Table 1. ^{1}H NMR spectral data of compounds **1** and **2** (400 MHz, $CDCl_3$, δ-values)

H	1	2	multiplicity
1	6.60	6.60	*br t*
2	2.62	2.62	*m*
3	2.37	2.37	*dt*
3′	1.43	1.43	*dtq*
5	2.47	2.47	*d*
6	4.80	4.80	*br d*
8	5.38	5.38	*dd*
9	3.38	3.38	*br dd*
9′	2.73	2.73	*br dd*
13	5.05	5.05	*br d*
13′	4.92	4.94	*dd*
14	9.31	9.31	*s*
15	1.62	1.62	*br d*
OCOR	2.24 *dd*	2.59 *qq*	
	2.19 *dd*	1.19 *d*	
	2.05 *tqq*	1.14 *d*	
	0.94 *d*		
	0.93 *d*		
OAc	2.07 *s*	2.08 *s*	

J [Hz]: 1,2 = 8.5; 1,9 ~ 1; 2,3 = 4.5; 2,3′ = 7; 3,3′ = 14; 3′,15 ~ 0.5; 5,6 = 9; 6,13′ = 1; 8,9 = 11; 8,9′ = 7.5; 9,9′ = 14; 13,13′ = 13; O*i*Val: 2,2′ = 15; 2,3 = 6; 3,4 = 3,5 = 6.5; O*i*Bu: 2,3 = 2,4 = 7.

3 ml min^{-1}, MeOH–H_2O, 3 : 1) affording 3 mg **2** (R_t 2.3 min) and 20 mg **1** (R_t 3.8 min).

Glaucogalamensolide isovalerate (**1**). Crystals, mp 138°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2750, 1700 (C=CCHO), 1780 (γ-lactone), 1745 (CO_2R); MS *m/z* (rel. int.): 360.157 $[M-HOAc]^+$ (2) (calc. for $C_{20}H_{24}O_6$: 360.157), 345 $[360-Me]^+$ (0.5), 276 $[360-O{=}C{=}CHCHMe_2]^+$ (8), 258 $[360-RCO_2H]^+$ (6), 229 $[258-CHO]^+$ (17), 85 $[RCO]^+$ (85), 57 $[85-CO]^+$ (100); $[\alpha]_D$ $-114°$ ($CHCl_3$; *c* 0.6).

Glaucogalamensolide isobutyrate (**2**). Crystals, mp 183°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2750, 1700 (C=CCHO), 1780 (γ-lactone), 1745 (CO_2R); MS *m/z* (rel. int.): 346.142 $[M-HOAc]^+$ (2) (calc. for $C_{19}H_{22}O_6$: 346.142), 318 $[M-RCO_2H]^+$ (0.8), 258 $[318-HOAc]^+$ (13), 229 $[258-CHO]^+$ (60), 71 $[RCO]^+$ (100).

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SESQUITERPENE LACTONES AND FLAVONOIDS FROM *HELENIUM RADIATUM*

Elisa Petenatti, Mauricio J. Pestchanker, Ming Guo and Eduardo Guerreiro

Departamento de Química Orgánica, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, Chacabuco y Pedernera, 5700 San Luis, Argentina

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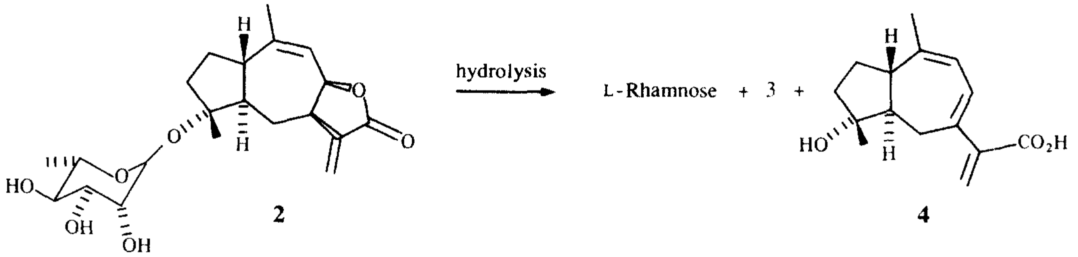
Key Word Index—*Helenium radiatum*; Compositae; flavones; pseudoguaianolide; guaianolide rhamnopiranoside.

