

FUROLABDANES AND LINEAR DITERPENES FROM *GUTIERREZIA RESINOSA*

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Key Word Index—*Gutierrezia resinosa*; Compositae; diterpenes; furolabdanes; linear diterpenes; nerylgeraniol derivatives.

Abstract—The aerial parts of *Gutierrezia resinosa* gave 15 new diterpenes including 12 labdanes and three nerylgeraniol derivatives. The structures were elucidated by high field NMR spectroscopy.

INTRODUCTION

The genus *Gutierrezia* has been studied by many groups. In addition to flavanoids, labdanes and a few linear diterpenes are common [1 and lit. cited therein]. In continuation of our investigations of Chilean Compositae, we have reinvestigated *G. resinosa* (H. et A.) Blake which has already been studied for flavones [2–4].

RESULTS AND DISCUSSION

The extract of the aerial parts of *G. resinosa* afforded the labdanes 1–12 and the nerylgeraniol derivatives 13–15.

The structure of the main constituent 1 followed from the ¹H NMR spectrum of its methyl ester 1a (Table 1) which was close to that of methyl polyalthoate [5] which has a 8(17) double bond. The corresponding Δ⁷ isomer has been reported from *G. lucida* [6]. However, this acid belongs to the *ent*-series, while the optical rotation of 1a required the presence of a normal labdane. The ¹³C NMR data also agree with the structure and the configuration at C-4 (see Experimental) which also followed from the NOE of H-19 and H-20 (8%) and H-6a (4%).

The ¹H NMR spectra of 2a–6a and 7aAc (Table 1) only differ in the signals of the ester groups and in small shift differences. In the case of 3a all signals could be assigned by spin decoupling. The resulting sequences required the presence of a 2α-(2-methyl)-butyrate of 1a. The ester signals in the spectra of 2a and 4a–6a showed that we were dealing with the corresponding isobutyrate, angelate, isovalerate and 4-methylsenecioate. The acid 7 was isolated as the 2-*O*-acetate of the methyl ester.

The ¹H NMR spectrum of 9a (Table 2) was in part similar to that of the 4-*epi* isomer isolated from *G. lucida* [7]. However, due to the changed configuration at C-4 some signals were shifted. In particular, the chemical shift of H-20 was altered as in similar cases. Furthermore, the IR band at 1250 cm⁻¹ required an equatorial carbomethoxy group [8] as in all the other labdanes (1a–6a, 7aAc, 8a, 10aAc, 11aAc and 12aAc).

The ¹H NMR data of 8a (Table 2) clearly indicated that

the isomeric 16,15-olide was present. Accordingly, H-14 was drastically deshielded.

The lactones 10 and 11 could only be separated as the acetates of their methyl esters. Again the position of the lactone carbonyl clearly followed from the chemical shifts of H-14. In the case of 11aAc some signals were split, indicating the presence of 16-epimers.

The diol 12 was isolated as its diacetate of the methyl ester. The ¹H NMR data (Table 2) clearly show the presence of the diacetate of the diol 12 which is almost certainly the precursor of the main constituent 1.

