, H-6 (10%) and H-11 β (7%) allowed the assignment of the methyl singlets. H-9 showed effects with H-5 (10%), H-1 α (5%), H-14 (3%) and H-15 (3%) establishing the *trans*-decalin configuration. The ^1H NMR spectra (Table 2) of **9** and **10** showed that the corresponding isobutyrate and angelate were present, while that of **11** (Table 2) differed from that of **8** in the chemical shifts and in the coupling of H-12 which required the presence of a 12-*epi*-isomer of **8**. The lactone without an ester group at C-6 was named gutiespinolide.

The ^1H NMR spectra of **12a** and **13a** (Table 2) showed that again methyl esters were present. The spectrum of **12a** differed from that of **1a** by the absence of furane proton signals which were replaced by a triplet of triplets at δ 7.10 and a double triplet at 4.75 (2H). These signals and their splitting are typical for 16,15-olides. This was supported by the molecular formula ($\text{C}_{26}\text{H}_{38}\text{O}_6$) and the IR band at 1770 cm^{-1} . The lactone **12** we have named espinasanolide-2-methylbutyrate.

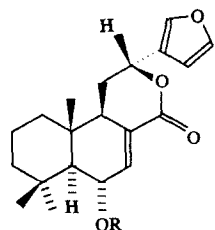
The ^1H NMR spectrum of **14a** (Table 3) required the presence of an alicyclic diterpene. The corresponding *O*-acetate has been reported previously as the result of esterification and acetylation of the polar parts from a *Heteropappus* species [24].

The ^1H NMR spectrum of **15a** (Table 3) was similar to that of gutiesolbriolide from a *Gutierrezia* species [16]. However, an additional signal of an olefinic methyl and the absence of a signal for a methylol group showed that the corresponding 17-desoxy derivative was present. Furthermore, the H-10 signal was shifted downfield requiring a *Z*-configuration of the Δ^{10} -bond. The ^1H NMR spectral data of **16a** (Table 3) showed that the isomeric lactone, the 17-desoxyiso-gutiesolbriolide was present. Accordingly, the spectrum was close to that of the corresponding 17-hydroxy derivative [16].

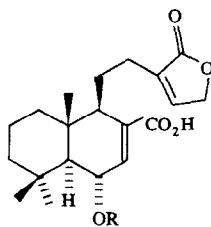
The ^1H NMR spectrum of **17a** (Table 3) was similar to that of the methyl ester of centipedic acid [25]. The additional hydroxy group followed from the broadened singlet at δ 4.55 while the configuration of the Δ^{10} -double bond was deduced from the chemical shift of H-10. The last diterpene (**18a**) differed in the ^1H NMR spectrum



- 1** R = MeBu
2 R = *i* Bu
3 R = Prop
4 R = COCH₂CH₂ Ph
5 R = Ac
6 R = H
7 R = Ang



- 8** R = MeBu
9 R = *i* Bu
10 R = Ang
11 R = MeBu, **12** *epi*



- 12** R = MeBu
13 R = Ang

(Table 3) by the absence of the low field triplet of H-10. The molecular formula required the presence of a dihydro derivative. As most signals were nearly identical with those of **17a** the 10,11-dihydro derivative of the latter was very likely and this was established by spin decoupling. Furthermore, the spectrum of the crude alcohol **18** showed a pair of doublets (δ 4.12 and 4.02, $J = 11$ Hz) for H-17 which required a chiral carbon in its proximity.

The chemistry of this *Gutierrezia* species agrees well with that of 10 other species of the genus while six further species have been studied so far only for flavones. Further studies may show whether these species also contain furanolabdanes which, however, are also reported from related genera of tribe Astereae (*Solidago* [26], *Xanthocephalum* [27], *Baccharis* [28], *Nidorella* [29]). Ner-ylgeraniol derivatives with an acid and a furane moiety were isolated also from related genera (*Grangea* [25], *Olearia* [30], *Chiliotrichium* [31], *Nardophyllum* [31] and *Solidago* [32]).

