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A DIMERIC GERMACRANOLIDE AND OTHER SESQUITERPENE LACTONES FROM *MIKANIA* SPECIES*

FERDINAND BOHLMANN,† ALFONS ADLER,† JASMIN JAKUPOVIC,† ROBERT M. KING‡ and HAROLD ROBINSON‡

†Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany;
‡Smithsonian Institution, Department of Botany, Stop No. 166, Washington, DC 20560, U.S.A.

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Key Word Index—*Mikania goyazensis*; *M. pohlii*; Compositae; sesquiterpene lactones; germacranolides; eudesmanolides; dimeric germacranolide; geranyl geraniol derivatives.

Abstract—The investigation of two *Mikania* species, both previously placed in the genus *Kanimia*, afforded in addition to known compounds several new germacranolides, one being a dimeric lactone, and a new eudesmanolide. Furthermore, two geranyl geraniol derivatives were isolated. The structures were elucidated by spectroscopic methods and a few chemical transformations. The chemotaxonomy is discussed briefly.

INTRODUCTION

From the large genus *Mikania* (Compositae, tribe Eupatorieae) with *ca* 300 species, the chemical results so far have shown that some species contain highly oxygenated germacranolides such as mikanolides, scandenolide and miscandenin[1–6], while others only afforded diterpenes, mainly kaurene derivatives[2,3,5–7]. We now have investigated two further species, both previously placed in the genus *Kanimia*. The chemistry of these two species is very uniform, both containing mainly highly oxygenated germacranolides, several of them not isolated previously.

RESULTS AND DISCUSSION

The roots of *Mikania goyazensis* (B. L. Robins.) K. et R. (*Kanimia goyazensis*) afforded germacrene D, α-humulene, the thymol derivatives **1–5** and desacetyl laurenobiolide (**10**)[8]. The aerial parts contained germacrene D, α-humulene, sitosterol, stigmasterol, lup-12-en-3β-ol, linoleic and linolenic acid as well as its methyl ester, isocomene (**30**)[9], β-isocomene (**31**)[10], modhephene (**32**)[11], phytol, geranylnerol, which could only be separated from the latter after oxidation to the aldehyde **7**, and 16-hydroxygeranylgeraniol (**8**), which was isolated as its diacetate **9**. The structure clearly followed from the ^{1}H NMR spectral data (Experimental), when compared with those of similar compounds. Furthermore, a complex mixture of sesquiterpene lactones was isolated, the main constituent being **10**[8]. Finally, seven further lactones were obtained, the germacranolides **13**, **17**, **18**, **20**, **21**, the eudesmanolide **23**[12] and the dimeric lactone **25**. The ^{1}H NMR spectrum of **13** (Table 1) at room temperature showed broad, unresolved signals, indicating a very flexible system. However, in deuteriobenzene at elevated temperatures a much clearer spectrum was obtained, allowing extensive decoupling. Nearly all signals could be assigned in this way, showing that either a 6,12 or an 8,12-*cis*-germacranolide was present. As the signal of H-6 and H-8 nearly had the same chemical shifts, acetylation was necessary to decide where the hydroxyl group had to be placed. The chemical shift of H-6 in the spectrum of the acetate **14** obtained clearly showed that the hydroxyl was at C-6. The position of the epoxide group followed from the chemical shift of H-1 and the couplings of H-1 supported the proposed stereochemistry. **13** therefore was 1β, 10α-epoxy-6α-hydroxy-1,10H-inunolide. **17**, **18** and **20** were obviously germacranolides with an exocyclic double bond; this followed from the typical broadened singlets around δ5. **17** and **18** were isomers, as was clear from the ^{1}H NMR spectra (Table 2) which further showed that the same substitution and stereochemistry at C-5 through C-8 as in **16** was present. However, again 6,12 or 8,12-lactones were possible. We therefore acetylated both lactones. Surprisingly both afforded the known keto acetate chrysanolide (**19**) [13]. Clearly **17** and **18** were the 1-epimeric hydroperoxides, which were transformed to the ketone **19** by thermal elimination of acetic acid. A clear decision on the stereochemistry at C-1 was difficult. The proposed assignment seemed the more likely as in the spectrum of **18** the signal of H-14 was shifted downfield when compared with that of **17**. This deshielding differences would be expected, if a conformation was present with both the 4-methyl and the 10-methylene groups above the plane. Such a con-