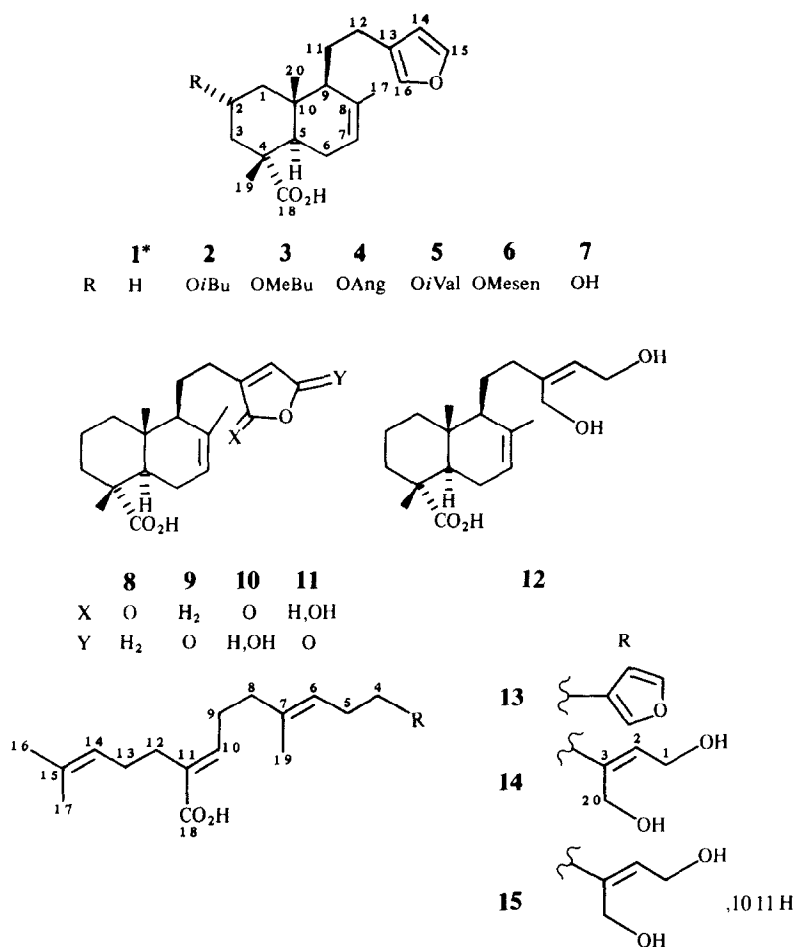
The ¹H NMR spectrum of 13a in C₆D₆ (Table 3) showed that a linear diterpene with a β-substituted furan moiety was present. The downfield shift of H-10 indicated an *E*-configured double bond. Spin decoupling showed that the carbomethoxy group has to be placed at C-11. Accordingly, we were dealing with the 10*E*-isomer of centipedic acid [9].

The ¹H NMR data of 14aAc (Table 3) indicated that the furan moiety of 13a was replaced by a diacetoxy butene unit. The configuration of the Δ² bond follows from the chemical shifts of H-2 and H-1. The ¹H NMR spectrum of 15aAc (Table 3) indicated that the 10,11-dihydro derivative of 14aAc was present. The data were in part close to those of the corresponding furan derivative from a *Pteronia* species [10].

The chemistry of *G. resinosa* again shows that labdane derivatives are characteristic for this genus. In particular, furolabdanes and their derivatives are common and have been reported from 12 species [1, 7, 11–16]. So far from three species linear diterpenes have been isolated [1, 13, 14]. From a few species only flavones are reported, but perhaps these species may also contain diterpenes. From one species clerodanes are reported [17].

EXPERIMENTAL

The air-dried aerial parts (265 g, collected in September 1990 in the Region de Coquimbo, Chile, voucher Niem., 89132, deposited in the Herbarium of the University of Chile) were extracted with MeOH-Et₂O-petrol (1:1:1) and the resulting