EXPERIMENTAL

The air-dried plant material (45 g, collected in December 1988 in N. Chile, voucher AH-15, deposited in the Herbarium of the University of Chile, Santiago) was extracted with MeOH-Et₂O-petrol (1:1:1). CC (silica gel) of the extract after defatting with MeOH gave 10 mg germacrene D and polar fractions which were combined. After esterification with CH₂N₂ MPCC (silica gel, θ 30–60 μ , petrol and Et₂O-petrol mixtures) gave 1 g **1a** and four mixtures. HPLC of the first one (RP 8, MeOH-H₂O, 9:1, flow rate 3 ml/min) gave 4 mg **3a** (R_f 4.8 min), 20 mg **2a** (R_f 5.7 min), 20 mg **1a** (R_f 7.6 min) and 10 mg of a mixture of **1a** and **7a** (*ca* 10:1; R_f 7.8 min). HPLC (same conditions) of the second mixture gave 3 mg **4a** (R_f 7.3 min) while the third mixture afforded by HPLC (same conditions) 6 mg **5a** (R_f 3.7 min). TLC of the last mixture (Et₂O-petrol, 3:1) gave three bands. HPLC of the first one (RP 8, MeOH-H₂O, 17:3) gave 15 mg **6a** (R_f 4.9 min), 35 mg **8** (R_f 9.1 min), 2 mg of a mixture of **8** and **10** (*ca* 4:1) and a mixture which gave by TLC

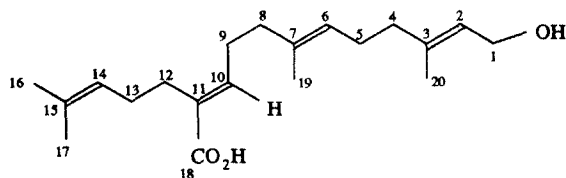
(Et₂O-petrol, 1:1) 3 mg **11** (R_f 0.70) and 4 mg **9** (R_f 0.56). HPLC of the second band (same conditions) gave 5 mg **6a**, 5 mg **8** and two mixtures. The first one gave by TLC (Et₂O-petrol, 1:1) 4 mg **15a** (R_f 0.40) and a mixture which after acetylation (Ac₂O, 70°, 1 hr) gave by TLC (Et₂O-petrol, 1:1) 2 mg **17a** (R_f 0.70), 1 mg **18a**, not free from **17a** (R_f 0.67) and 2 mg **16a** (R_f 0.45). The second mixture gave by TLC (Et₂O-petrol, 1:1) 4 mg **14a** (R_f 0.45). The third band gave by HPLC (MeOH-H₂O, 17:3) 8 mg **12a** (R_f 7.7 min) and 2 mg of a mixture of **12a** and **13a** (R_f 7.8 min).

Gutierrezianolic acid [2-methylbutyrate] (**1**). Purified as its methyl ester **1a**; oil; IR $\nu_{\max}^{\text{CCl}_4}$ cm⁻¹: 1725 (CO₂R), 875 (furan); MS m/z (rel. int.): 430.272 [M]⁺ (0.5) (calc. for C₂₆H₃₈O₅: 420.272), 399 [M-OMe]⁺ (1), 328 [M-RCO₂H]⁺ (23), 233 [328-CH₂CH₂C₄H₃O]⁺ (74), 85 [RCO]⁺ (62), 82 [methylfuran]⁺ (100), 57 [85-CO]⁺ (88); [x]_B²⁺ + 54° (CHCl₃; *c* 1.2).

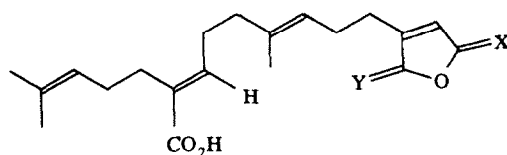
Isobutyrate methyl ester (**2a**). Oil; IR $\nu_{\max}^{\text{CCl}_4}$ cm⁻¹: 1725 (CO₂R), 875 (furan); MS m/z (rel. int.): 416.256 [M]⁺ (0.4) (calc. for C₂₅H₃₆O₅: 416.256), 328 [M-RCO₂H]⁺ (11), 233 [M-CH₂CH₂C₄H₃O]⁺ (62), 82 (100), 71 [RCO]⁺ (65).

Propionate methyl ester (**3a**). Oil; IR $\nu_{\max}^{\text{CCl}_4}$ cm⁻¹: 1740 (CO₂R), 1720 (C=CCO₂R), 875 (furan); MS m/z (rel. int.): 328.204 [M-RCO₂H]⁺ (3.6) (calc. for C₂₁H₂₈O₃: 328.204), 297 [328-OMe]⁺ (3), 233 (22), 82 (100), 57 [RCO]⁺ (40).