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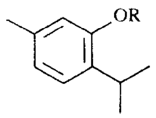
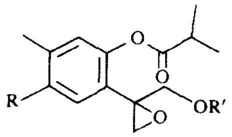
*Part 412 in the series "Naturally Occurring Terpene Derivatives". For Part 411 see Bohlmann, F., Ziesche, J. and Gupta, R. K. (1982) *Phytochemistry* **21**, 1331.

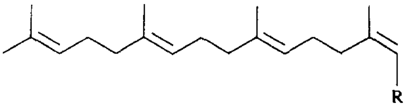


1 R = H

2 R = *i*Bu

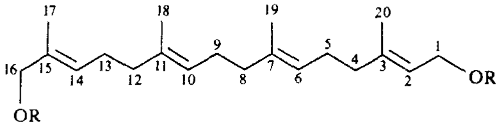


	3	**4**	**5**
R	H	H	OMe
R′	Ac	*i*Bu	Ac



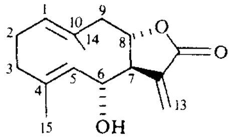
6 R = CH_2OH

7 R = CHO



8 R = H

9 R = Ac



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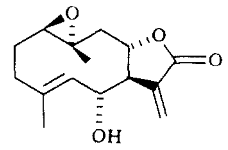

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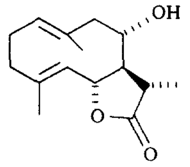

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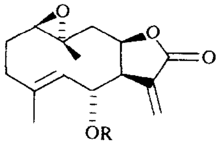
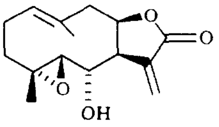


13 R = H

14 R = Ac



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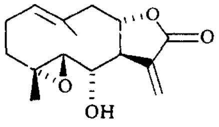

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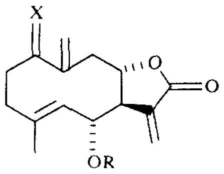
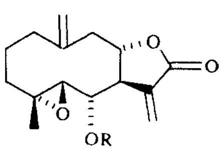
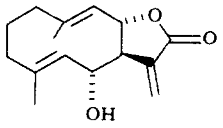


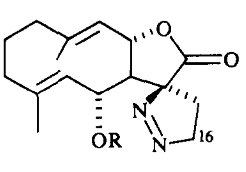




	17	**18**	**19**
R	H	H	Ac
X	α-OOH,H	β-OOH,H	=O

20

21



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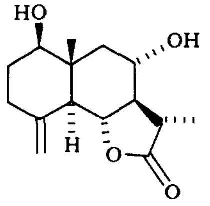

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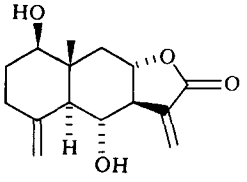

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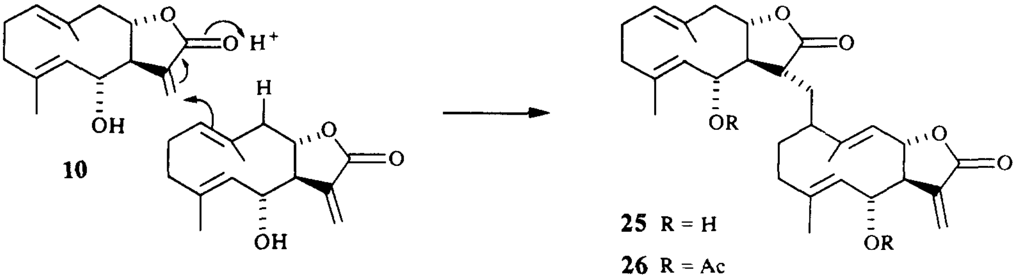