***1a–15a** are the corresponding methylesters,

7aAc, 10aAc, 11aAc, 14aAc and **15aAc** are the acetates of the methylesters

extract was sepd after defatting (MeOH, -20°) as reported previously [18]. CC fractions were combined to give 3 fractions. The first (Et₂O–petrol, 1:3), after addition of CH₂N₂, gave by TLC (EtOAc–petrol, 1:19) 1.0 g **1a**, 300 mg of a mixture of **1a** and **13a** (1/1) and a mixture of **2a–6a** (1/2). The mixture 1/1 was sepd by repeated TLC, finally on AgNO₃ coated silica gel affording an enriched mixture of **13a**. HPLC (MeOH–H₂O, 19:1, always RP 8, flow rate 3 ml min⁻¹) gave 5 mg pure **13a** (*R*_f 6.3 min). HPLC (MeOH–H₂O, 9:1) of 1/2 gave 20 mg **2a** (*R*_f 7.0 min), 100 mg **3a** (*R*_f 8.7 min), 50 mg **4a** (*R*_f 9.4 min), 10 mg **5a** (*R*_f 11.0 min) and 15 mg **6a** (*R*_f 11.7 min). CC 2 was shaken with NaHCO₃ soln to remove the acids which were esterified by addition of CH₂N₂. HPLC (MeOH–H₂O, 17:3) gave 30 mg **9a** (*R*_f 4.8 min), 25 mg **8a** (*R*_f 5.8 min) and a mixture which, after acetylation (Ac₂O, 1 hr, 70^o), gave by HPLC (MeOH–H₂O, 17:3) 3 mg **11aAc** (*R*_f 6.2 min) and 3 mg **10aAc** (*R*_f 7.0 min), CC 3 did not show any acetate methyl signals in the ¹H NMR. After acetylation (CHCl₃–Ac₂O–DMAP, 1 hr, 65^o), methylation (CH₂N₂) and filtration over silica gel HPLC (MeOH–H₂O, 9:1) gave 2 mixtures (3/1 and 3/2). TLC of 3/1 (EtOAc–petrol, 1:3) gave 5 mg **7aAc** (*R*_f 0.80) and 5 mg **12aAc** (*R*_f 0.68). Repeated HPLC (MeOH–H₂O, 17:3) of 3/2 gave 20 mg **14aAc** (*R*_f 8.7 min) and 2 mg **15aAc** (*R*_f 9.5 min).

15,16-Epoxyabda-7,13(16),14-trien-18-oic acid (**1**). ¹H NMR (CDCl₃): δ 0.80 (s, H-20), 1.21 (s, H-19), 1.73 (*br s*, H-17), 5.36 (*br s*, H-7), 6.28 (*br s*, H-14), 7.35 (*t*, H-15), 7.22 (*br s*, H-16); addition of CH₂N₂ gave **1a**; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹: 1730, 1250 (eCO₂Me); 885 (furan); MS *m/z* (rel. int.): 330.219 [M]⁺ (8) (calc. for C₂₁H₃₀O₃: 330.219), 248 [M–methylfuran]⁺ (20), 188 [248–HCO₂Me]⁺ (16), 123 (70), 81 (100); ¹³C NMR (CDCl₃, C-1–C-20): δ 37.0, 18.0, 36.2, 46.6, 54.1, 26.9, 121.7, 135.2, 45.0, 38.0, 25.5, 27.5, 125.1, 111.0, 142.7, 138.7, 13.9, 179.1, 22.1, 16.9; OMe 51.8; [α]_D²⁴ + 43 (CHCl₃; *c* 2.23).

2α-Isobutyryloxy-15,16-epoxyabda-7,13(16),14-trien-18-oic acid (**2**). Isolated as its methylester **2a**; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹: 1735, 1250 (CO₂R); MS *m/z* (rel. int.): 416.256 [M]⁺ (0.5) (calc. for C₂₅H₃₆O₅: 416.256), 301 (12), 247 (16), 187 (46), 119 (69), 100 (100), 81 (25), 71 [RCO]⁺ (26).

2α-[2-methylbutyryloxy]-15,16-epoxyabda-7,13(16),14-trien-18-oic acid (**3**). Isolated as its methylester **3a**; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹: 1735, 1250 (CO₂R); MS *m/z* (rel. int.): 430.272 [M]⁺ (6) (calc. for C₂₆H₃₈O₅: 430.272), 328 [M–RCO₂H]⁺ (18), 247 (12), 187 (23), 119 (51), 107 (61), 95 (84), 82 (100); [α]_D²⁴ + 24 (CHCl₃; *c* 2.14).

