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A EUDESMANOLIDE FROM *PLUCHEA DIOSCORIDIS**

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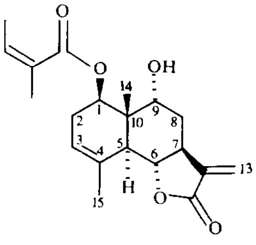
Key Word Index—*Pluchea dioscoridis*; Compositae; sesquiterpene lactones; eudesmanolides; 1β-angeloyloxy-9α-hydroxy-α-cyclocostunolide.

Abstract—From the aerial parts of *Pluchea dioscoridis* a new eudesmanolide was isolated and identified as 1β-angeloyloxy-9α-hydroxy-α-cyclocostunolide.

Pluchea dioscoridis (L.) DC. [= *Conyza dioscoridis* (L.) Desf.] is very common in Egypt. Previous work led to the isolation of a sesquiterpene lactone [1, 2], a thiophene acetylene [2], flavonoids [3] and sterols and triterpenes [4]. A reinvestigation of the aerial parts afforded in addition to **2** [2] a closely related lactone, the angelate **1**. The mass spectrum showed no molecular ion as the fragment *m/z* 246 resulted by the elimination of angelic acid. Accordingly *m/z* 328 was formed by elimination of water and the molecular formula was, therefore, most likely to be $C_{20}H_{26}O_5$. In agreement with this assumption the IR spectrum showed bands for a γ-lactone (1775 cm^{-1}) and for a hydrogen bonded unsaturated ester (3480, 1700, 1650 cm^{-1}). The ^1H NMR spectrum (Table 1) showed that an angelate was present. Spin decoupling allowed the assignment of all signals. Irradiation at δ3.11 (H-7, $CDCl_3$–C_6D_6) collapsed the typical methylene signals to singlets, the triplet at 3.73 to a doublet and the signals at δ2.00 and 1.61 to two- and three-fold doublets, respectively. The latter two signals showed in addition to a geminal coupling further ones due to a double triplet at δ3.45 which itself was coupled with a signal at δ4.04 which disappeared after deuterium exchange. The triplet at δ3.73 was coupled with a complex signal at δ2.81 which itself showed couplings with an olefinic signal and with two allylic ones (δ2.25 and 2.09) which were also coupled with the olefinic proton and with the olefinic methyl (δ1.84 *ddd*). The latter was also coupled with the allylic protons which were altered when



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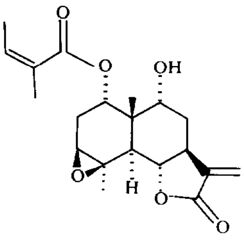

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Table 1. ^1H NMR spectral data of compounds **1** and **2** (400 MHz, TMS as internal standard)

	1		
	$CDCl_3$	$CDCl_3$–C_6D_6 (2:1)	**2** [$CDCl_3$–C_6D_6 (2:1)]
H-1	5.34 *dd*	5.26 *dd*	4.71 *br d*
H-2α	2.42 *br d*	2.25 *dddq*	2.17 *ddd*
H-2β	2.25 *m*	2.09 *dddq*	1.92 *ddd*
H-3	5.35 *br s*	5.19 *dddq*	2.60 *br d*
H-5	2.97 *br d*	2.81 *ddq*	2.80 *d*
H-6	3.98 *t*	3.73 *t*	3.64 *dd*
H-7	3.23 *ddddd*	3.11 *ddddd*	3.12 *ddddd*
H-8α	2.18 *ddd*	2.00 *ddd*	1.81 *ddd*
H-8β	1.87 *ddd*	1.61 *dddd*	1.51 *dddd*
H-9	3.60 *dt*	3.45 *dt*	3.61 *dt*
H-13	6.05 *d*	5.98 *d*	5.99 *d*
H-13′	5.36 *d*	5.13 *d*	5.12 *d*
H-14	0.92 *s*	0.78 *s*	1.05 *s*
H-15	1.87 *br s*	1.84 *ddd*	1.40 *s*
OH	4.15 *dd**	4.04 *dd**	3.00 *dd*
OAng	6.20 *qq*	6.02 *qq*	5.95 *qq*
	2.02 *dq*	1.93 *dq*	1.98 *dq*
	1.90 *dq*	1.81 *dq*	1.83 *dq*

*Exchangeable with D_2O.

J(Hz): Compound **1**: 1, 2α = 7.5; 1, 2β = 10; 2α, 2β = 18; 2α, 3 = 4.5; 2β, 3 = 2.5; 2α, 5 = 2β, 5 = 2α, 15 = 2β, 15 = 1.5; 3, 5 = 2.5; 3, 15 = 1.5; 5, 6 = 6, 7 = 11; 7, 8α = 3.5; 7, 8β = 12; 7, 13 = 3.5; 7, 13′ = 3; 8α, 8β = 14; 8α, 9 = 3.5; 8β, 9 = 3; 8β, OH = 1.5; 9, OH = 3; compound **2**: 1, 2α ~ 1; 1, 2β = 5; 2α, 2β = 17; 2α, 3 ~ 1; 2β, 3 = 3; 5, 6 = 11.5; 6, 7 = 11; 7, 8α = 3; 7, 8β = 12; 7, 13 = 3.3; 7, 13′ = 3.0; 8α, 8β = 14; 8α, 9 = 3; 8β, 9 = 3; 8β, OH = 2; 9, OH = 2; OAng: 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.5.

