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EUDESMANOLIDES FROM *DIMEROSTEMMA LIPPIOIDES**

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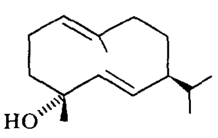
Key Word Index—*Dimerostemma lippioides*; Heliantheae; Compositae; sesquiterpene lactones; eudesmanolides.

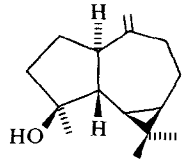
The Brazilian genus *Dimerostemma* is placed by Stuessy [1] in the subtribe Verbesininae (tribe Heliantheae, Compositae). So far nothing is known about the chemistry of this small genus.

We have now investigated *D. lippioides* (Baker) Blake. The aerial parts afforded germacrene D, α-humulene, bicyclogermacrene, 4α-hydroxygermacra-1(10),5-diene (**1**), spathulenol (**2**) and the isomeric acids **3** and **4**. The polar fractions gave three sesquiterpene lactones, the eudesmanolides **5**–**7**. The structures followed from the ^1H NMR data (Table 1), though **6** and **7** could not be separated even by HPLC. Compounds **5**–**7** are closely related to the β-cyclocostunolides from *Zexmenia phyllocephala* [2]. The small couplings of 1-H required an α-position of the ester residues, while the stereochemistry at C-5 through C-8 followed from the sequence of axial, axial-couplings. The presence of the 4,15-epoxide was deduced from the typical doublets in the spectrum of **6** at δ 3.42 and 2.44. The large difference in the chemical shifts of the epoxide protons and the chemical shift of the 10-methyl group favoured a β-epoxide. As could be seen from models one of the epoxide protons is deshielded by the lactone oxygen, while the 10-methyl group is deshielded by the epoxide oxygen. The relative position of the ester groups in **6** and **7** was supported by the differences in the chemical shifts of 6-, 7- and 8-H, which were typical for compounds with saturated and unsaturated ester groups. However, the signal of 1-H was identical in both compounds. We therefore assign the structures as **6** and **7**, though the relative position of the ester groups could not be established by partial saponification. The diol, which is derived from the esters **5**–**7**, we have named dimerostemmolide.

The roots afforded only bicyclogermacrene. The



1



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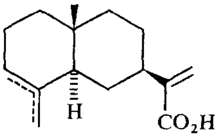
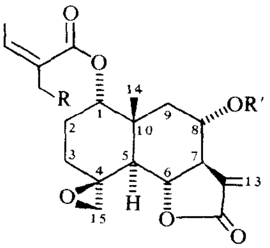


3 Δ4(15)
4 Δ3(4)



5 R = H, R′ = H
6 R = OH, R′ = Ang
7 R = OH, R′ = Mebu

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*Part 313 in the series 'Naturally Occurring Terpene Derivatives'. For Part 312 see: Bohlmann, F., Zdero, C., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 739.

Table 1. ^1H NMR spectral data of compounds **5**–**7** (270 MHz, TMS as internal standard)

	5($CDCl_3$)	**5**(C_6H_6)	**6**	($CDCl_3$)	**7**
1-H	4.86 *dd*	4.66 *dd*		4.95 *br. dd*	
3-H	2.30 *m*	2.15 *m*		2.25 *m*	
5-H	2.40 *d*	2.26 *d*	2.62 *d*		2.60 *d*
6-H	3.86 *dd*	3.32 *dd*	3.94 *dd*		3.91 *dd*
7-H	2.51 *dddd*	2.15 *m*	2.80 *dddd*		2.76 *dddd*
8-H	3.98 *ddd*	3.43 *ddd*	5.28 *ddd*		5.21 *ddd*
9-H	1.88 *m*	1.7 *m*	1.90 *dd*		1.84 *dd*
9'-H				1.70 *m*	
13-H	6.15 *d*	6.23 *d*		6.12 *d*	
13'-H	5.97 *d*	6.02 *d*	5.55 *d*		5.54 *d*
14-H	1.12 *s*	0.33 *s*	1.31 *s*		1.29 *s*
15-H	3.21 *br. d*	2.48 *dd*	3.43 *d*		3.42 *d*
15'-H	2.89 *d*	2.09 *d*	2.45 *d*		2.44 *d*
OCOR	6.19 *qq*	5.79 *qq*		6.43 *br. q*	
	2.06 *dq*	2.00 *dq*		2.13 *br. d*	
	1.99 *dq*	1.80 *dq*		4.32 *br. s*	
OCOR'	—	—	6.17 *qq*		2.38 *tq*
			2.00 *dq*		1.70 *m*
			1.88 *dq*		1.49 *ddq*
					0.91 *t*
					1.15 *d*
OH	4.14 *s*	4.11 *s*			