2α-Angeloyloxy-15,16-epoxyabda-7,13(16),14-trien-18-oic acid (**4**). Isolated as its methylester **4a**; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹: 1735 (CO₂R), 1720, 1650 (C=CCO₂R); MS *m/z* (rel. int.): 428.256

Table 1. ¹H NMR spectral data of compounds **1a–6a** and **7aAc** (400 MHz, CDCl₃, δ-values)

H	1a	2a	3a	4a	5a	6a	7aAc
1α	*	1.02 <i>t</i>	1.03 <i>t</i>	1.06 <i>t</i>	1.06 <i>t</i>	1.11 <i>t</i>	1.08 <i>t</i>
1β	*	1.89 <i>m</i>	1.88 <i>m</i>	1.85 <i>m</i>	1.86 <i>m</i>	1.86 <i>m</i>	1.90 <i>m</i>
2	*	4.98 <i>tt</i>	4.99 <i>tt</i>	5.08 <i>tt</i>	5.01 <i>tt</i>	5.04 <i>tt</i>	4.99 <i>tt</i>
3α	*	1.79 <i>t</i>	1.80 <i>t</i>	1.85 <i>m</i>	} 1.86 <i>m</i>	1.82 <i>t</i>	1.81 <i>t</i>
3β	*	1.89 <i>m</i>	1.88 <i>m</i>	1.85 <i>m</i>		1.85 <i>m</i>	1.90 <i>m</i>
6α	1.95 <i>br d</i>	2.08 <i>br d</i>	2.09 <i>br d</i>	2.17 <i>br d</i>	2.15 <i>br d</i>	2.15 <i>br d</i>	2.13 <i>br d</i>
6β	1.80 <i>m</i>	1.95 <i>m</i>	1.94 <i>m</i>	1.96 <i>m</i>	1.95 <i>m</i>	1.95 <i>m</i>	1.95 <i>m</i>
7	5.35 <i>br d</i>	5.37 <i>br d</i>	5.37 <i>br d</i>	5.37 <i>br d</i>	5.37 <i>br d</i>	5.37 <i>br d</i>	5.37 <i>br d</i>
12	2.63 <i>ddd</i>	2.64 <i>ddd</i>	2.64 <i>ddd</i>	2.64 <i>ddd</i>	2.63 <i>ddd</i>	2.63 <i>ddd</i>	2.64 <i>ddd</i>
12'	2.37 <i>ddd</i>	2.38 <i>ddd</i>	2.38 <i>ddd</i>	2.38 <i>ddd</i>	2.38 <i>ddd</i>	2.37 <i>ddd</i>	2.38 <i>ddd</i>
14	6.28 <i>br s</i>	6.27 <i>br s</i>	6.27 <i>br s</i>	6.27 <i>br s</i>	6.27 <i>br s</i>	6.28 <i>br s</i>	6.29 <i>br s</i>
15	7.35 <i>t</i>	7.34 <i>t</i>	7.34 <i>t</i>	7.33 <i>t</i>	7.35 <i>t</i>	7.34 <i>t</i>	7.36 <i>t</i>
16	7.22 <i>br s</i>	7.23 <i>br s</i>	7.23 <i>br s</i>	7.22 <i>br s</i>	7.22 <i>br s</i>	7.23 <i>br s</i>	7.23 <i>br s</i>
17	1.73 <i>br s</i>	1.73 <i>br s</i>	1.73 <i>br s</i>	1.73 <i>br s</i>	1.73 <i>br s</i>	1.73 <i>br s</i>	1.73 <i>br s</i>
19	1.21 <i>s</i>	1.28 <i>s</i>	1.29 <i>s</i>	1.31 <i>s</i>	1.29 <i>s</i>	1.31 <i>s</i>	1.29 <i>s</i>
20	0.79 <i>s</i>	0.87 <i>s</i>	0.87 <i>s</i>	0.89 <i>s</i>	0.87 <i>s</i>	0.90 <i>s</i>	0.88 <i>s</i>
OCOR	—	2.50 <i>qq</i>	2.32 <i>tq</i>	6.07 <i>qq</i>	2.28 <i>dd</i>	5.63 <i>tq</i>	2.04 <i>s</i>
		1.15 <i>d</i>	1.65 <i>ddq</i>	1.98 <i>dq</i>	2.07 <i>dd</i>	2.16 <i>dq</i>	
		1.16 <i>d</i>	1.47 <i>ddq</i>	1.87 <i>dq</i>	0.94 <i>d</i>	1.07 <i>t</i>	
			0.90 <i>t</i>			2.15 <i>d</i>	
			1.13 <i>d</i>				
OMe	3.63 <i>s</i>	3.65 <i>s</i>	3.65 <i>s</i>	3.65 <i>s</i>	3.65 <i>s</i>	3.65 <i>s</i>	3.66 <i>s</i>

*Overlapped multiplets.

