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ENT-CLERODANE DERIVATIVES FROM *CHROMOLAENA CONNIVENS*

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Key Word Index—*Chromolaena connivens*, *C. turnariensis*; Compositae, diterpenes; clerodane; prostaglandin-like acids.

Abstract—The aerial parts of *Chromolaena connivens* afforded in addition to widespread compounds four *ent*-clerodane derivatives and two epimeric prostaglandin-like acids. A second species, *C. turnariensis*, only gave widespread compounds. The structures were elucidated by high field NMR techniques.

INTRODUCTION

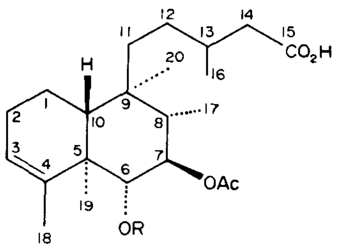
In continuation of our investigations of *Chromolaena* species [1], we have now studied the constituents of the Bolivian species, *C. connivens* (Rusby) K. et R. which is placed in the subgenus Chromolaena [2]. The aerial parts afforded germacrene D, caryophyllene epoxide, the flavanones sakuranetin, the corresponding 7-*O*-methyl ether and naringenin, *ent*-labd-13*E*-en-8,15-diol [3], the prostaglandin-like acids **5** [4] and **6** [5] as well as the *ent*-clerodanes **1**–**4** which were isolated as their methyl esters **1a**–**4a**.

The structures of these *ent*-clerodane derivatives were deduced from the ^{1}H NMR spectra (Table 1). These were nearly identical with those of the corresponding Δ^{13} derivatives which have been isolated from *C. laevigata* [6], except for the signals for the side chain. These signals were similar to those of the corresponding 13,14-dihydrokolavenic acids which only differ in the nature of the oxygen functions [6]. The aerial parts of *C. tunariensis* (Hieron.) K. et R. only gave germacrene D, caryophyllene, α-humulene, coumarin and *o*-hydroxycinnamic acid, the *E*-isomer of the coumarin precursor.

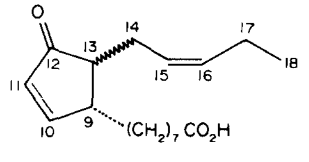
Table 1. ^{1}H NMR spectral data of compounds **1a**–**4a** (400 MHz, $CDCl_3$)

H	1a	2a	3a	4a	Multiplicity
3	5.21	5.21	5.21	5.22	*br s*
6	4.98	4.89	4.91	4.86	*d*
7	5.12	5.08	5.09	5.06	*dd*
8	1.77	1.74	1.74	1.75	*m*
13	1.85	1.84	1.85	1.84	*m*
14	2.29	2.29	2.29	2.28	*dd*
14′	2.14	2.14	2.15	2.14	*dd*
16	0.94	0.94	0.93	0.93	*d*
17	0.79	0.78	0.77	0.79	*d*
18	1.56	1.55	1.56	1.57	*br s*
19	1.23	1.21	1.21	1.20	*s*
20	0.85	0.85	0.83	0.83	*s*
OAc	1.95	2.00	2.00	2.00	*s*
OCOR	6.12 *qq* 2.03 *dq* 1.87 *dq*	2.48 *qq* 1.14 *d*	2.29 *tq* 1.74 *ddq* 1.35 *ddq* 0.91 *t* 1.10 *d*	2.02 *s*	

J = [Hz]: 6, 7 = 7, 8 = 10; 8, 17 = 13, 16 = 7; 13, 14 = 6.5; 13, 14′ = 7.5; 14, 14′ = 15; OAng: 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.5; O*i*Bu: 2′, 3′ = 2′, 4′ = 7; OMeBu: 2′, 3_1′ = 2′, 3_2′ = 2′, 5′ = 3_1′, 4′ = 3_2′, 4′ = 7; 3_1′, 3_2′ = 14.



	1	**2**	**3**	**4**
R	Ang	*i*Bu	MeBu	Ac



5 13αH **6** 13βH

1a–**6a** are the corresponding methyl esters

These results indicate a close relationship of *C. connivens* to *C. laevigata* which is also placed in the subgenus *Chromolaena* [2]. However, the latter species also contains furocadinenes which are characteristic for the genus. Prostaglandin-like acids have been reported from two other *Chromolaena* species of the same subgenus but several other types of natural products are also present.