J (Hz): 1, 2 ~ 3; 5, 6 = 11; 6, 7 = 11; 7, 8 = 8, 9 = 10; 7, 13 = 3.2; 7, 13' = 2.8; 8, 9' = 4.5; 9, 9' = 13.5; 15, 15' = 5; OAng: 3', 4' = 7; 3', 5' = 1; O-Mebu: 2', 3' = 2', 5' = 7; $3'_1$, $3'_2$ = 14.

isolation of **3**–**7** supported the placement of this genus in the subtribe Verbesininae as eudesmane derivatives are common in representatives of this tribe, though eudesmanolides are rare. They are reported only from *Zexmenia* [2], *Podanthus* [3] and *Steiractinia* [4]. Different kinds of lactones were isolated from a few species belonging to Verbesininae [5].

EXPERIMENTAL

The air-dried plant material (collected in north eastern Brazil, voucher RMK 8224) was extracted with Et_2O–petrol and the resulting extract was separated first by CC (Si gel, act. grade II) and further by repeated TLC (Si gel). Known compounds were identified by comparing their IR and ^1H NMR spectra with those of authentic samples. The roots (50 g) afforded 10 mg bicyclogermacrene and the aerial parts (460 g) 95 mg germacrene D, 5 mg α-humulene, 65 mg bicyclogermacrene, 24 mg **1**, 18 mg, **2**, 10 mg **3**, 10 mg **4**, 4 mg **5** (Et_2O–petrol, 3:1) and 45 mg **6** and **7** (*ca* 2:3) (Et_2O–petrol, 3:1).

*Dimerostemmolide-*1*-angelate* (**5**). Not completely pure colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3460 (OH), 1780 (γ-lactone), 1725 ($C{=}CCO_2R$); MS *m/e* (rel. int.): 262.120 ($M - C_4H_7CO_2H$, 3) ($C_{15}H_{18}O_4$), 83 ($C_4H_7CO^+$, 100), 55 (83 – CO, 95); CI (isobutane): 363 (M + 1, 11), 263 ($M + 1 - RCO_2H$, 16), 245 ($263 - H_2O$, 24), 101 ($C_4H_7CO_2H + 1$, 100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+10.0 \quad +12.5 \quad +15.0 \quad +16.7} (c = 0.12,\ CHCl_3).$$

*8-O-Angeloyl- and [2-methylbutyryl]-dimerostemmolide-*1*-[5-hydroxyangelate]* (**6** *and* **7**). Colourless gum which could not be separated by TLC or HPLC, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1785 (γ-lactone), 1740 (CO_2R), 1725, 1655 ($C{=}CCO_2R$); MS *m/e* (rel. int.): 360 ($M - C_4H_7CO_2H$, $C_4H_9CO_2H$), 244.110 ($360 - RCO_2H$, 24) ($C_{15}H_{16}O_3$), 99 ($MeCH{=}C(CH_2OH)CO^+$, 38), 83 ($C_4H_7CO^+$, 82), 55 (83 – CO, 100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+125.6 \quad +131.2 \quad +149.6 \quad +256.7}$$

($c = 1.1$, $CHCl_3$).

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