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A GERMACRANOLIDE FROM *MATTFELDANTHUS NOBILIS**

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Key Word Index—*Mattfeldanthus nobilis*; Vernonieae; Compositae; new germacranolide.

Mattfeldanthus is a small new genus [1] in the tribe Vernonieae. We have investigated one species collected in north-eastern Brazil. The roots of *M. nobilis* (H. Robins.) H. Robins. afforded the pentaynene **1** [2], polyisoprene, lupeol, lupeol acetate and its isomer **5** [3], while the aerial parts contained the enetetraynene **2** [2], germacrene D (**3**), bicyclogermacrene (**4**), lupeol, lupeol acetate and a new sesquiterpene lactone, which was identified as the diacetate of artemisiifolin (**6**). The ^1H NMR spectrum of **6** was very uncharacteristic; only a few signals could be assigned (Table 1). This is characteristic for 8,12-lactones [4–6]. In C_6D_6 the ^1H NMR spectrum indicated that a mixture of several conformers was present, while at 75° again a very unclear spectrum was obtained, indicating a rapid equilibrium of the conformers. Addition of diazomethane afforded two pyrazolines. The less polar one was identical with the adduct already prepared by acetylation and diazomethane addition to artemisiifolin [5]. Inspection of the ^1H NMR spectra in connection with models allows a clear assignment of all NMR signals by double resonance (Table 1). Furthermore, the stereochemistry of the two pyrazolines obtained by

Table 1. ^1H NMR data of compounds **6**, **8**, **9** and **10**

	6 $CDCl_3$	**6** C_6D_6 75°	**6** 25°	**8** $CDCl_3$	**9**	**10**
1-H				4.98 *m*	5.10 *m*	4.98 *m*
2-H				2.22 *m*	2.24 *m*	2.24 *m*
2′-H					1.9 *m*	1.9 *m*
3-H				2.45 *m*	2.5 *ddd*	2.47 *ddd*
3′-H					1.9 *m*	1.9 *m*
5-H				4.84 *d* (*br*)		1.70 *d*(*br*)
6-H		5.28 *m*	5.33, 5.15 *dd*	5.44 *dd*	5.39 *dd*	5.61 *dd*
7-H				2.22 *m*	3.79 *dd*	2.79 *dd*
8-H				4.14 *dd* (*br*)	4.22 *dd* (*br*)	5.02 *dd* (*br*)
9α-H				2.45 *m*	2.66 *dd*	2.55 *dd*
9β-H				2.84 *d* (*br*)	3.05 *d* (*br*)	3.06 *d* (*br*)
11-H	—	—	—	2.59 *dq*	—	—
13-H	6.39 *s* (*br*)	6.38 *s* (*br*)	6.44, 6.38 *s* (*br*)	1.40 *d*	2.3 *m*	2.31 *m*
13′-H	5.94 *s* (*br*)	5.64 *s* (*br*)	5.67, 5.34 *s* (*br*)		1.9 *m*	1.90 *m*
14-H	1.72, 1.68	1.32 *s* (*br*)	1.63, 1.61,	1.50 *s* (*br*)	1.47 *s* (*br*)	1.58 *s*(*br*)
	1.61 *s* (*br*)		1.28, 1.26 *s* (*br*)	4.73 *d*	4.74 *d*	4.78 *d*
15-H				4.59 *d*	4.66 *d*	4.72 *d*
16-H						4.84 *ddd*
16′-H					4.70 *m*	4.7 *m*
OAc	2.10 *s*		1.83, 1.75, 1.71	2.09 *s*	2.10 *s*	2.11 *s*
	2.07 *s*		1.69 *s*	2.06 *s*	1.85 *s*	1.87 *s*

J (Hz): **6**: 5,6 = 7,8 = 10; **8**: 5,6 = 6,7 = 10; 7,8 = 9; 7,11 = 10; 8,9α = 10; 9α,9β = 12; 11,13 = 7; 15,15′ = 12; **9** and **10**: 5, 6 = 6, 7 = 10; 7, 8 = 9; 7, 11 = 10; 8,9α = 10; 9α,9β = 12.5; 13, 16 = 4; 13, 16′ = 13′, 16 = 10; 13′, 16′ = 8; 15, 15′ = 10; 16, 16′ = 18.