EXPERIMENTAL

The air-dried part (290 g) of *Chromolaena connivens* (voucher RMK 964, deposited in the US National Herbarium, Washington, collected in Feb. 1987 in Bolivia) was extracted and worked-up as reported previously [7]. CC and TLC afforded 50 mg germacrene D, 9 mg caryophyllene epoxide, 180 mg 7-*o*-methyl sakuranetin, 200 mg sakuranetin, 60 mg naringenin, 1.3 g *ent*-labd-13*E*-ene-8,15-diol and a mixture of acids which were converted to the methyl esters by addition of CH_2N_2. TLC (Et_2O–petrol, 1:1) gave two mixtures. HPLC of one-tenth of the less polar one (RP 8, 100 bar, flow rate, 3 ml/min, $MeOH-H_2O$, 17:3) afforded 30 mg **1a** (R_t 13.9 min), 50 mg **2a** (R_t 12.3 min) and 30 mg **3a** (R_t 15.0 min). HPLC of one tenth of the second fraction ($MeOH-H_2O$, 4:1) gave 15 mg **4a** (R_t 17.0 min), 10 mg **5a** and 12 mg **6a**.

The aerial parts (420 g) of *C. tunariensis* (voucher RMK 9634, collected in Feb. 1987 in Bolivia) gave 20 mg germacrene D, 20 mg caryophyllene, 20 mg α-humulene, 900 mg coumarin and 450 mg *o*-hydroxycinnamic acid. Known compounds were identified by comparing the 400 MHz ^1H NMR spectra with those of authentic material.

7β-Acetoxy-6α-angeloyloxy-13,14-*dihydrokolavenic acid* (**1**). Isolated as its methyl ester **1a**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R); MS *m/z* (rel. int.): 476.314 $[M]^+$ (0.3) (calc. for $C_{28}H_{44}O_6$: 476.314), 416 $[M-HOAc]^+$ (3.3), 316 $[416-RCO_2H]^+$ (33), 187 (71), 83 $[RCO]^+$ (100).

7β-Acetoxy-6α-isobutyryloxy-13,14-*dihydrokolavenic acid* (**2**). Isolated as its methyl ester **2a**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740/CO_2R; MS *m/z* (rel. int.) 464.314 $[M]^+$ (0.2) (calc. for $C_{27}H_{44}O_6$: 464.314), 404 (2.6), 316 (42), 187 (100), 71 $[RCO]^+$ (51).

7β-Acetoxy-6α-[2-methyl butyryloxy]-13,14-*dihydrokolavenic acid* (**3**). Isolated as its methyl ester **3a**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735 (CO_2R); MS *m/z* (rel. int.): 478.329 $[[M]^+$ (0.1) (calc. for $C_{28}H_{46}O_6$: 478.329), 418 (1.5), 316 (29), 187 (65), 85 $[RCO]^+$ (31), 57 $[85-CO]^+$ (100); $[\alpha]_D^{24°}$ −23 ($CHCl_3$; *c* 0.46).

6α,7β-Diacetoxy-13,14-*dihydrokolavenic acid* (**4**). Isolated as its methyl ester **4a**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R); MS *m/z* (rel. int.): 436 $[M]^+$ (0.3), 376.261 $[M-HOAc]^+$ (1.9) (calc. for $C_{23}H_{36}O_4$: 376.261), 316 (39), 187 (100).

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DITERPENOIDS FROM *DYPTERIX ODORATA*

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Key Word Index—*Dipterix odorata*; Leguminosae; diterpenoids cassane type; structure elucidation; HRGC-MS-C data, 3β-acetoxy vouacapenol.

Abstract—A new cassane diterpene was isolated from the bark of seeds of *Dipterix odorata* together with four known diterpenoids with the same skeleton.

INTRODUCTION

Dipterix odorata Willd (Aubl.) (≡*Coumarouna odorata* Aubl.) belongs to the order Rosales. It is a tall tree (~50 m) indigenous to the Amazonian area, growing in dry plains, known locally as Cumaru or Serrapia in Venezuela. Its seeds are a rich source of coumarin, which is important in the perfumery industry [1].

From the bark and heartwood of this plant earlier workers isolated several isoflavones besides lupeol, betulin and a mixture of methyl esters of fatty acids [2, 3].

RESULTS AND DISCUSSION

Chromatographic fractionation of the petrol extract from the bark of the seed yielded two cassane-type diterpenes, vouacapenic acid (**1**) [4] and β-acetoxy vouacapenol (**2**) which were identified by spectroscopic methods. Chemical transformations performed with vouacapenic acid (**1**) afforded vouacapenol (**3**) and its acetate (**4**) and the hydrocarbon derivative **5** which were identified as minor components in the isolated fractions by HRGC-MS and by co-injection with authentic sam-