Abstract—The aerial parts of *Helenium radiatum* afforded two known flavones, the pseudoguaianolide 9-*O*-desacetylspathulin-2-*O*-angelate and the guaianolide 2-desoxypleniradin-4-*O*-α-L-rhamnopyranoside. The structures were elucidated by spectroscopic methods and chemical transformations.

INTRODUCTION

As part of a general phytochemical study of the Argentinian region of Cuyo we have reinvestigated *Helenium radiatum* (Less.) Bierner known heretofore as *H. alternifolium* (Spreng.) Cabr. [1]. In previous studies on Argentinian samples of this genus, the pseudoguaianolides tenulin, brevilin A, linifolin A and the flavone jaceosidin, were isolated from material collected in Tucuman and alternilin from that collected in Buenos Aires [2].



RESULTS AND DISCUSSION

The methanolic extract of the aerial parts of *H. radiatum*, collected in San Luis, Argentina, gave the flavones jaceosidin and nepetin, the pseudoguaianolide 9-*O*-desacetylspathulin-2-*O*-angelate (**1**) [3] and the guaianolide rhamnopiranoside (**2**).

The presence of the glycoside **2** was inferred from the signals at δ5.03 (1H, *d*, $J = 1.5$ Hz and the signals between, δ3.00 and 4.50 and 1.27 (3H, *d*, $J = 6$ Hz) in the ^{1}H NMR spectrum. This was further supported by the signals at δ95.0, 72.4, 71.9, 71.2, 67.8 and 17.1 in the ^{13}C NMR spectrum. The additional signals in the ^{1}H NMR spectrum were close to those of the guaianolide 2-desoxypleniradin [4]. The proton signals were assigned by COSY experiments. These ^{1}H shift were then used in a two dimensional heteronuclear ^{1}H–^{13}C correlation experiment. Furthermore, the EI mass spectral fragmentation pattern and ^{13}C NMR data also supported this structure.

The single sugar produced by mild acid hydrolysis of **2** was identified, as the trimethylsilyl ether derivative, by comparison with a standard sample of L-rhamnose by GC techniques, as well as by co-chromatography with the above standard. The configuration at C-1 of the L-rhamnosyl group was determined as α from the chemical shift of H-1 and its coupling constant.

Beside L-rhamnose, hydrolysis of **2** afforded two products. One of them was characterized as 2-desoxypleniradin (**3**) which showed the same pattern of **2** in ^{1}H NMR, the second product, which exhibited higher polarity, was characterized by the ^{1}H NMR, IR and UV spectra as 7(8),9,11(13)-guaitrien-4-ol-12-oic acid (**4**). The formation of **4** in the hydrolytic conditions employed may be due to hydrolysis of the lactone moiety followed by a dehydration step whose driving force is the formation of a highly conjugate system. The *cis* junction of the lactonic ring is in total agreement with the fast dehydration suffered by **3**, in the hydrolytic medium. All the data of **2** indicated that this lactone was 2-desoxypleniradin-4-*O*-α-L-rhamnopyranoside. Though their concentrations are very high the corresponding aglycone was not detected.

Table 1. ^{1}H NMR spectral data of compound **2** (360 MHz CDCl$_3$, TMS as int. standard)

H	
1	2.95–3.10 *m*
2	1.6–1.9 *m*
3	1.8–2.0 *m*
5	2.09 *ddd* (10, 10, 2)
6	1.3 *m*, 1.9 *m*
7	3.0–3.15 *m*
8	5.24 *dm* (9)
9	5.30 *br s*
13a	6.25 *d* (3)
13b	5.56 *d* (3)
14	1.75 *s*
15	1.20 *s*
1′	5.04 *s*
2′	3.75–3.90 *m* 3H
3′	
5′	
4′	3.45 *dd* (9, 9)
6′	1.29 *d* (6)

Coupling constants (Hz) are given in parentheses.

Table 2. ^{13}C NMR spectral data of compound **2** (90 MHz, CDCl$_3$).

C	
1	41.9
2	36.4
3	25.7[a]
4	86.9
5	47.7
6	25.5[a]
7	41.1
8	77.9
9	122.6
10	139.0[b]
4-Me	20.6
10-Me	22.5
11	137.5[b]
12	170.4
13	121.3
1′	95.1
2′	72.3
3′	71.7
4′	73.4
5′	67.8
6′	17.4

[a, b] Assignments may be interchanged.