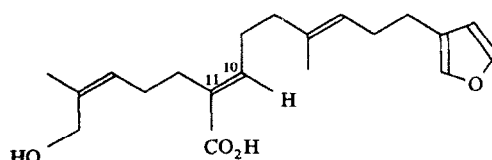
3-Phenylpropionate methyl ester (**4a**). Oil; IR $\nu_{\max}^{\text{CCl}_4}$ cm⁻¹: 1735 (CO₂R), 1725 (C=CCO₂R), 875 (furan); MS m/z (rel. int.): 328.204 [M-RCO₂H]⁺ (18) (calc. for C₂₁H₃₈O₃: 328.204), 233 (63), 105 [phenyl CH₂CH₂]⁺ (72), 91 [C-H₃]⁺ (79), 82 (100).



14



15 X=O, Y=H₂ **16** X=H₂, Y=O



17

18 10.11 H

1a-7a and **12a-16a** are the methyl esters

17a and **18a** are methyl esteracetates

Table 1. ¹H NMR spectral data of compounds **1a**–**7a** (400 MHz, CDCl₃, δ-values)

H	1a *	2a *	3a *	4a *	5a *	6a *
5	1.54 <i>d</i>	1.55 <i>d</i>	1.54 <i>d</i>	1.52 <i>d</i>	1.54 <i>d</i>	1.18 <i>d</i>
6	5.60 <i>ddd</i>	5.60 <i>ddd</i>	5.61 <i>ddd</i>	5.60 <i>ddd</i>	5.59 <i>ddd</i>	4.38 <i>ddd</i>
7	6.25 <i>t</i>	6.23 <i>t</i>	6.29 <i>t</i>	6.19 <i>t</i>	6.31 <i>t</i>	6.49 <i>t</i>
9	2.21 <i>dt</i>	2.21 <i>dt</i>	2.21 <i>dt</i>	2.21 <i>dt</i>	2.21 <i>dt</i>	2.17 <i>dt</i>
11	1.76 <i>m</i>	1.76 <i>dddd</i>	1.75 <i>dddd</i>	1.74 <i>m</i>	1.76 <i>m</i>	1.75 <i>m</i>
11'	1.38 <i>m</i>	1.38 <i>m</i>	1.38 <i>m</i>	1.38 <i>m</i>	1.38 <i>m</i>	1.34 <i>m</i>
12	2.75 <i>ddd</i>	2.76 <i>ddd</i>	2.75 <i>ddd</i>	2.75 <i>ddd</i>	2.76 <i>ddd</i>	2.74 <i>ddd</i>
12'	2.37 <i>ddd</i>	2.38 <i>ddd</i>	2.38 <i>ddd</i>	2.37 <i>ddd</i>	2.38 <i>ddd</i>	2.38 <i>ddd</i>
14	6.24 <i>br s</i>	6.24 <i>br s</i>	6.25 <i>br s</i>	6.25 <i>br s</i>	6.25 <i>br s</i>	6.25 <i>br s</i>
15	7.32 <i>t</i>	7.33 <i>t</i>	7.33 <i>t</i>	7.33 <i>t</i>	7.33 <i>t</i>	7.33 <i>t</i>
16	7.19 <i>br s</i>	7.20 <i>br s</i>	7.20 <i>br s</i>	7.20 <i>br s</i>	7.20 <i>br s</i>	7.19 <i>br s</i>
18	0.91 <i>s</i>	0.91 <i>s</i>	0.91 <i>s</i>	0.90 <i>s</i>	0.91 <i>s</i>	1.15 <i>s</i>
19	0.96 <i>s</i>	0.96 <i>s</i>	0.95 <i>s</i>	0.89 <i>s</i>	0.98 <i>s</i>	1.08 <i>s</i>
20	0.95 <i>s</i>		0.97 <i>s</i>	0.92 <i>s</i>	0.97 <i>s</i>	0.87 <i>s</i>
OCOR	2.34 <i>tq</i>	2.52 <i>qq</i>	2.33 <i>dq</i> †	2.65 <i>dt</i> †	2.07 <i>s</i>	—
	1.70 <i>ddq</i>	1.17 <i>d</i>	1.16 <i>t</i>	2.62 <i>dt</i> †		
	1.35 <i>m</i>	1.16 <i>d</i>		2.97 <i>br t</i> †		
	0.91 <i>t</i>			7.21 <i>br d</i>		
	1.13 <i>d</i>			7.28 <i>br t</i>		

*OMe 3.73 s; †not first order.