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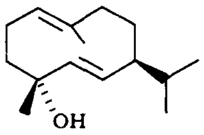
25 R = H

26 R = Ac



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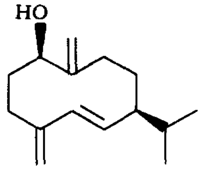

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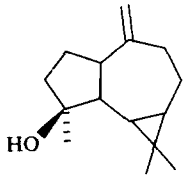

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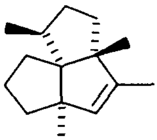

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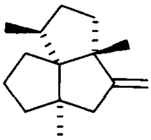

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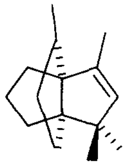

32

formation would also agree with the couplings observed. The ^{1}H NMR spectrum of **20** (Table 2) showed that again an epoxide was present. Spin decoupling allowed the assignment of H-5 through H-8, and from the couplings the stereochemistry could be deduced. As the chemical shifts of H-6 and H-8 were nearly the same as in the spectrum of **16**, again an 8,12-lactone was proposed. Unfortunately, confirmation by acetylation was not successful since the compound was destroyed during this treatment. Since, however, the chemical shift of H-5 through H-9 were nearly identical with those of **16**, an 8,12-lactone is the most probable formula. The ^{1}H NMR spectrum of **21** (Table 2) showed that this lactone must have a 9,10-double bond, which also clearly followed from the results of spin decoupling. Irradiation of H-7 collapsed the double doublets at 4.59 and 4.55 to doublets and also changed the signals of the exo-methylene protons to broadened singlets. As the signal at 4.55 was further coupled with a broadened doublet at δ5.03, the sequence H-5 through H-9 was established. **21** could also be written as a 6,12-lactone. We therefore prepared the pyrazoline derivative **22** by addition of diazomethane.

Table 1. ^{1}H NMR spectral data of compounds **11**, **13**, **14** and **16** (400 MHz, CDCl$_3$, TMS as int. standard)

	11	**13**	C$_6$D$_6$, 70°	**14** (C$_6$D$_6$, 100°)	**16**
H-1	2.67 *dd*	2.71 *brd*	2.30 *dd*	2.38 *dd*	5.35 *br*
H-3	2.36 *ddd* 2.24 *ddd*	2.42 *m* 2.2 *m*	1.95 *m* 1.70 *m*	2.00 *m* 1.70 *m*	2.15 *m*
H-5	5.22 *brd*	5.24 *brd*	4.85 *brd*	4.90 *brd*	2.64 *d*
H-6	4.34 *ddd*	4.39 *brt*	3.76 *dd*	5.14 *dd*	3.43 *brdd*
H-7	2.85 *dddd*	2.97 *m*	2.65 *dddd*	2.79 *dddd*	2.99 *dddd*
H-8	4.03 *brdd*	4.11 *m*	3.79 *ddd*	3.85 *ddd*	4.01 *ddd*
H-9	2.04 *brdd*	2.07 *m*	1.99 *dd*	2.00 *dd*	2.15 *m*
H-9′	1.55 *m*	1.61 *m*	1.72 *dd*	1.73 *dd*	1.75 *m*
H-13	6.38 *dd*	6.39 *dd*	6.39 *dd*	6.32 *dd*	6.57 *dd*
H-13′	6.24 *dd*	6.19 *dd*	5.92 *dd*	5.58 *dd*	6.28 *dd*
H-14	1.27 *s*	1.43 *s*	1.05 *s*	1.08 *s*	1.79 *d*
H-15	1.76 *d*	1.84 *brs*	1.37 *brs*	1.54 *d*	1.27 *s*
OAc	—	—	—	1.71 *s*	—
OH	1.73 *d*	—	—	—	—

