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KAURANE DERIVATIVES FROM *ROBINSONIA EVENIA*

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Key Word Index—*Robinsonia evenia*; Compositae; Senecioneae; diterpenes; *ent*-kauranes.

Abstract—Six new *ent*-kaurane angelates were isolated from the aerial part of *Robinsonia evenia* Phil. The structures were elucidated by spectroscopic methods.

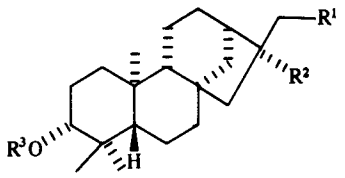
INTRODUCTION

Robinsonia D.C. is a South American genus of seven species, endemic to the Juan Fernandez Islands off Chile. The genus is the second largest of those of the Compositae found on the Islands. The Juan Fernandez islands, located 600 km off the coast of Chile at latitude 33°S consist of two major islands, Masatierra (= Isla Robinson Crusoe) and Masafuera (= Isla Alejandro Selkirk), separated in an east–west line by 150 km of ocean [1].

We recently described the isolation and structure elucidation of an *ent*-kaurane derivative from the leaves and stems of *Robinsonia thurifera* Dcne, from Chile [2, 3]. In our systematic examination of the diterpenes of *Robinsonia*, we have examinated the aerial parts of *Robinsonia evenia* Phil, which gave new *ent*-kaurane derivatives.

RESULTS AND DISCUSSION

The extract of the aerial parts of *R. evenia* afforded *ent*-kaurane-16β-ol and the kaurane derivatives **1**–**6**. The structure of **1** followed from the ^{1}H NMR spectrum (Table 1) which was close to that of the corresponding dicacetate recently isolated from a *Peteravenia* species [4] where the stereochemistry and the assignment of the methyl signals were deduced from the results of NOE difference spectroscopy. The replacement of the acetate by angelate groups caused the expected shifts of H-3 and H-17. The ^{1}H NMR spectra of **2** and **7** (Table 1), obtained by mild acetylation of **2**, were close to that of **1**. The chemical shift of H-3 in the spectra of **2** and **7** differed from that of **1** as expected. Comparison of the signals of the angelate residues in **1** and **2** indicated that the H-3′ signal of the angelate at C-3 differed from that of the 17-angelate proton by a small upfield shift. The spectrum of **3** clearly indicated that the oxygen function at C-17 was missing (1.36 *s*). The other signals were nearly identical with those of **1**. The absence of the 16-hydroxy group in compound **4** followed from the ^{1}H NMR spectrum by the presence of a doublet at δ3.40 (Table 1). Again the other signals were close to those of **1**. The ^{1}H NMR spectrum (Table 1) of



	1	2	3	4	5	6	7	8
R^1	OAng	OAng	H	OH	OH	OH	OAng	OAc
R^2	OH	OH	OH	H	OH	OMe	OH	OH
R^3	Ang	H	Ang	Ang	Ang	Ang	Ac	Ang

compound **5** and of the corresponding 17-*O*-acetate (**8**) indicated that **5** was the 17-*O*-desacyl derivative of **1**. Accordingly, the H-17 signals were shifted upfield and the chemical shifts of H-3 and H-17 in the spectrum of the corresponding acetate differed from those of **7** in the expected way, H-3 being shifted downfield and H-17 upfield.

The spectral data of **6** (Table 1) required the presence of a methoxy derivative of **5**. Thus H-17 was a broadened singlet at δ3.72 and a three proton singlet at δ3.16 was obviously due to a methoxy group which had to be placed at C-16 as the remaining signals were nearly identical with those of **5**.

The ^{13}C NMR spectrum of **4** (see Experimental) also supported the structures. As followed from the optical rotation of 16-hydroxy kaurane it belongs to the *ent*-series. It is likely, therefore, that all of the diterpenes were *ent*-kauranes.

