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TWO FURTHER 6,12-*CIS*-GERMACRANOLIDES FROM *MONTANOA TOMENTOSA* SUBSP. *XANTHIIFOLIA*

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Key Word Index—*Montanoa tomentosa* subsp. *xanthiifolia*; Compositae; sesquiterpenes; lactones; 6,12-*cis*-germacranolides; kaurane derivatives.

Abstract—The aerial parts of *Montanoa tomentosa* subsp. *xanthiifolia* gave two further 6,12-*cis*-germacranolides while the roots contained large amounts of kaurane derivatives.

INTRODUCTION

From the genus *Montanoa* (tribe Heliantheae) mostly the rare 6,12-*cis*-germacranolides were isolated [1]. Only from *M. tomentosa*, belonging to the monotypic subgenus *Montanoa*, were other lactones reported [2]. We have now studied *M. tomentosa* subsp. *xanthiifolia* Sch. Bip. from Costa Rica.

RESULTS AND DISCUSSION

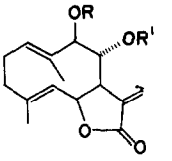
The aerial parts gave in addition to widespread diterpenes the isomeric lactones **1** and **2**, the structures of which were easily assigned by comparison of their ^{1}H NMR spectral data (Table 1) with those of corresponding germacranolides [3, 4]. The nature of the ester group followed from the typical ^{1}H NMR signals and their relative position, from the chemical shifts of H-8 and H-9 respectively, and from the downfield shift of the H-1 signal in the spectrum of **2**. The presence of a 6β,12-lactone led to the typical coupling $J_{6,7} \sim 6$ Hz and the small coupling $J_{7,13}$. Compounds **1** and **2** are obviously the precursors of the 4,5-epoxides isolated from other *Montanoa* species [1].

The roots gave large amounts of *ent*-kaurenic acid, its $\Delta^{9(11)}$-dehydro derivative, beyerenic acid, 15α-cinnamoyloxy-*ent*-kaurenic acid [5] and its $\Delta^{9(11)}$-dehydro derivative [6], *ent*-kaurenal and its $\Delta^{9(11)}$-dehydro derivative, 15α-angeloyloxy-*ent*-kaurenic acid and borneyl cinnamate.

EXPERIMENTAL

The air dried plant material (collected near Tilarán, Costa Rica voucher 1029081 National Herbarium, Costa Rica) was extracted with Et_2O–petrol–MeOH (1:1:1) and the extracts separated by the usual procedures [6]. The CC silica gel fractions of the extract (4.3 g) of the roots (530 g) obtained with Et_2O–petrol (1:4) gave 1 g each of *ent*-kaurenic acid, its $\Delta^{9(11)}$-derivative and beyerenic acid (identified after conversion to their methyl esters and separation by TLC ($AgNO_3$ coated silica gel) by comparing their 400 MHz ^{1}H NMR spectra with those of authentic materials), 100 mg *ent*-kaurenal and its $\Delta^{9(11)}$-dehydro derivative and 10 mg borneylcinnamate. The CC fraction with Et_2O–petrol (1:1) gave by TLC 150 mg 15α-cinnamoyloxy-*ent*-kaurenic acid, 100 mg of its $\Delta^{9(11)}$-derivative and 5 mg 15α-angeloyloxy-*ent*-kaurenic acid (these compounds were identified by comparison with authentic samples).

The polar CC fractions (silica gel) of the extract of the



	1	2
R	Sen	H
R'	H	Sen

Table 1. ^{1}H NMR spectral data of compounds **1** and **2** (400 MHz, $CDCl_3$ TMS as int. standard)

H	1	2
1	5.30 *ddq*	5.61 *m*
2	2.20 *m*	2.30 *m*
2'		
3	2.29 *ddd*	
3'	2.00 *ddd*	2.08 *m*
5	4.94 *d* (*br*)	5.18 *d* (*br*)
6	5.15 *dd*	5.11 *dd*
7	3.17 *dd* (*br*)	3.11 *dd* (*br*)
8	4.02 *dd*	5.02 *d*
9	4.67 *d*	4.05 *d*
13	6.43 *s* (*br*)	6.24 *d*
13'	5.74 *s* (*br*)	5.53 *d*
14	1.63 *d* (*br*)	1.57 *d* (*br*)
15	1.69 *d*	1.70 *d*
OCOR	5.70 *qq*	5.59 *qq*
	2.16 *d*	2.12 *d*
	1.90 *d*	1.88 *d*