J (Hz): Compound **11**: 1, 2 = 11; 1, 2′ = 2; 2, 3 = 13; 2′, 3 = 6; 2, 3′ = 2.5; 2′, 3′ = 5.5; 3, 3′ = 13; 5, 6 = 6, 7 = 10; 5, 15 = 1.5; 7, 8 = 6.5; 7, 13 = 3; 7, 13′ = 2.8; 8, 9′ ~ 1; 8, 9 = 9; 6, OH = 3; 13, 13′ = 1; compounds **13/14**: 1, 2 = 10; 1, 2′ = 3; 5, 6 = 9; 5, 15 = 1.5; 6, 7 = 10; 7, 8 = 4; 7, 13 = 3; 7, 13′ = 2.6; 8, 9 = 4; 8, 9′ = 11; 9, 9′ = 14; 13, 13′ = 1; compound **16**: 5, 6 = 6, 7 = 9.5; 7, 8 = 6; 7, 13 = 3; 7, 13′ = 2.6; 13, 13′ = 1; 8, 9 = 2.5; 8, 9′ = 11.

Table 2. ^{1}H NMR spectral data of compounds **17–21** (400 MHz, CDCl$_3$, TMS as int. standard)

	17 (57°)	**18**	**19** (60°)	**20**	**21**
H-1	4.15 *brd*	4.15 *brd*	—	—	—
H-5	5.09 *brd*	5.28 *brd*	4.96 *brd*	2.68 *d*	5.03 *brd*
H-6	4.26 *dd*	4.44 *dd*	5.11 *dd*	3.40 *brdd*	4.59 *dd*
H-7	2.81 *dddd*	2.89 *dddd*	2.91 *dddd*	2.98 *dddd*	2.72 *dddd*
H-8	4.01 *ddd*	3.82 *ddd*	4.02 *brdd*	4.13 *ddd*	4.55 *dd*
H-9	2.99 *brd*	3.11 *ddd*	3.42 *brd*	3.07 *brd*	5.15 *brd*
H-9′	2.37 *dd*	2.30 *ddd*	2.15 *dd*	2.46 *dd*	
H-13	6.35 *dd*	6.29 *dd*	6.33 *dd*	6.44 *dd*	6.25 *dd*
H-13′	6.18 *dd*	6.22 *dd*	5.82 *dd*	6.28 *dd*	6.22 *dd*
H-14	5.28 *dd*	5.40 *dd*	5.79 *brd*	5.41 *brd*	1.78 *d*
H-14′	5.25 *brs*	5.33 *dd*	5.75 *brd*	5.29 *brs*	
H-15	1.73 *d*	1.60 *d*	1.74 *d*	1.38 *s*	1.67 *d*
OAc	—	—	2.03 *s*	—	—

J (Hz): Compound **17**: 1, 2 = 9; 1, 2′ = 4; 5, 6 = 6, 7 = 10; 5, 15 = 1; 7, 8 = 6.5; 7, 13 = 3; 13, 13′ = 1; 8, 9′ = 3; 8, 9′ = 10; 9, 9′ = 14; compound **18**: 1, 2 = 10; 5, 6 = 6, 7 = 10; 5, 15 = 1.5; 7, 8 = 7.5; 7, 13 = 3.5; 7, 13′ = 3; 13, 13′ = 1; 8, 9 = 2.5; 8, 9′ = 6.5; 9, 9′ = 16; 9, 14 = 9, 14′ = 2; 9′, 14 = 1.5; compound **19**: 5, 6 = 6, 7 = 10; 7, 8 = 5; 7, 13 = 3; 7, 13′ = 2.5; 8, 9 ~ 3; 8, 9′ = 11; 9, 9′ = 13.5; 9, 14 = 1.5; 9, 14′ = 2; compound **20**: 5, 6 = 6, 7 = 10; 7, 8 = 6; 7, 13 = 3.5; 7, 13′ = 3; 13, 13′ = 1; 8, 9 ~ 3; 8, 9′ = 11; 9, 9′ = 14; 9, 14 ~ 1; compound **21**: 5, 6 = 6, 7 = 7, 8 = 10; 7, 13 = 3; 13, 13′ = 1; 5, 15 = 9, 15 = 1.3.