The occurrence of *ent*-kaurane derivatives in *Robinsonia* may be of chemotaxonomic relevance as studies of other species have indicated that this type of diterpene seems to be widespread in the genus. So far more than 100 *Senecio* species have been studied but no kaurane derivatives have been isolated. This is true for the whole tribe Senecioneae. The only exception is the South African genus *Othonna*. From two species, kauranes are reported [5, 6] while most species afforded furoeremophilanes.

Table 1. ^{1}H NMR data of compounds **1–8** (400 MHz, $CDCl_3$)

H	1	2	3	4	5	6*	7	8
3	4.54 *dd*	3.20 *dd*	4.53 *dd*	4.54 *dd*	4.53 *dd*	4.54 *dd*	4.45 *dd*	4.54 *dd*
17 17′	4.29 *s*	4.29 *s*	1.36 *s*	3.40 *br d*	3.65 *br d* 3.77 *br d*	3.72 *br s*	4.28 *s*	4.22 *s*
18 19	0.87 *s*	0.98 *s* 0.77 *s*	0.87 *s* 0.86 *s*	0.86 *s*	0.88 *s*	0.89 *s*	0.87 *s* 0.83 *s*	0.86 *s*
20	1.04 *s*	1.02 *s*	1.05 *s*	1.03 *s*	1.05 *s*	1.05 *s*	1.03 *s*	1.04 *s*
O Ac	–	–	–	–	–	–	2.04 *s*	2.10 *s*
OCOR	6.03 *qq* 1.88 *dq* 1.99 *dq* 6.10 *qq* 1.90 *dq* 1.98 *dq*	6.10 *qq* 1.90 *dq* 1.99 *dg*	6.03 *qq* 1.88 *dq* 1.98 *dq*	6.03 *qq* 1.89 *dq* 1.98 *dq*	6.03 *qq* 1.88 *dq* 1.98 *dq*	6.03 *qq* 1.90 *dq* 1.99 *dq*	6.10 *qq* 1.90 *dq* 1.99 *dq*	6.03 *qq* 1.88 *dq* 1.98 *dq*

*OMe: 3.16 *s*.
J [Hz]: 2α,3β = 11; 2β,3β = 4.5; 17,17′ = 12, Compound **4**: 14,17 = 7; OAng 3,4 = 7; 3,5 = 4,5 = 1.5.

EXPERIMENTAL

Mps are uncorr. *Robinsonia evenia* was collected during the expeditions to the Juan Fernandez Islands (Chile) in January 1984 from Masatierra. The plant material was air-dried in the field. Vouchers are deposited at the Herbarium of the Ohio State University, U.S.A., with duplicates at the Herbarium of the Universidad de Concepcion, Chile. The dried and ground aerial parts of the plant (440 g) were extracted with petrol, $CHCl_3$ and EtOAc. The resulting extract (24 g) was chromatographed on a silica gel column using petrol–EtOAc gradient elution systems. The compounds isolated were crystallized from the same solvent mixture used to elute them from the column. Fractions 25–28 (EtOAc–petrol, 1:19) gave 41 mg **1**, fractions 68–83 (EtOAc–petrol, 1:4) 60 mg **3**, fractions 84–102 (EtOAc–petrol, 1:3) 82 mg **4**, fractions 131–138 (EtOAc–petrol, 1:3) 7 mg **2**, fractions 150–162 (EtOAc–petrol, 1:1) 28 mg **5**, fractions 162–172 10 mg **6** and fractions 173–180 (EtOAc–petrol, 4:1) 95 mg *ent*-kaurane-16β-ol, which was identified by comparison of its spectral data with those of authentic material.

ent-3β,17-*Diangeloyloxy*-16β-*hydroxykaurane* (**1**). Colourless crystals, mp 210–212°; MS *m/z* (rel. int.): 486.355 $[M]^+$ (0.5) (calc. for $C_{30}H_{46}O_5$: 486.355), 468 $[M-H_2O]^+$ (1.6), 373 $[M-CHOAng]^+$ (19), 273 $[373-HOAng]^+$ (21), 83 $[C_4H_7CO]^+$ (100).