J[Hz]: 5, 6=10.5; 6, 7=6, 9=7, 9~2.5; 9, 11~3; 11, 11'~13; 11, 12=4.5; 11, 12'=11', 12=12; 11', 12'=5.5; 12, 12'=14; 14, 15=15, 16=1.5; MeBu: 2, 3=2, 3'=2, 5=3, 4=3', 4=7; 3, 3'=14; *i*Bu: 2, 3=2, 4=7; Prop: 2, 3=7.5; COCH₂CH₂Ph: 2, 2'=14; 2, 3=2', 3=7; OAng: δ6.10 *qq*, 2.01 *dq*, 1.88 *dq* (other signals see **1a** except H-7, 6.32 *t*).

Table 2. ¹H NMR spectral data of compounds **8**–**11**, **12a** and **13a** (400 MHz, CDCl₃, δ-values)

H	8	9	11	12a
5	1.58 <i>d</i>	1.58 <i>d</i>	1.58 <i>d</i>	1.55 <i>d</i>
6	5.66 <i>dt</i>	5.65 <i>dt</i>	5.69 <i>dt</i>	5.60 <i>dt</i>
7	6.88 <i>t</i>	6.88 <i>t</i>	6.99 <i>t</i>	6.30 <i>t</i>
9	2.35 <i>dddd</i>	2.36 <i>dddd</i>	2.50 <i>ddd</i>	2.19 <i>dddd</i>
11α	2.03 <i>ddd</i>	2.04 <i>ddd</i>	2.05 <i>br d</i>	1.81 <i>m</i>
11β	1.96 <i>ddd</i>	1.97 <i>ddd</i>	1.70 <i>m</i>	1.48 <i>m</i>
12	5.61 <i>dddd</i>	5.62 <i>dddd</i>	5.29 <i>br dd</i>	2.68 <i>br t</i> 2.30 <i>br t</i>
14	6.29 <i>ddd</i>	6.29 <i>ddd</i>	6.43 <i>ddd</i>	7.10 <i>tt</i>
15	7.45 <i>t</i>	7.45 <i>t</i>	7.42 <i>t</i>	4.75 <i>dt</i>
16	7.37 <i>ddd</i>	7.37 <i>ddd</i>	7.47 <i>ddd</i>	—
18	0.92 <i>s</i>	0.92 <i>s</i>	0.91 <i>s</i>	0.92 <i>s</i>
19	0.91 <i>s</i>	0.91 <i>s</i>	0.95 <i>s</i>	0.97 <i>s</i>
20	0.98 <i>s</i>	0.98 <i>s</i>	1.01 <i>s</i>	0.96 <i>s</i>
OCOR	2.34 <i>tq</i>	2.51 <i>qq</i>	2.35 <i>tq</i>	2.35 <i>tq</i>
	1.70 <i>tq</i>	1.17 <i>d</i>	1.73 <i>m</i>	1.70 <i>tq</i>
	1.48 <i>m</i>	1.16 <i>d</i>	1.48 <i>m</i>	1.49 <i>m</i>
	0.91 <i>t</i>		0.93 <i>t</i>	0.91 <i>t</i>
	1.13 <i>d</i>		1.14 <i>d</i>	1.13 <i>d</i>

J[Hz]: Compounds **8**–**11**, **12a** and **13a**: 5, 6=10.5; 6, 7=7, 9=3; 9, 11=5; 9, 11'=12; 11, 11'=14; 11, 12=3; 11', 12=4.5; 12, 14=12, 16=14, 15=14, 16=15, 16~1 (compound **11**: 11, 12=1.5; 11', 12=11; compound **12a**: 12, 14=12, 15=14, 15~1.5); OMeBu: 2, 3=2, 5=3, 5=7; 3, 3'=14; *Oi*Bu: 2, 3=2, 4=7; OAng (**10**): δ6.10 *qq*, 2.02 *br d*, 1.86 *dq* (other signals as **8** except H-7, 6.94 *t*); OAng (**13a**): δ6.11 *qq*, 2.01 *dq*, 1.88 *dq* (other signals as in **12a** except H-7, 6.35 *t*).