The adduct obtained showed a negative cotton effect. Following the Geissman rule [14] an 8,12-*trans*-lactone was therefore present.

The structure elucidation of **25** caused some difficulties as the ^{1}H NMR spectrum (Table 3) could not be interpreted directly. Only at 120° in deuteriobenzene in a sealed tube could a relatively clear spectrum be obtained, allowing extensive spin decoupling. In this way it could be shown that a dimeric lactone was present. All signals of one part of the molecule could be assigned. They were nearly identical with those of **21**, however, since as shown by spin decoupling, H-1$_1$ was coupled with protons belonging to the second part of the molecule further decoupling the sequence H-1$_1$, H-13, H-11, H-7, H-6 could be established, so the mode of linking of the two lactones could be

Table 3. ^{1}H NMR spectral data of compounds **25** and **26** (400 MHz, TMS as int. standard)

	25 (C_6D_6, 120°)	**26** ($CDCl_3$)		**25**	**26**
H-1	4.83 *m*	4.92 *brd*	H-1_1	3.06 *ddd*	3.05 *m*
H-5	4.59 *brd*	4.92 *brd*	H-2_1	1.64 *m*	—
H-6	4.00 *brdd*	5.44 *brdd*	H-$2'_1$	1.42 *m*	—
H-7	2.00 *m*	2.48 *m*	H-3_1	2.07 *brdd*	—
H-8	3.72 *m*	4.12 *brdd*	H-$3'_1$	1.83 *ddd*	—
H-9	2.77 *brd*	2.76 *brd*	H-5_1	4.83 *brd*	4.60 *brd*
H-9′	2.25 *m*	2.40 *brdd*	H-6_1	4.30 *dd*	5.46 *brdd*
H-11	2.60 *ddd*	2.60 *ddd*	H-7_1	2.52 *dddd*	2.99 *m*
H-13	2.25 *m*	—	H-8_1	4.75 *dd*	4.75 *dd*
H-13′	1.64 *m*	—	H-9_1	5.12 *brd*	5.20 *brd*
H-14	1.33 *brs*	1.51 *brs*	H-13_1	6.30 *dd*	6.25 *brd*
H-15	1.43 *brs*	1.62 *brs*	H-$13'_1$	6.09 *dd*	5.72 *brd*
OAc	—	2.10 *s*	H-14_1	1.65 *brs*	1.80 *brs*
		2.08 *s*	H-15_1	1.76 *d*	1.86 *brs*

J (Hz): 5, 6 = 9; 6, 7 = 10; 7, 11 = 10; 8, 9′ = 10; 9, 9′ = 13; 11, 13 = 5; 11, 13′ = 5; 13, 1_1 = 5; 13′, 1_1 = 10; 1_1, 2_1 = 10; 1_1, $2'_1$ = 5; 2_1, 3_1 ~ 1; 2_1, $3'_1$ = 6; $2'_1$, 3_1 = 6; $2'_1$, $3'_1$ = 3_1, $3'_1$ = 13; 5_1, 6_1 = 10; 6_1, 7_1 = 7_1, 8_1 = 9; 8_1, 9_1 = 10; 7_1, 13_1 = 3.5; 7_1, $13'_1$ = 3; 13_1, $13'_1$ = 1.

assigned. Though not all signals of the second part could be interpreted completely, the assignment of H-1 and H-5 through H-9 showed what the complete structure was. The stereochemistry at C-7 and C-11 followed from the coupling observed. The ^{1}H NMR spectrum of the diacetate **26** (Table 4) further supported the proposed structure. The mass spectrum of **25** also agreed with the structure. Though the molecular ion was very weak, the $[M-H_2O]^+$ fragment was *m/z* 478.272 leading to $C_{30}H_{38}O_5$, while the diacetate **26** showed fragments of $[M-HOAc]^+$ and $[M-2\times HOAc]^+$, also in agreement with the proposed molecular formula. The ^{13}C NMR data also supported the structure, though an assignment of the signals was not attempted as too many similar carbons were present. **25** was most likely formed by dimerization of **10** induced by proton attack as shown in the scheme. **25** we have named mikagoyanolide.