J [Hz]: 1α,1β=1α,2=2,3α=3α,3β~12; 6α,6β=11; 6β,7~3; 11,12=11',12'~10; 11',12=11,12'~5; 12,12'=14; 14,15=15,16=1.5; iBu: 2,3=2,4=7; Mebu: 2,3=3,4=7; 3,3'=14; Ang: 3,4=7; 3,5=4,5=1.5; iVal: 2,2'=14; 2,3=2',3=3,4=3,5=7; MeSen: 2,4=2,6=1; 4,5=7.5.

Table 2. ¹H NMR spectral data of compounds **8a**, **9a**, **10aAc**, **11aAc** and **12aAc** (400 MHz, CDCl₃, δ-values)

H	8a	9a	10aAc	11aAc	12aAc
7	5.35 <i>br d</i>	5.38 <i>br d</i>	5.37 <i>br d</i>	5.39 <i>br d</i>	5.34 <i>br d</i>
12	2.52 <i>ddd</i>	2.60 <i>ddd</i>	2.56 <i>ddd</i>	2.58, 2.52 <i>ddd</i>	2.36 <i>br d</i>
12'	2.27 <i>m</i>	2.37 <i>ddd</i>	2.30 <i>m</i>	2.37, 2.26 <i>ddd</i>	*
14	7.13 <i>tt</i>	5.86 <i>tt</i>	6.89 <i>br s</i>	5.98 <i>br s</i>	5.58 <i>br t</i>
15	4.78 <i>dt</i>	—	6.89 <i>br s</i>	—	4.67 <i>d</i>
16	—	{ 4.77 <i>dd</i> 4.72 <i>dd</i>	—	6.86, 6.85 <i>br s</i>	{ 4.67 <i>d</i> 4.63 <i>d</i>
17	1.71 <i>br s</i>	1.67 <i>br s</i>	1.71 <i>br s</i>	1.67 <i>br s</i>	1.68 <i>br s</i>
19	1.21 <i>s</i>	1.21 <i>s</i>	1.22 <i>s</i>	1.22 <i>s</i>	1.21 <i>s</i>
20	0.79 <i>s</i>	0.80 <i>s</i>	0.80 <i>s</i>	0.81, 0.80 <i>s</i>	0.78 <i>s</i>
OAc	—	—	2.16 <i>s</i>	2.18 <i>s</i>	2.07 <i>s</i>
OMe	3.64 <i>s</i>	3.63 <i>s</i>	3.64 <i>s</i>	3.64 <i>s</i>	3.64 <i>s</i>

J [Hz]: 6,7=3.5; 11,12=11',12'=12; 11,12'=6; 11',12=5; 12,12'=15; 12,14=1; compound **8a**: 12,14=12,15~1.5; compound **9a**: 16,16'=16; 14,16=1.5; compound **10aAc**: 12,14=12,15~1.5; compound **11aAc**: 12,14=12',14~1.5; compound **12aAc**: 14,15=7; 16,16'=12.

[M]⁺ (1) (calc. for C₂₆H₃₆O₅: 428.256), 328 [M–RCO₂H]⁺ (7), 247 (12), 187 (26), 83 [RCO]⁺, 82 (100).

2α-Isovaleryloxy-15,16-epoxylabda-7,13(16),14-trien-18-oic acid (**5**). Isolated as its methylester **5a**; IR ν_{max}^{CCl₄} cm⁻¹: 1730 (CO₂R); MS *m/z* (rel. int.): 430.272 [M]⁺ (5) (calc. for C₂₆H₃₈O₅: 430.272), 328 [M–RCO₂H]⁺ (20), 247 (13), 187 (25), 119 (55), 82 (100).