Table 3. ^1H NMR spectral data of compounds **14a**–**18a** (400 MHz, CDCl_3 , δ -values)

H	14a	15a	16a	17a	18a
1	4.15 <i>br d</i>	—	4.77 <i>dq</i>	7.34 <i>t</i>	7.34 <i>t</i>
2	5.41 <i>br t</i>	5.84 <i>tt</i>	7.11 <i>tt</i>	7.20 <i>br s</i>	7.20 <i>br s</i>
4	2.32 <i>br t</i>	2.45 <i>br t</i>	2.35 <i>m</i>	2.44 <i>br t</i>	2.43 <i>br t</i>
5	2.12 <i>br dt</i>	2.28 <i>br dt</i>	2.25 <i>m</i>	2.25 <i>m</i>	2.25 <i>m</i>
6	5.13 <i>br t</i>	5.12 <i>br t</i>	5.14 <i>br t</i>	5.19 <i>br t</i>	5.14 <i>br t</i>
10	6.73 <i>t</i>	6.69 <i>t</i>	6.70 <i>t</i>	6.75 <i>t</i>	2.33 <i>m</i>
14	5.13 <i>br t</i>	5.12 <i>br t</i>	5.13 <i>br t</i>	5.41 <i>br t</i>	5.36 <i>br t</i>
16	1.67 <i>br s</i>	1.67 <i>br s</i>	1.68 <i>br s</i>	1.74 <i>br s</i>	1.74 <i>br s</i>
17	1.59 <i>br s</i>	1.58 <i>br s</i>	1.59 <i>br s</i>	4.55 <i>br s</i>	4.55 <i>br s</i>
19	1.61 <i>br s</i>	1.63 <i>br s</i>	1.61 <i>br s</i>	1.59 <i>br s</i>	1.54 <i>br s</i>
20	1.67 <i>br s</i>	4.73 <i>br s</i>	—	6.27 <i>br s</i>	6.27 <i>br s</i>
OMe	3.73 <i>s</i>	3.73 <i>s</i>	3.73 <i>s</i>	3.73 <i>s</i>	3.67 <i>s</i>

J [Hz]: Compounds **14a**–**18a**: 4, 5 = 5, 6 = 9, 10 = 13, 14 = 7 (compound **15a**): 2, 4 = 2, 20 = 1; compound **14a**: 1, 2 = 7; compound **16a**: 1, 2 = 1, 4 = 2, 4 ~ 1; compounds **17a** and **18a**: 1, 2 = 1, 20 = 1.5; OAc: δ 2.07 and 2.06 s.

Angelate methyl ester (7a). Oil, not free from **1a**; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 1730 (CO_2R), 875 (furan); MS m/z (rel. int.): 428.256 $[\text{M}]^+$ (2) (calc. for $\text{C}_{26}\text{H}_{36}\text{O}_5$: 428.256), 328 $[\text{M} - \text{RCO}_2\text{H}]^+$ (25), 233 (65), 83 $[\text{RCO}]^+$ (100), 82 (71).

Gutespinolide-[2-methylbutyrate] (8). Oil; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 1735 (CO_2R), 870 (furan); MS m/z (rel. int.): 414.241 $[\text{M}]^+$ (12) (calc. for $\text{C}_{25}\text{H}_{34}\text{O}_5$: 414.241), 330 $[\text{M} - \text{O} = \text{C} = \text{CHCHMe}_2]^+$ (62), 312 $[\text{M} - \text{RCO}_2\text{H}]^+$ (31), 297 $[\text{312} - \text{Me}]^+$ (75), 236 (60), 85 $[\text{RCO}]^+$ (78), 57 $[\text{85} - \text{CO}]^+$ (100); $[\alpha]_{\text{D}}^{24} + 85^\circ$ (CHCl_3 ; c 2.66).

Gutespinolide isobutyrate (9). Oil; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 1735 (CO_2R), 870 (furan); MS m/z (rel. int.): 400.225 $[\text{M}]^+$ (5) (calc. for $\text{C}_{24}\text{H}_{32}\text{O}_5$: 400.225), 330 (11), 312 (14), 297 (10), 236 (32), 71 $[\text{RCO}]^+$ (100).

Gutespinolide angelate (10). Oil, not free from **8**; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 1725 ($\text{C} = \text{CCO}_2\text{R}$), 870 (furan); MS m/z (rel. int.): 412.225 $[\text{M}]^+$ (30) (calc. for $\text{C}_{25}\text{H}_{32}\text{O}_5$: 412.225), 330 (57), 312 (41), 297 (70), 236 (55), 83 $[\text{RCO}]^+$ (100).

12-epi-Gutespinolide-[2-methylbutyrate] (11). Oil; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 1730 (CO_2R), 870 (furan); MS m/z (rel. int.): 414.241 $[\text{M}]^+$ (14) (calc. for $\text{C}_{25}\text{H}_{34}\text{O}_5$: 414.241), 330 (56), 312 (34), 297 (70), 236 (62), 85 $[\text{RCO}]^+$ (74), 57 (100).