Table 4. ^{1}H NMR spectral data of compound **24** (400 MHz, $CDCl_3$, TMS as int. standard)

H-1	3.58 *ddd**
H-5	1.93 *brd*
H-6	4.13 *ddd**
H-7	2.59 *dddd*
H-8	3.98 *ddd*
H-9	2.53 *ddd*
H-9′	1.90 *m*
H-13	6.18 *dd*
H-13′	5.98 *dd*
H-14	0.80 *s*
H-15	5.10 *brs*
H-15′	4.77 *brs*
OH	2.16 *d*

*With D_2O *dd*.

J (Hz): 1, 2 = 11; 1, 2′ = 4.5; 1, OH = 4; 5; 5, 6 = 6, 7 = 10; 6, OH = 2; 7, 13 = 3; 7, 8 = 8, 9′ = 12; 8, 9 = 3.5; 9, 9′ = 12.

The roots of *Mikania pohlii* (Baker) K. et R. (*Kanimia pohlii* Baker) afforded germacrene D, α-humulene, **1**, **2**, **5**, **10**, **12**[15] and **25**, while the aerial parts gave germacrene D, α-humulene, bicyclogermacrene, caryophyllene-1,10-epoxide, phytol, nerolidol, lup-12-en-3β-ol, β-amyrin, stigmasterol, linolenic acid and its methyl ester, **10**, **13**, **15**[8], **25** and **27**–**29** as well as three further sesquiterpene lactones, the epoxides **11** and **16** and the eudesmanolide **24**. The structure of the latter clearly followed from the ^{1}H NMR spectrum (Table 4), since the corresponding acetate is a known substance[16]. The ^{1}H NMR spectrum of **11** and **16** showed that isomeric epoxides were present, both derived from **10**. Consequently the couplings of H-6 through H-9 were nearly the same. In the spectrum of **11** the H-6 signal could be assigned by spin decoupling. Irradiation of the olefinic proton (H-5) collapsed the threefold doublet at δ4.34 to a double doublet, while further decoupling showed that the latter was coupled with H-7 and with a doublet at δ1.73, which disappeared after the deuterium exchange, indicating that the hydroxyl group was again at C-6. From the couplings of H-1, the stereochemistry at C-1 and C-10 was deduced. In the spectrum of **16** (Table 2) the H-5 signal was a doublet at δ2.64, while that of H-1 was a broad signal at δ5.35. As the remaining signals were similar to those of **11** the presence of a 5, 6-epoxide was very likely. The broadened double doublet at δ3.43 was the signal of H-6, as could be established by spin decoupling. As the threefold doublet at δ4.01 was sharp, the presence of an 8,12-lactone was very likely. **16** has already been obtained by epoxidation of **10**[8]. The spectral data agreed nicely.

The chemistry of the two species is very uniform. Obviously all the lactones are closely related, **10** being most probably the common precursor of all the other lactones isolated, though the co-occurrence of *cis*- and *trans*-8,12-lactones is unexpected. The chemical evidence would support the removal of the two species previously belonging to *Kanimia* into a separate subgenus of *Mikania*.

EXPERIMENTAL

The air-dried plant material, collected in north-eastern Brazil, was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing their ^1H NMR spectra with those of authentic material.

Mikania goyazensis (*voucher RMK* 8280). The roots (7 g) afforded 5 mg germacrene D, 0.5 mg α-humulene, 1 mg **1**, 2 mg **2**, 6 mg **3**, 3 mg **4**, 5 mg **5** and 23 mg **10**, while the aerial parts (260 g) gave 200 mg germacrene D, 10 mg α-humulene, 10 mg linoleic acid, 10 mg linolenic acid, 42 mg of its methylester, 12 mg lup-12-en-3β-ol, 20 mg sitosterol, 20 mg stigmasterol, 2 mg phytol, 5 mg **6**, 10 mg **8** (isolated as its diacetate 9), 1.9 g **10**, 10 mg **13**, 36 mg **17**, 20 mg **18**, 10 mg **20**, 20 mg **21**, 15 mg **23**, 40 mg **25**, 8 mg **30**, 2 mg **31** and 18 mg **32** (the lactones were separated by mixtures of CH_2Cl_2–C_6H_6, 1:1, with different amounts of Et_2O, several developments).