2α-[4-methylseneciolyoxy]-15,16-Epoxyabda-7,13(16),14-trien-18-oic acid (**6**). Isolated as its methylester **6a**; IR ν_{max}^{CCl₄} cm⁻¹: 1735 (CO₂R), 1715, 1695 (C=CCO₂R); MS *m/z* (rel. int.): 442.288 [M]⁺ (0.5) (calc. for C₂₇H₄₀O₅: 442.288), 301 (6), 247 (9), 187 (18), 119 (20), 95 [RCO]⁺ (100).

2α-Hydroxy-15,16-epoxylabda-7,13(16),14-trien-18-oic acid (**7**). Isolated as the acetate of its methylester **7aAc**; IR ν_{max}^{CCl₄} cm⁻¹:

Table 3. ¹H NMR spectral data of compounds **13a**, **14aAc** and **15aAc** (400 MHz, CDCl₃, δ-values)

H	13a		14aAc	15aAc*
	CDCl ₃	C ₆ D ₆		
1	7.35 <i>t</i>	7.19 <i>t</i>	4.66 <i>br d</i>	4.67 <i>br d</i>
2	6.28 <i>br s</i>	6.14 <i>br s</i>	5.56 <i>br t</i>	5.55 <i>br t</i>
4	2.45 <i>br t</i>	2.54 <i>br t</i>	2.14 <i>m</i>	2.13 <i>m</i>
5	2.30 <i>m</i>	2.36 <i>br q</i>		
6	5.19 <i>ttq</i>	5.21 <i>ttq</i>	5.12 <i>br t</i>	5.07 <i>br t</i>
8	2.30 <i>m</i>	2.00 <i>br t</i>	2.30 <i>br t</i>	1.95 <i>br t</i>
9	2.09 <i>m</i>	2.21 <i>br q</i>	2.07 <i>br q</i>	1.34 <i>m</i> 1.61 <i>m</i>
10	6.73 <i>br t</i>	6.96 <i>br t</i>	6.71 <i>br t</i>	1.58 <i>m</i> 1.45 <i>m</i>
12	2.09 <i>m</i>	2.19 <i>br t</i>	2.07 <i>m</i>	1.61 <i>m</i> 1.45 <i>m</i>
13	2.30 <i>m</i>	2.34 <i>br q</i>	2.25 <i>br q</i>	2.26 <i>m</i>
14	5.14 <i>ttq</i>	5.31 <i>ttq</i>	5.12 <i>br t</i>	5.07 <i>br t</i>
16	1.68 <i>br s</i>	1.71 <i>br s</i>	1.67 <i>br s</i>	1.68 <i>br s</i>
17	1.60 <i>br s</i>	1.64 <i>br s</i>	1.61 <i>br s</i>	1.58 <i>br s</i>
19	1.60 <i>br s</i>	1.49 <i>br s</i>	1.58 <i>br s</i>	1.57 <i>br s</i>
20	7.21 <i>br s</i>	7.14 <i>br s</i>	4.63 <i>br s</i>	4.64 <i>br s</i>
OMe	3.74 <i>s</i>	3.52 <i>s</i>	3.72 <i>s</i>	3.67 <i>s</i>
OAc	—	—	2.06 <i>s</i> 2.05 <i>s</i>	2.07 <i>s</i> 2.05 <i>s</i>

*H-11 2.35 *m*.

J [Hz]: 4,5=5,6=8,9=9,10=12,13=13,14~7; 6,8=6,19=14,16=14,17~1.5; compound **13a**: 1,2=1,20=1.5; compounds **14aAc** and **15aAc**: 1,2=7.

1745 (CO₂R); MS *m/z* (rel. int.): 388.225 [M]⁺ (17) (calc. for C₂₃H₃₂O₅: 388.225), 328 [M-HOAc]⁺ (31), 247 (22), 246 (29), 187 (30), 119 (36), 95 (33), 82 (100), 81 (77).