Espinanolide-[2-methylbutyrate] (12). Isolated as its methyl ester **12a**; Oil; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 1770 (γ -lactone), 1720 (CO_2R); MS m/z (rel. int.): 446.267 $[\text{M}]^+$ (0.15) (calc. for $\text{C}_{26}\text{H}_{38}\text{O}_6$: 446.267), 415 $[\text{M} - \text{OMe}]^+$ (1.5), 414 $[\text{M} - \text{MeOH}]^+$ (2), 312 $[\text{414} - \text{RCO}_2\text{H}]^+$ (12), 297 $[\text{312} - \text{Me}]^+$ (100), 85 $[\text{RCO}]^+$ (24), 57 $[\text{85} - \text{CO}]^+$ (49).

Angelate methyl ester (13a). Oil, not free from **12a**; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 1770 (γ -lactone), 1720 ($\text{C} = \text{CCO}_2\text{R}$); MS m/z (rel. int.): 444.251 $[\text{M}]^+$ (0.3) (calc. for $\text{C}_{26}\text{H}_{36}\text{O}_6$: 444.251), 412 (2), 312 $[\text{412} - \text{RCO}_2\text{H}]^+$ (15), 297 (100), 83 $[\text{RCO}]^+$ (97).

Nerylgeraniol-18-oic acid (14). Isolated as its methyl ester **14a**; oil; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 3600 (OH), 1720 ($\text{C} = \text{CCO}_2\text{R}$); MS m/z (rel. int.): 316.240 $[\text{M}]^+$ (1) (calc. for $\text{C}_{21}\text{H}_{32}\text{O}_3$: 316.240), 285 $[\text{M} - \text{OMe}]^+$ (0.8), 284 $[\text{M} - \text{MeOH}]^+$ (0.7), 257 $[\text{285} - \text{CO}]^+$ (1.2), 187 $[\text{257} - \text{C}_5\text{H}_{10}]^+$ (6), 69 $[\text{C}_5\text{H}_9]^+$ (100).

Methyl ester of 10Z-desoxygutesinobriolide (15a). Oil; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 1790 (γ -lactone), 1720 ($\text{C} = \text{CCO}_2\text{R}$); MS m/z (rel. int.): 346.215 $[\text{M}]^+$ (2) (calc. for $\text{C}_{21}\text{H}_{30}\text{O}_4$: 346.215), 314 $[\text{M} - \text{MeOH}]^+$ (10), 69 $[\text{C}_5\text{H}_9]^+$ (100).

Methyl ester of 10Z-desoxyisogutesinobriolide (16a). Oil; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 1770 (γ -lactone), 1720 ($\text{C} = \text{CCO}_2\text{R}$); MS m/z (rel. int.): 346.214 $[\text{M}]^+$ (0.6) (calc. for $\text{C}_{21}\text{H}_{30}\text{O}_4$: 346.215), 314 $[\text{M}$

$-\text{MeOH}]^+$ (8), 245 $[\text{314} - \text{C}_5\text{H}_9]^+$ (6), 69 $[\text{C}_5\text{H}_9]^+$ (100).

17-Hydroxy-10E-centipedic acid (17). Isolated as its methyl ester acetate **17a**; oil; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 1740 (OAc), 1720 ($\text{C} = \text{CCO}_2\text{R}$), 865 (furan); MS m/z (rel. int.): 388.225 $[\text{M}]^+$ (0.2) (calc. for $\text{C}_{23}\text{H}_{32}\text{O}_5$: 388.225), 328 $[\text{M} - \text{AcOH}]^+$ (3), 81 $[\text{C}_5\text{H}_5\text{O}]^+$ (100).

17-Hydroxy-10,11-dihydrocentipedic acid (18). Isolated as its methyl ester acetate **18a**; oil, not free from **17a**; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 1740 (CO_2R), 870 (furan); MS m/z (rel. int.): 390.241 $[\text{M}]^+$ (0.2) (calc. for $\text{C}_{23}\text{H}_{34}\text{O}_5$: 390.241), 330 $[\text{M} - \text{AcOH}]^+$ (5), 299 $[\text{330} - \text{OMe}]^+$ (1.7), 81 $[\text{C}_5\text{H}_5\text{O}]^+$ (100).

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