Mikania pohlii (*voucher RMK* 8199). The roots (10 g) gave 3 mg germacrene D, 3 mg α-humulene, 5 mg **1**, 14 mg **2**, 10 mg **5**, 15 mg **10**, 10 mg **12** and 8 mg **25**, while the aerial parts afforded 270 mg germacrene D, 110 mg α-humulene, 160 mg bicyclogermacrene, 1 mg caryophyllene-1,10-epoxide, 20 mg phytol, 5 mg nerolidol, 40 mg lup-12-en-3β-ol, 8 mg β-amyrin, 3 mg stigmasterol, 100 mg linolenic acid, 3 mg of its methyl ester, 1.9 g **10**, 1 mg **11**, 15 mg **13**, 15 mg **15**, 10 mg **16**, 5 mg **17**, 5 mg **18**, 2 mg **24**, 40 mg **25**, 3 mg **27**, 8 mg **28** and 3 mg **29**.

16-*Acetoxygeranyl geraniol acetate* (**9**). Colourless gum, obtained by acetylation of **8** (1 hr Ac_2O, 70°), IR $\nu^{CCl_4}_{max}$ cm^{-1}: 1735, 1235 (OAc); MS *m*/*z* (rel. int.): 330.256 $[M-HOAc]^+$ (1) ($C_{22}H_{34}O_2$), 270 $(330-HOAc)^+$ (1), 55 (100); ^1H NMR ($CDCl_3$): 4.55 *br d* (H-1), 5.36 *br t* (H-2), 5.11 *br t* (H-6, 10), 5.45 *br t* (H-14), 4.40 *br s* (H-16), 1.64 *br s* (H-17), 1.54 *br s* (H-18, 19), 1.76*dt* (H-20), 2.07 and 2.04 *s* (OAc, *J*(Hz): 1, 2 = 5, 6 = 9, 10 = 13, 14 = 7; 1, 20 = 2, 20 = 1).

1β,10α-*Epoxy*-1,10H-*desacetyl laurenobiolide* (**11**). Colourless gum, IR$\nu^{CHCl_3}_{max}$ cm^{-1}: 3616 (OH), 1773 (γ-lactone); MS *m*/*z* (rel. int.): 264.136 $[M]^+$ (7) ($C_{15}H_{20}O_4$), 97 (98), 69 (100), 57 (95).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-28 \quad -28 \quad -40 \quad -66} \quad (CHCl_3;\ c = 0.05).$$

1β,10α-*Epoxy*-6α-*hydroxy*-1,10H-*inunolide* (**13**). Colourless gum, IR$\nu^{CHCl_3}_{max}$ cm^{-1}: 3616 (OH), 1761 (γ-lactone); MS *m*/*z* (rel. int.): 264.136 $[M]^+$ (1) ($C_{15}H_{20}O_4$), 97 (100), 81 (92), 55 (87), $[\alpha]_D = -28$ ($CHCl_3$; *c* 0.05).

1α-*Hydroperoxy*-1-*desoxo-chrysanolide* (**17**). Colourless gum, IR$^{CHCl_3}_{max}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone); MS *m*/*z* (rel. int.): 228.115 $[M-H_2O, H_2O_2]^+$ (20) ($C_{15}H_{16}O_3$), 55 (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-22 \quad -23 \quad -27 \quad -53} \quad (CHCl_3;\ c\ 0.29).$$

5 mg **17** was heated for 1 hr with Ac_2O. TLC afforded 3 mg **19**, MS *m*/*z* (rel. int.): 304 $[M]^+$ (3), 262.120 $[M-\text{ketene}]^+$ (30) ($C_{15}H_{18}O_4$), 244 $[262-H_2O]^+$ (21), 216 $[244-CO]^+$ (23), 80 (100).