EXPERIMENTAL

Air-dried aerial parts (460 g, voucher Del Vitto 2841, deposited in the Herbario de la Universidad Nacional de San Luis) were extracted with MeOH (24 hr × 3) at room temp and the resulting extract worked-up in the usual fashion. CC silica gel eluted with C_6H_6–EtOAc mixts, gave the following compounds in order of elution: jaceosidin (C_6H_6–EtOAc) (9:1), 9-*O*-desacetylspathulin-2-*O*-angelate (C_6H_6–EtOAc) (6:1), nepetin (C_6H_6–EtOAc) (3:1) and 2-desoxypleniradin-4-*O*-α-L-rhamnopiranoside (EtOAc). Complete purification of the compounds was achieved by rechromatography over Sephadex LH-20 for the flavonoids and by crystallization for the lactones, affording 0.21 g, 2.05 g, 0.17 g and 1.65 g respectively. Known compounds were identified by comparison with previously reported data and by comparison with authentic material.

2-*Desoxypleniradin*-4-O-*α*-L-*rhamnopyranoside* (**2**). Mp 163–164°; IR $\nu^{\mathrm{KBr}}_{\mathrm{max}}\ \mathrm{cm}^{-1}$: 3500 (OH), 1765 (γ-lactone); MS *m*/*z* (rel. int.): 248 $[\mathrm{M}-C_6H_{10}O_4]^+$ (2), 231 $[C_{15}H_{19}O_2]^+$ (51), 230 $[248-H_2O]$ (100), 215 (14), 188 (26), 145 (62), 129 (28), 105 (30).

$$[\alpha]^{\lambda}_{24^\circ}=\frac{589 \quad 578 \quad 546 \quad 436\ \mathrm{nm}}{-134.8 \quad -138.8 \quad -156.9 \quad -254.3}\ (\mathrm{CHCl_3};\ c\ 1.02)$$

7(8),9,11(13)-*Guaiatrien*-4-*ol*-12-*oic acid* (**4**). ^{1}H NMR (60 MHz, $\mathrm{CDCl_3}$): δ1.18 (3H, *s*, H-15), 1.74 (3H, *br s*, H-14), 5.47 (1H, *d*, $J=2$ Hz), 5.60 (1H, *d*, $J=2$ Hz) (H-8 and H-9), 5.75 (1H, *s*, H-13b), 6.35 (1H, *s*, H-13a).

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A CLERODANE DITERPENE AND OTHER CONSTITUENTS OF *CLERODENDRON INERME*

BASUDEB ACHARI, CHANDANA CHAUDHURI, CHITTA R. SAHA, PRADEEP K. DUTTA and SATYESH C. PAKRASHI*

Indian Institute of Chemical Biology, Calcutta-700032, India

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Key Word Index—*Clerodendron inerme*; Verbenaceae; clerodane diterpene; clerodermic acid; flavonoids.

Abstract—A new clerodane diterpene clerodermic acid was isolated from *Clerodendron inerme* and the structure deduced from spectral data. The known compounds friedelin, 5-hydroxy-7,4′-dimethoxyflavone, salvigenin, acacetin and apigenin were also found.

INTRODUCTION

Clerodendron inerme L., like many other species of the genus, is a recognized medicinal plant having alterative and febrifugal properties [1]. An alcoholic extract of the plant has also been reported to exhibit uterine stimulant activity [2]. Chemical investigations on the leaves and stems have so far shown the presence of a number of common triterpenes [3], a neolignan [4], diterpenoids [3, 5], sterols [3, 6] and flavones [7]. Reinvestigation of the leaves of this plant has now revealed the presence of salvigenin (5-hydroxy-6,7,4′-trimethoxyflavone, **4**) and 5-hydroxy-7,4′-dimethoxyflavone (**3**), not reported earlier from any *Clerodendron* species, in addition to apigenin (**6**), acacetin (5,7-dihydroxy-4′-methoxyflavone, **5**) and friedelin (**2**) detected in related species and a new diterpene acid, clerodermic acid, the structure determination of which is discussed below.

RESULTS AND DISCUSSION

Clerodermic acid (**1a**), mp 161–162°, $[\alpha]^{27^\circ}_{\mathrm{D}}-70^\circ$, exhibited in its IR spectrum a broad absorption band in the region 3300–2500 cm^{-1} together with a strong absorption at 1670 cm^{-1}, indicative of a conjugated carboxyl

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*Author to whom correspondence should be addressed.