Labda-7,13-dien-16,15-olid-18-oic acid (**8**). Isolated as its methylester **8a**; IR ν_{max}^{CCl₄} cm⁻¹: 1790, 1765, 1650 (butenolide), 1735 (CO₂R); MS *m/z* (rel. int.): 346.214 [M]⁺ (6) (calc. for C₂₁H₃₀O₄: 346.214), 286 [M-HCO₂Me]⁺ (92), 271 [286-Me]⁺ (56), 189 (64), 109 (96), 81 (100); [α]_D²⁴ +41 (CHCl₃; *c* 2.15).

Labda-7,13-dien-15,16-olid-18-oic acid (**9**). Isolated as its methylester **9a**; IR ν_{max}^{CCl₄} cm⁻¹: 1790, 1760, 1650 (butenolide), 1735 (CO₂R); MS *m/z* (rel. int.): 346.214 [M]⁺ (4) (calc. for C₂₁H₃₀O₄: 346.214), 286 [M-HCO₂Me]⁺ (20), 271 [286-Me]⁺ (8), 179 (30), 109 (100), 81 (58); [α]_D²⁴ +48 (CHCl₃; *c* 0.91).

15-Hydroxylabda-7,13-dien-16,15-olid-18-oic acid (**10**). Isolated as the acetate **10aAc**; IR ν_{max}^{CCl₄} cm⁻¹: 1800, 1780, 1750, 1735 (butenolide, OAc, CO₂R); MS *m/z* (rel. int.): 404.220 [M]⁺ (0.3) (calc. for C₂₃H₃₂O₆: 404.220), 344 [M-HOAc]⁺ (4), 329 [344-Me]⁺ (23), 285 (12), 269 (43), 187 (20), 109 (100).

16-Hydroxylabda-7,13-dien-15,16-olid-18-oic acid (**11**). Isolated as the acetate **11aAc**; IR ν_{max}^{CCl₄} cm⁻¹: 1800, 1780, 1745, 1735, 1650 (butenolide, OAc, CO₂R); MS *m/z* (rel. int.): 404.220 [M]⁺ (0.1) (calc. for C₂₃H₃₂O₆: 404.220), 344 [M-HOAc]⁺ (10), 284 [344-HCO₂Me]⁺ (35), 269 [284-Me]⁺ (24), 189 (42), 173 (75), 109 (100).

15,16-Dihydroxylabda-7,13-dien-18-oic acid (**12**). Isolated as the diacetate **12aAc**; IR ν_{max}^{CCl₄} cm⁻¹: 1750 (OAc, CO₂R); MS *m/z* (rel. int.): 374.246 [M-HOAc]⁺ (6) (calc. for C₂₃H₃₄O₄: 374.246), 314 [374-HOAc]⁺ (48), 299 [314-Me]⁺ (50), 255 [314-CO₂Me]⁺ (48), 248 (83), 188 (80), 173 (100), 119 (86), 81 (90).

10E-Centipedic acid (**13**). Isolated as its methylester **13a**; IR ν_{max}^{CCl₄} cm⁻¹: 1730 (CO₂R), 890 (furan); MS *m/z* (rel. int.): 330.219 [M]⁺ (1) (calc. for C₂₁H₃₀O₃: 330.219), 179 (20), 121 (40), 109 (100), 93 (62), 81 (66), 69 (51).

20-Hydroxynerylgeraniol-18-oic acid (**14**). Isolated as its diacetate methylester **14aAc**; IR ν_{max}^{CCl₄} cm⁻¹: 1745 (OAc, CO₂R); MS *m/z* (rel. int.): 374.246 [M-HOAc]⁺ (1) (calc. for C₂₃H₃₄O₄: 374.246), 314 [374-HOAc]⁺ (10), 187 (24), 133 (50), 119 (48), 81 (64), 69 (100).

20-Hydroxy-10,11-dihydroneerylgeraniol-18-oic acid (**15**). Isolated as its diacetate methylester **15aAc**; IR ν_{max}^{CCl₄} cm⁻¹: 1750 (OAc, CO₂R); MS *m/z* (rel. int.): 376.261 [M-HOAc]⁺ (0.4) (calc. for C₂₃H₃₆O₄: 376.261), 316 [376-HOAc]⁺ (24), 133 (60), 119 (73), 93 (74), 81 (76), 69 (100).

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