1β-*Hydroperoxy*-1-*desoxo-chrysanolide* (**18**). Colourless gum, IR $\nu^{CHCl_3}_{max}$ cm^{-1}: 3600 (OH), 1730 (γ-lactone); MS *m*/*z* (rel. int.): 246 $[M-H_2O_2]^+$ (1), 228 $[246-H_2O]^+$ (1), 218 $[246-CO]^+$ (6), 203 $[218-Me]^+$ (3), 57 (100). Acetylation as above afforded **19**.

5α, 6β-*Epoxy*-5, 6H-1-*desoxo-chrysanolide* (**20**). Colourless gum, IR$\nu^{CHCl_3}_{max}$ cm^{-1}: 3600 (OH), 1760 (γ-lactone); MS *m*/*z* (rel. int.): 246.125 $[M-H_2O]^+$ (1) ($C_{15}H_{18}O_3$), 57 (100).

6α-*Hydroxy-germacra*-4, 9-*dien*-8α, 12-*olide* (**21**). Colourless gum, IR$\nu^{CHCl_3}_{max}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone); MS *m*/*z* (rel. int.): 248.141 $[M]^+$ (3) ($C_{15}H_{20}O_3$), 230 $[M-H_2O]^+$ (25), 55 (100). To 5 mg **21** in Et_2O excess CH_2N_2 was added. TLC (Et_2O) afforded **22**. ^1H NMR ($CDCl_3$): 5.60 *dd* (H-8, *J* = 10, 10 Hz), 5.13 *brd* (H-9, *J* = 10 Hz), 4.95 *brd* (H-5, *J* = 10 Hz), 4.43 *ddd* (H-6, *J* = 10, 10, 2 Hz), 1.87 *brs* (H-15), 1.65 (H-14, *J* = 1.5), 4.80 *t* (H-16, *J* = 8), 1.66 *dt* and 1.46 *dt* (H-13, *J* = 13, 8 Hz); CD (MeCN): $\Delta\epsilon_{322} = -9$.

Desacetyl-β-cyclopyrethrosin (**24**). Colourless gum, IR$\nu^{CHCl_3}_{max}$ cm^{-1}: 3620 (OH), 1775 (γ-lactone); MS *m*/*z* (rel. int.): 264.136 $[M]^+$ (8) ($C_{15}H_{20}O_4$), 246 $[M-H_2O]^+$ (8), 228 $[246-H_2O]^+$ (7), 108 (100), 107 (89), 69 (95).

Mikagoyanolide (**25**). Colourless gum, IR$\nu^{CHCl_3}_{max}$ cm^{-1}: 3620 (OH), 1770 (γ-lactone) MS *m*/*z* (rel. int.): 496 $[M]^+$ (0.3), 478.272 $[M-H_2O]^+$ (6) ($C_{30}H_{38}O_5$), 460 $[478-H_2O]^+$ (3), 218.131 $[C_{14}H_{18}O_2]^+$ (10), 57 (100). ^{13}C NMR ($CDCl_3$): 178.7, 170.7, 144.3, 138.4, 135.9, 135.5, 132.5, 131.3, 130.5, 129.8, 126.9, 123.0, 79.6, 79.5, 75.9, 71.2, 52.5, 44.0, 38.8, 37.2, 37.0, 36.1, 35.9, 35.5, 26.2, 25.2, 18.1, 17.7, 16.8, 15.4 (assignment was not attempted).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-26 \quad -28 \quad -33 \quad -61} \quad (CHCl_3;\ c\ 0.4).$$

10 mg **25** on heating with Ac_2O (1 hr, 70°) afforded 10 mg **26**, colourless gum, IR$\nu^{CHCl_3}_{max}$ cm^{-1}: 1775 (γ-lactone), 1740, 1240 (OAc); MS *m*/*z* (rel. int.): 520 $[M-HOAc]^+$ (3), 478 $[520-\text{ketene}]^+$ (8), 460.261 $[520-HOAc]^+$ (9) ($C_{30}H_{36}O_4$), 55 (100).

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