ent-17-*Angeloyloxy*-3β,16β-*dihydroxykaurane* (**2**). Colourless crystals, mp 180–182°; IR ν_{max}^{Nujol} cm^{-1}: 3520, 3400 (OH), 1710 (C=CCO_2R); MS *m/z* (rel. int.): 404.293 $[M]^+$ (1) (calc. for $C_{25}H_{40}O_4$: 404.293), 386 $[M-H_2O]^+$ (7), 291 $[M-CH_2OAng]^+$ (50), 273 [291] $-H_2O$] (32), 83 $[C_4H_7CO]$ (100). Acetylation (Ac_2O, 1 hr, 70°) gave **7**; colourless oil; IR ν_{max}^{Nujol} cm^{-1}: 3480 (OH), 1740, 1250 (OAc), 1720 (C=CCO_2R).

ent-3β-*Angeloyloxy*-16β-*hydroxykaurane* (**3**). Colourless crystals, mp 178–180°; IR ν_{max}^{Nujol} cm^{-1}: 3570, 3480 (OH), 1740 (OAc), 1710 (C=CCO_2R); MS *m/z* (rel. int.): 388.297 $[M]^+$ (0.05) (calc. for $C_{25}H_{40}O_3$: 388.297, 370 $[M-H_2O]^+$ (4), 270 $[370-HOAng]^+$ (22), 83 $[C_4H_7CO]$ (100); ^{13}C NMR ($CDCl_3$, C-1–C-20): 38.4 *t*, 23.7 *t*, 80.8 *d*, 38.8 *s*, 56.5 *d*, 20.1 *t*, 41.8 *t*, 45.1 *s*, 55.2 *d*, 39.0 *s*, 18.1 *t*, 26.8 *t*, 48.9 *d*, 37.6 *t*, 57.8 *t*, 79.2 *s*, 24.5 *q*, 28.4 *q*, 16.9 *q*, 17.8 *q*, OAng: 167.0 *s*, 127.1 *s*, 137.2 *d*, 15.7 *q*.

ent-3β-*Angeloyloxy*-17*hydroxykaurane* (**4**). Colourless crystals, mp 125–128°; IR ν_{max}^{Nujol} cm^{-1}: 3300 (OH), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 388.298 $[M]^+$ (0.5), 288 $[M-HOAng]^+$ (52), 83 $[C_4H_7CO]$ (100).

ent-3β-*Angeloyloxy*-16β,17-*dihydroxykaurane* (**5**). Colourless crystals, mp 138–140°; IR ν_{max}^{Nujol} cm^{-1}: 3400, 3300 (OH), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 404 [M] (0.1), 386 $[M-H_2O]^+$ (1.1), 373 $[M-CH_2OH]^+$ (42), 273 $[373-HOAng]^+$ (48), 83 $[C_4H_7CO]^+$ (100). Acetylation (Ac_2O, 1 hr, 70°) gave **8**; colourless crystals, mp 166–178°; IR ν_{max}^{Nujol} cm^{-1}: 3520 (OH), 1740 (OAc), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 446 $[M]^+$ (0.1), 428 $[M-H_2O]^+$ (0.3), 373 $[M-CH_2OAc]^+$ (9), 328 $[428-HOAng]^+$ (16), 273 $(373-HOAng]^+$ (24), 83 $[C_4H_7CO]^+$ (100).

ent-3β-*Angeloyloxy*-16β-*methoxy*-17-*hydroxykaurane* (**6**). Colourless crystals, mp175–178°; MS *m/s* (rel. int.): 388 $[M-CH_2O]^+$ (2.6), 387 $[M-OMe]^+$ (100), 287 $[378-HOAng]^+$ (12), 83 $[C_4H_7CO]^+$ (100).

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