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);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-186 \quad -195 \quad -225 \quad -412} \; (\text{CHCl}_3;\ c = 0.4).$$

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);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-135 \quad -141 \quad -163 \quad -291} \; (\text{CHCl}_3;\ c = 0.6).$$

REFERENCES

1. Seaman, F. C., Malcolm, A. J. and Fischer, N. H. (1984) *Phytochemistry* **23**, 1063.
2. Seaman, F. C., Malcolm, A. J., Fronczek, F. R., Lee, I. Y. and Fischer, N. H. (1984) *Phytochemistry* **23**, 646.
3. Herz, W. and Govindan, S. V. (1980) *J. Org. Chem.* **45**, 1113.
4. Bohlmann, F., Schmeda-Hirschmann, G., Jakupovic, J., Castro, V., Cicció, J. F. and Calvo, G. (1984) *J. Nat. Prod.* **47**, 663.
5. Bohlmann, F. and Le Van, N. (1978) *Phytochemistry* **17**, 1957.
6. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1984) *Phytochemistry* **23**, 1979.

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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-

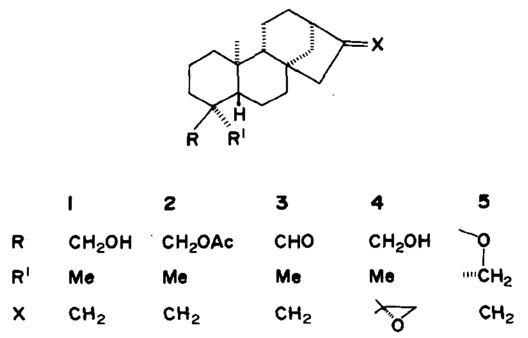

Table 1. ^{1}H and ^{13}C NMR spectral data of **2**–**5** (400 MHz and 100.6 MHz respectively, $CDCl_3$, TMS as int. standard)

H	**2**	**3***	**4**	**5**	C	**2**†	**3**†	**4**†	C	**2**	**3**	**4**
13	2.63 *dd*(*br*)	2.65 *dd*(*br*)		2.64 *dd*(*br*)	1	39.8	39.8	39.9	11	18.2	18.0	19.3
14	1.96 *dd*(*br*)	1.97 *dd*(*br*)	1.97 *dd*	1.95 *dd*	2	17.9	17.0	17.9	12	33.2	33.1	29.1
14′	1.08 *m*	1.09 *dd*(*br*)			3	35.8	32.2	35.2	13	44.0	44.4	42.7
15	2.05 *m*	2.11 *d*(*br*)	1.69 *dd*	2.09 *d*(*br*)	4	36.5	49.8	37.5	14	40.9	40.4	40.7
15′		2.04 *ddd*	1.62 *d*	2.02 *ddd*	5	50.2	48.4	49.2	15	49.1	49.0	48.9
17	4.79 *s*(*br*)	4.80 *s*(*br*)	2.85 *d*	4.80 *s*(*br*)	6	20.2	23.0	19.8	16	155.8	155.4	66.4
17′	4.73 *s*(*br*)	4.74 *s*(*br*)	2.77 *d*	4.75 *s*(*br*)	7	39.9	39.4	38.6	17	103.0	103.2	50.4
18	3.84 *d*	9.19 *s*	3.41 *d*	—	8	44.1	43.8	45.3	18	73.1	206.6	72.1
18′	3.62 *d*		2.08 *d*	—	9	56.0	55.7	55.8	19	18.0	13.9	18.2
19	0.79 *s*	1.03 *s*	0.75 *s*	2.70 *dd* 2.54 *d*	10	39.2	38.0	39.1	20	17.4	17.7	17.5
20	1.05 *s*	1.05 *s*	1.04 *s*	0.95 *s*								

Signals assigned by spin decoupling.

*H-3α 1.87 (*ddd*, $J = 13, 3, 3$ Hz), H-3β, 0.80 (*ddd*, $J = 13, 13, 3$).

†Multiplicity as required.

J (Hz): 12, 13 = 13, 14 ~ 4; 13, 14′ ~ 2; 14, 14′ = 12; 15, 15′ = 17; 15, 17 = 2.5; compounds **2** and **4**: 18, 18′ = 11; compound **4**: 17, 17′ = 5; compound **5**: 3, 19 = 1.

teristically from those of the epimeric aldehyde. Furthermore the ^{13}C NMR shift of C-5 was typically different in these isomers. As the shift of C-20 was the same as in **1** and **2** an aldehyde group at C-10 could be excluded.

As followed from the molecular formula, compound **4** has a second oxygen function. The ^{1}H NMR data of **4** (Table 1) were very similar to those of **1**. However, the signals of the exo-methylene protons were replaced by a pair of doublets at δ2.85 and 2.77. Accordingly, the presence of an epoxide of **1** was very likely. The ^{13}C NMR data established this to be the case. The signals at δ66.4 and 50.4 were obviously those of C-16 and C-17. The stereochemistry was deduced by comparing the ^{1}H NMR spectrum with that of the corresponding epoxy-*ent*-kaurene [5, 6]. The configuration at C-4 followed from the NMR data which were nearly identical with those of **1**. Furthermore **4** was prepared by epoxidation of **1** which gave as expected mainly the α-epoxide.

