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GERMACRANOLIDES FROM *PROTEOPSIS ARGENTEA**

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Key Word Index—*Proteopsis argentea*; Compositae; sesquiterpene lactones; goyazensolanolide; eremantholanolides.

Abstract—*Proteopsis argentea* (tribe Vernonieae) afforded in addition to known compounds three new sesquiterpene lactones, closely related to those isolated from *Eremanthus* species, indicating a close relationship between these genera.

INTRODUCTION

Representatives of the small Brazilian genus *Proteopsis* have not previously been investigated chemically. Therefore, we have studied the constituents of *P. argentea* Mart. ex Zucc. to see if there is any phytochemical relationship to other genera of the tribe Vernonieae. In addition to widespread polyacetylenes, triterpenes and the angelate **5**, three new sesquiterpene lactones were isolated, a goyazensanolide and two eremantholanolides.

RESULTS AND DISCUSSION

The aerial parts of *P. argentea* afforded, in addition to large amounts of polyisoprene, lupeol, lupenone, lupeyl acetate, its isomers **3** and **4** [1], traces of **1** and **2** and **5** [2], three further sesquiterpene lactones, 6α-[2,3-epoxybutyryloxy]-goyazensolanolide (**6**), 16-[1-methylprop-1*Z*-enyl]-eremantholanolide (**7**) and 16-[1-methyl-1,2-epoxypropyl]-eremantholanolide (**8**). The structures clearly followed from their ^{1}H NMR data (Table 1), which were very similar to those of already known compounds of these types [2–7]. Compound **6** was the epoxide of the angelate **5**, consequently the angelate signals were replaced by the typical epoxybutyrate signals (2.99 *q*, 1.26 *d* and 1.45 *s*). Compound **7** was the *Z*-isomer of the corresponding lactone isolated from *Eremanthus bicolor* [2]. The corresponding signals of the side chain protons were clearly different due to the influence of the deshielding effect of the 16-hydroxy group, while all the other signals were nearly identical with those of the *E*-isomer. Compound **8** was the epoxide of **7**, consequently the signals of the side chain protons had undergone typical shifts (3.48 *q*, 1.53 *d* and 1.51 *s*). Also the chemical shift of the epoxide proton was influenced by the deshielding effect of the 16-hydroxy group. The shifts of 7- and 9-H were also different from those of **7**, which supported the 16α-configuration of the side chain. Compounds **7** and **8** are obviously formed by reductive cyclization of the corresponding 8α-angelate and epoxybutyrate. This makes it rather remarkable that the 6α-ester can be isolated from the plant. However, the same observation was made within *Eremanthus* species.

The roots gave polyisoprene, lupeyl acetate and also compounds **1**–**7**.

Table 1. ^{1}H NMR spectral data of compounds **6**–**8** (270 MHz, $CDCl_3$, TMS as internal standard)

	6	**7**	**8**
2-H	5.72 *s*	5.62 *s*	5.61 *s*
5-H	5.99 *dq*	6.04 *dq*	6.02 *dq*
6-H	5.20 *ddq*	4.98 *ddq*	4.99 *ddq*
7-H	3.82 *dddd*	2.80 *dd*	2.87 *dd*
8-H	4.56 *ddd*	4.12 *ddd*	4.10 *ddd*
9α-H	2.49 *dd*	2.01 *dd*	1.96 *dd*
9β-H	2.27 *dd*	2.54 *dd*	2.50 *dd*
13-H	6.35 *d*	1.23 *s*	1.34 *s*
13′-H	5.57 *d*		
14-H	1.53 *s*	1.45 *s*	1.50 *s*
15-H	2.08 *dd*	2.05 *dd*	2.06 *dd*
R	—	5.59 *qq*	3.48 *q*
	—	1.78 *dq*	1.53 *d*
	—	1.85 *dq*	1.51 *s*
OCOR	2.99 *q*	—	—
	1.26 *d*	—	—
	1.45 *s*	—	—
OH	—	3.90 *s*	3.89 *s*

J (Hz): Compound **6**: 5, 6 = 3; 5, 15 = 1.7; 6, 7 = 5; 6, 15 = 2.5; 7, 8 = 2.5; 7, 13 = 3.2; 7, 13′ = 2.8; 8, 9α = 12; 8, 9β = 2; 9α, 9β = 14; OCOR: 3′, 4′ = 5.5; compounds **7**/**8**: 5, 6 = 2; 5, 15 = 1.5; 6, 7 = 7; 6, 15 = 2; 7, 8 = 8; 8, 9α = 12; 8, 9β = 2.5; 9α, 9β = 14; R (**7**): 3′, 4′ = 7; 3′, 5′ = 4′, 5 = 1.5; (**8**): 3′, 4′ = 5.5.