J (Hz): 1, 2 = 8; 1, 2' = 9; 1, 14 = 1.5; 2, 3 = 2', 3 = 3.5; 2, 3' = 2', 3' = 9; 3, 3' = 11.5; 5, 6 = 11; 5, 15 = 1.5; 6, 7 = 6; 7, 8 = 8; 7, 13 = 7, 13' = 1; 8, 9 = 9.

aerial parts (from 320 g) (Et_2O and Et_2O–MeOH, 1:9) were further separated by repeated TLC (silica gel PF 254, C_6H_6–CH_2Cl_2–Et_2O, 4.5:4.5:1, three developments) affording 4 mg **1** (R_f 0.18) and 6.3 mg **2** (R_f 0.2) (the total amount of **1** and **2** was about 100 mg, but a lot of material was lost during the lengthy separations).

8α-Hydroxy-9β-senecioyloxy-trans,trans-*germacra*-1(10),4-*dien*-cis-6,12-*olide* (**1**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone), 1725, 1645 (C=CCO_2R); MS *m/z* (rel. int.): 346.178 $[M]^+$ (0.7) (calc. for $C_{20}H_{26}O_5$: 346.178), 246 $[M-RCO_2H]^+$ (3.5), 231 $[246-Me]^+$ (3), 228 $[246-H_2O]^+$ (6), 213 $[228-Me]^+$ (4), 83 $[C_4H_7CO]^+$ (100);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-186 \quad -195 \quad -225 \quad -412} \ (CHCl_3;\ c = 0.4).$$

9β-Hydroxy-8α-senecioyloxy-trans,trans-*germacra*-1(10),4-*dien*-cis-6,12-*olide* (**2**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3590 (OH), 1780 (γ-lactone), 1733, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 346.178 $[M]^+$ (0.2) (calc. for $C_{20}H_{26}O_5$: 346.178), 246 $[M-RCO_2H]^+$ (3.5), 231 $[246-Me]^+$ (2), 228 $[246-H_2O]^+$ (4), 213 $[228-Me]^+$ (2), 83 $[C_4H_7CO]^+$ (100);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-135 \quad -141 \quad -163 \quad -291} \ (CHCl_3;\ c = 0.6).$$

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4β,19-EPOXY-NORKAURENE AND OTHER DITERPENES FROM *MIKANIA BANISTERIAE*

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Key Word Index—*Mikania banisteriae*; Compositae; diterpenes; kaurane derivative; norkaurane derivative.

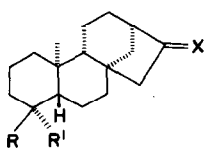
Abstract—The aerial parts of *Mikania banisterae* afforded four new diterpenes, *ent*-kaur-16-en-18-al, 18-acetoxy-*ent*-kaurene, 18-hydroxy-16α,17-epoxy-*ent*-kaurane and 4β-19-epoxy-18-nor-*ent*-kaurene.

INTRODUCTION

From the large genus *Mikania* (tribe Eupatorieae, subtribe Mikaniinae) so far mainly highly oxygenated sesquiterpene lactones have been reported [1]. However, there are also several species in which these compounds are replaced by a large variety of diterpenes [2]. We have studied a species from Costa Rica, *M. banisteriae* DC.

RESULTS AND DISCUSSION

The aerial parts gave *ent*-kaur-16-en-18-oic acid, 4-*epi*-abietic acid, ozic acid and four further diterpenes, the kaurane derivatives **2**–**4** and the nor-kaurene **5**. The hydroxy derivative **1** has been isolated previously from a *Sideritis* species [3] and the acetate **2** has been prepared from **1** [3]. The ^{13}C NMR data agreed nicely with those reported [4]. The ^1H and ^{13}C NMR data (Table 1) of **3** showed clearly that this compound was the 4-epimer of the known *ent*-kaur-16-en-19-al. Accordingly, the ^1H NMR shifts of the methyl singlets differed charac-



	1	2	3	4	5
R	CH_2OH	CH_2OAc	CHO	CH_2OH	
R'	Me	Me	Me	Me	
X	CH_2	CH_2	CH_2		CH_2