The molecular formula of **5** indicated that a nor-diterpene was present. The ^{1}H NMR spectrum (Table 1) was in part very similar to that of the kaurene derivative. However, as there was only one methyl singlet (δ0.95) no methyl group was present at C-4. Two signals at δ2.70 and 2.54 indicated the presence of an epoxide which could only be placed at C-4 as the Δ^{15}-double bond was still present. The configuration of the epoxide followed from the *W*-coupling (double doublet at δ2.70) as inspection of a model showed that a *W*-coupling only was possible with an α-epoxide. The corresponding 4(18)-exo-methylene derivative, which most likely is the precursor of **5**, has not been reported.

EXPERIMENTAL

The air dried aerial parts (500 g) (collected near El Empalme, Costa Rica, voucher 982331 National Herbarium, Costa Rica) were extracted with Et_2O–petrol–MeOH (1:1:1) and the extract was separated as reported previously [7]. CC fractions (silica gel) were as follows: 1 (petrol), 2 (Et_2O–petrol, 1:10), 3 (Et_2O–petrol, 1:3) and 4 (Et_2O–petrol, 1:1, and Et_2O). TLC (silica gel PF 254) of fraction 2 (C_6H_6–CH_2Cl_2, 1:1) gave 10 mg **3** (R_f 0.45) and 10 mg **2** (R_f 0.40). The ^{1}H NMR spectrum of fraction 3 indicated the presence of *ent*-kaurenic acid and a mixture of acids. After addition of CH_2N_2, TLC (Et_2O–petrol, 1:4) gave 300 mg methyl *ent*-kaurenoate, 10 mg methyl 4-*epi*-abietoate and 10 mg ozic acid methyl ester. (The 400 MHz ^{1}H NMR spectra of these esters were identical with those of authentic material.) TLC of fraction 4 (C_6H_6–CH_2Cl_2–Et_2O, 4.5:4.5:1) gave 3 mg **5** (R_f 0.7), 20 mg 28-hydroxy-*ent*-kaur-16-ene (R_f 0.55) and 10 mg **4** (R_f 0.45).

18-*Acetoxy*-ent-*kaur*-16-*ene* (**2**). Colourless oil, identical to a sample obtained by acetylation of **1** (^{1}H NMR and co-TLC), NMR: Table 1.

Ent-*kaur*-16-*en*-18-*al* (**3**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2690, 1735 (CHO), 3065, 890 ($C{=}CH_2$); MS m/z (rel. int.): 286.230 $[M]^+$ (61) (calc. for $C_{20}H_{30}O$: 286.230), 271 $[M-Me]^+$ (20), 257 $[M-CHO]^+$ (64), 243 $[271-CO]^+$ (60), 123 (81), 105 (78), 91 (97), 81 (91), 79 (78), 55 (100); $[\alpha]_D^{+} = -53$ ($CDCl_3$; c 0.5).

18-*Hydroxy*-16α,17-*epoxy-kaurane* (**4**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH); MS m/z (rel. int.): 304.240 $[M]^+$ (9) (calc. for $C_{20}H_{32}O_2$: 304.240), 273 $[M-CH_2OH]^+$ (100), 255 $[273-H_2O]^+$ (59), 156 (46), 123 (61), 81 (52), 55 (56). To 10 mg of **1** (obtained by $LiAlH_4$-reduction of 4-*epi*-*ent*-kaurenic acid) in 2 ml $CHCl_3$, 15 mg *m*-chloroperbenzoic acid was added. After 1 hr, separation by TLC (C_6H_6–CH_2Cl_2–Et_2O, 4:4:1) gave 7 mg **6**, identical with the natural compound (^{1}H NMR and co-TLC).

4β,19-*Epoxy*-18-*nor*-ent-*kaurene* (**5**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3060, 890 ($C{=}CH_2$); MS m/z (rel. int.): 272.214 $[M]^+$ (52) (calc. for $C_{19}H_{28}O$: 272.214), 257 $[M-Me]^+$ (37), 254 $[M-H_2O]^+$ (21), 241 $[M-CH_2OH]^+$ (21), 229 $[257-CO]^+$ (21), 105 (76), 91 (100), 81 (76), 79 (78), 55 (88).

REFERENCES

1. Bohlmann, F., Tsankova, E., King, R. M. and Robinson, H. (1984) *Phytochemistry* **23**, 1099.
2. Bohlmann, F., Singh, P., Jakupovic, J., Robinson, H. and King, R. M. (1982) *Phytochemistry* **21**, 705.
3. González, A. G., Fraga, B. M., Hernández, M. G. and Luis, J. G. (1973) *Phytochemistry* **12**, 2721.
4. González, A. G., Fraga, B. M., Hernández, M. G. and Hanson, J. R. (1981) *Phytochemistry* **20**, 846.
5. Hanson, J. R. (1967) *Tetrahedron* **23**, 801.
6. Bohlmann, F., Adler, A., Schuster, A., Gupta, R. K., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 1899.
7. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1984) *Phytochemistry* **23**, 1979.