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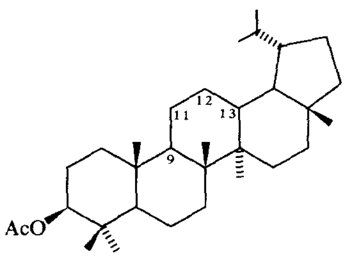
* Part 312 in the series 'Naturally Occurring Terpene Derivatives'. For Part 311 see Bohlmann, F., Ahmed, M., Jakupovic, J. and Jeffrey, C. (1981) *Phytochemistry* **20**, 251.

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

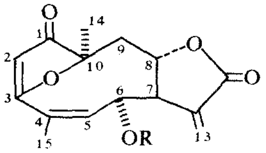
1

$Me\,CH{=}CH[C{\equiv}C]_4CH{=}CH_2$

2

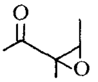


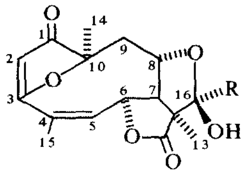
3 Δ9, 11
4 Δ12, 13



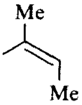
5 R = Ang

6 R =





7 R =



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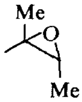

The chemistry of *Proteopsis argentea* indicated a close relationship of this genus to *Eremanthus*. Goyazensolanolides, however, were also reported from *Vanillosmopsis* [6], *Centratherum* [7] and *Lychnophora* [2]. Further investigations are necessary to obtain a clear picture of the chemical relationships in this taxonomically difficult tribe [8].

EXPERIMENTAL

The air-dried plant material (voucher RMK 8388, collected in north-eastern Brazil) was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated first by CC and further by repeated TLC (Si gel, GF 254). The aerial parts (1 kg) (extract treated first with MeOH to remove *ca* 3 g of polyisoprene) afforded 0.2 mg **1**, 0.2 mg **2**, 50 mg lupenone, 50 mg lupeyl acetate, 150 mg lupeol, 30 mg **3**, 20 mg **4**, 30 mg **5**, 20 mg **6** (Et_2O–petrol, 3:1), 100 mg **7** (Et_2O–petrol, 3:1) and 50 mg **8** (Et_2O–petrol, 3:1), while the roots (140 g) gave 100 mg polyisoprene, 1 mg **1**, 0.2 mg **2**, 50 mg lupeyl acetate, 25 mg **3**, 25 mg **4**, 2 mg **5**, 5 mg **6** and 3 mg **7**. Known compounds were identified by comparing the IR and NMR spectra with those of authentic material.

6α-[*2,3-Epoxybutyryloxy*]-*goyazensolanolide* (**6**). Colourless crystals (Et_2O–petrol) mp 168°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1785 (lactone), 1722 (CO, CO_2R), 1600 (C=COR); MS *m/e* (rel. int.): 374.137 (M^+, 100) ($C_{20}H_{22}O_7$), 259 (M − O_2CR, 9), 258 (M − RCO_2H, 8).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,\text{nm}}{-15.8 \quad -14.5 \quad -9.5 \quad +97.1 \quad +1035}$$

(c = 0.38, $CHCl_3$).

16α-[*1-Methylprop-1Z-enyl*]-*eremantholanolide* (**7**). Colourless crystals (Et_2O–petrol) mp 115°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1780 (lactone), 1710, 1585 (O=C—C=COR); MS *m/e* (rel. int.): 360.157 (M^+, 5), 342 (M − H_2O, 48), 83 ($C_4H_7CO^+$, 100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,\text{nm}}{-38.5 \quad -38.7 \quad -39.4 \quad +0.3 \quad +460.8}$$

(c = 2.6, $CHCl_3$).

16α-[*1-Methyl-1,2-epoxypropyl*]-*eremantholanolide* (**8**). Colourless crystals (Et_2O–petrol) mp 162.5°, IR $\nu_{max}^{CHCl_4}$ cm^{-1}: 3590 (OH), 1777 (lactone), 1710, 1590 (O=C C=COR); MS *m/e* (rel. int.): 376.153 (M^+, 18) ($C_{20}H_{24}O_7$), 358 (M − H_2O, 15), 332 (376 − CO_2, 31), 305 (M − C_4H_7O, 17), 95 ($C_5H_3O_2$, 100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,\text{nm}}{0 \quad +2.6 \quad +10.0 \quad +123.5 \quad +914.7}$$

(c = 0.34, $CHCl_3$).

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