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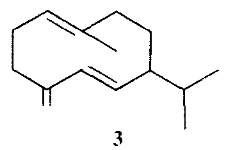
*Part 284 in the series "Naturally Occurring Terpene Derivatives". For Part 283 see Bohlmann, F., Zdero, C., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19**, 2381.

$Me[C \equiv C]_5CH = CH_2$

1

$MeCH = CH[C \equiv C]_4CH = CH_2$

2



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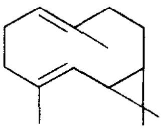

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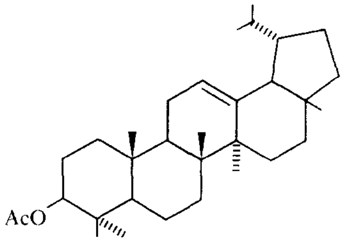

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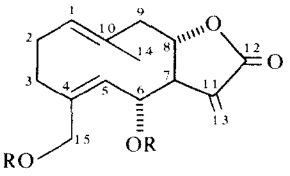
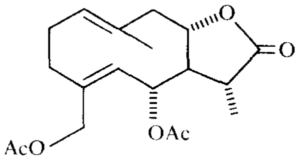
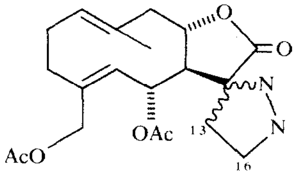


6 R = Ac
7 R = H



8



9 (α-adduct)
10 (β-adduct)

addition from the α-side was recognized by the downfield shift of the 7-H signal, caused by the deshielding effect of the azo group, while in the other isomer the 8β-H was slightly shifted downfield by the same group. Surprisingly the ^{1}H NMR spectrum of the 11,13-dihydro compound, obtained by sodium borohydride reduction, was very clear. Nearly all the signals were assigned (Table 1).

So far an 8,12-germacranolide has been isolated only from one *Vernonia* species [7], while lupeol and its derivatives, as well as the polyines **1** and **2**, are widespread in the tribe. Further investigations are necessary to establish relationships of the genus *Mattfeldanthus*.

EXPERIMENTAL

The air-dried plant material, collected in north-eastern Brazil, voucher RMK 8034, was chopped and extracted with Et_2O–petrol (1:2). The resulting extracts were first separated by CC (Si gel, act. grade II) and further by TLC (Si gel GF 254). Known compounds were identified by comparison of the IR and ^{1}H NMR spectra with those of authentic material. The roots (90 g) afforded 0.5 mg **1**, 80 mg polyisoprene, 20 mg lupeol, 200 mg lupeol acetate, and 100 mg **5**, while the aerial parts (800 g) gave 0.5 mg **2**, 10 mg **3**, 15 mg **4**, 8 mg lupeol, 100 mg lupeol acetate and 100 mg 6 (Et_2O–petrol, 3:1).

Artemisiifolin diacetate (**6**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770, 1660 (methylene lactone), 1745, 1235 (OAc); MS: M$^+$ *m/e* (rel. int.): 348.157 (M$^+$, 8%) ($C_{19}H_{24}O_6$); 306 (1, M − ketene); 288 (2, M − HOAc); 228 (71, 288 − HOAc); 43 (100, MeCO$^+$).

10 mg **6** in 1 ml MeOH were reduced with 20 mg $NaBH_4$. After 5 min dil H_2SO_4 was added. TLC (Et_2O–petrol, 3:1) afforded 5 mg **8**, colourless gum; ^{1}H NMR (see Table 1). To 20 mg **6** in 2 ml Et_2O excess ethereal CH_2N_2 soln was added. The crystalline pyrazoline mixture (**9** and **10**, *ca* 1:2) was separated by TLC (Et_2O–$CHCl_3$, 1:1). The less polar fraction afforded colourless crystals (**10**), mp 157° (decomp.) (lit. [5,6] 155–157°); ^{1}H NMR (see Table 1). The polar fractions afforded colourless plates (**9**), mp 157° (decomp.).

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