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*Part 467 in the series "Naturally Occurring Terpene Derivatives". For Part 466 see Bohlmann, F., Zdero, C., Jakupovic, J. and Greger, H. (1983) *Phytochemistry* **22**, 503.

the double doublet at δ 5.26 was irradiated. The chemical shift of the latter indicated that we were dealing with the proton under the angelate residue while the signal at δ 3.45 obviously had to be assigned to the proton under the hydroxyl group. Thus the whole sequence H-1 through H-9 was established.

The stereochemistry followed from the observed couplings. The angelate residue at C-1 was equatorial while the hydroxyl group at C-9 was axial as the couplings $J_{8,9}$ were both small. The presence of a hydrogen bridge between the hydroxyl group and the ester group led to an unusual double doublet for the hydroxy proton (δ 4.04). Spin decoupling showed that this signal was coupled with H-9 and H-8β. Inspection of a model showed that $J_{8\beta,\mathrm{OH}}$ was a *W* coupling. Also the small coupling $J_{9,\mathrm{OH}}$ agreed with the angle which was revealed by the model. It is interesting that the stereochemistry at C-1 is different in the two lactones. The ^{1}H NMR data of **2** are presented in Table 1. The nature of the chemical constituents of this species indicated that it cannot be placed in the genus *Conyza*, as no sesquiterpene lactones have been reported from this genus [5].

EXPERIMENTAL

The aerial parts (4 kg) of the plant collected near Alexandria were extracted by percolation with petrol (40–60°) and the extract was dissolved in 2 l. EtOH (95 %). The soln was separated from insoluble waxy material and the solvent evaporated. The residue was dissolved in 0.5 l. EtOH and gradually treated with 0.5 l. H_2O. Filtration gave 60 g insoluble material which was separated by CC (Si gel). Elution with EtOAc–petrol (1:5) gave 1.1 g **1**. The soln in EtOH–H_2O (1:1) was extracted with petrol and $CHCl_3$. The $CHCl_3$ soln after evaporation and recrystallization afforded 2.1 g **2**.

1β-Angeloyloxy-9α-hydroxy-α-cyclocostunolide (**1**). Colourless crystals, mp 122–123° (MeOH–petrol), IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 3480 (OH, hydrogen bonded), 1775 (γ-lactone), 1700, 1650 (C=CCO$_2$R, hydrogen bonded); MS *m/z* (rel. int.): 328.168 $[M-H_2O]^+$ (0.3) ($C_{20}H_{24}O_4$), 246 $[M-\mathrm{AngOH}]^+$ (31), 228 $[246-H_2O]^+$ (11), 213 $[228-\mathrm{Me}]^+$ (14), 83 $[C_4H_7CO]^+$ (58), 55 $[83-CO]^+$ (100).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\mathrm{nm}}{+190 \quad +200 \quad +229 \quad +406}\ (\mathrm{CHCl_3};\ c\ 1.67).$$

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TETRAHYDROLIGULARENOLIDE AND RELATED EREMOPHILANES FROM *SENECIO AUREUS*

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Key Word Index—*Senecio aureus*; Compositae; liferoot; eremophilanes; tetrahydroligularenolide; *trans*-9-oxofuranoeremophilane; ligularenolide; dehydrofukinone.

Abstract—An investigation of the eremophilane constituents of the medicinal herb, *Senecio aureus*, led to the isolation of tetrahydroligularenolide, furanoeremophilane, ligularenolide, and dehydrofukinone. Tetrahydroligularenolide has not been previously isolated as a natural product. While ligularenolide and dehydrofukinone are known compounds, they have not been previously reported as constituents of *S. aureus*.

Senecio aureus L. (golden ragweed, liferoot, squawweed), a perennial of the family Compositae, has been utilized as a pectoral, emmenagogue and a vulnerary by the peoples of Appalachia [1] and by Catawba Indian women to hasten labour during childbirth [2]. Despite the purported beneficial effects of this medicinal herb, a variety of toxic furanoeremophilanes [3] have been isolated from many species of the genus *Senecio*. Previous investigations [3, 4] of the eremophilane sesquiterpene constituents of *S. aureus* uncovered several furanoeremophilanes, analogues of which have been found by Jennings [5] to be hepatotoxic agents in *Tetradymia glabrata*, a range plant toxic to livestock. The two groups of furanoeremophilanes reported are, however, completely exclusive. This