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GUAIANOLIDES FROM *ELEPHANTOPUS CAROLINIANUS*

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Key Word Index—*Elephantopus carolinianus*; Compositae; sesquiterpene lactones; guaianolides.

Abstract—The roots of *Elephantopus carolinianus* afforded two guaianolides as well as two known elephantopin derivatives which were the main constituents of the aerial parts.

From *Elephantopus carolinianus* Willd., the presence of desoxyelephantopin, a type of sesquiterpene lactone which seems to be characteristic for this genus [1–8], has been reported [1]. Re-investigation of the aerial parts afforded, in addition to desoxyelephantopin [5], the C-1-epimer isodesoxyelephantopin [4] as evidenced from the ^{1}H NMR spectrum. The roots also contained minute amounts of these lactones and two further sesquiterpene lactones, the guaianolides **1** and **2**. The structures followed from the ^{1}H NMR spectra (Table 1) which were close to those of similar lactones [9–12]. The nature of the ester side chain at C-8 was deduced from the splitting and the chemical shifts of the corresponding signals. The stereochemistry was identical to that of 8β-acyloxypreeupatundin [10] and 5-desoxyeuparotin derivatives [10], respectively, as followed from the couplings observed. The presence of an ω-coupling between H-9 and H-14 in the spectrum of **2** agreed with a 10α-epoxide [12].

EXPERIMENTAL

The air-dried plant material was extracted with Et_2O–petrol (1:2) at room temp. The polar CC fractions of the extract (Et_2O and Et_2O–MeOH, 10:1) of the aerial parts (150 g) gave by TLC (SiO_2 PF 254; detection by UV 255 nm: Et_2O, two developments) 35 mg isodeoxyelephantopin and 43 mg deoxyelephantopin (increasing polarity); their ^{1}H NMR spectra agreed with those reported previously [4, 5]. Furthermore, the structure and stereochemistry were established by spin decoupling of the 400 MHz ^{1}H NMR spectra. The polar CC fractions (Et_2O and Et_2O–MeOH, 10:1) of the roots (5 g) afforded by repeated TLC (SiO_2 as above; Et_2O–petrol, 4:1) 1 mg **1** (R_f, 0.35), 1 mg isodeoxyelephantopin (R_f, 0.5), a mixture which gave by TLC (Et_2O–CH_2Cl_2–C_6H_6, 1:1:1) 1 mg deoxyelephantopin (R_f, 0.6) and 3.6 mg **2** (R_f, 0.55). Due to the minute amount, **1** and **2** could not be induced to crystallize although they were homogeneous by TLC in different solvent mixtures.

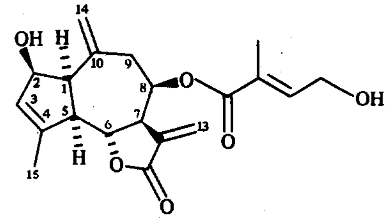
8β-[*4′-Hydroxytigloyloxy*]-*preeupatundin* (**1**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540 (OH), 1780 (γ-lactone), 1705 (C=CCO_2R); MS *m*/*z* (rel. int.): 342 $[M - H_2O]^+$ (2), 244.110 $[M - RCO_2H]^+$ (6) ($C_{15}H_{16}O_3$), 226 $[244 - H_2O]^+$ (21), 99 $[RCO]^+$ (72), 71 $[99 - CO]^+$ (90), 55 (100); CI (isobutane) 361 $[M + 1]^+$ (2), 245 $[361 - RCO_2H]^+$ (100). $[\alpha]_D \sim -15$, $CHCl_3$, $c = 0.1$.

8β-[*4′-Hydroxytigloyloxy*]-*5-desoxy-8-desacyleuparotin* (**2**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540 (OH), 1780 (γ-lactone), 1705 (C=CCO_2R); MS *m*/*z* (rel. int.): 260.105 $[M - RCO_2H]^+$ (3) ($C_{15}H_{16}O_4$), 242 $[260 - H_2O]^+$ (6), 99 $[RCO]^+$ (44), 71 $[99 - CO]^+$ (4), 55 (100); CI (isobutane): 377 $[M + 1]^+$ (1), 261 $[377 - RCO_2H]^+$ (100).

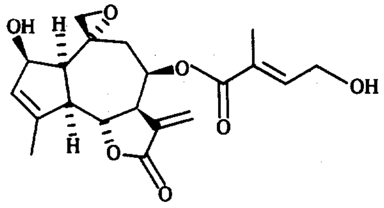
Table 1. ^{1}H NMR spectral data of compounds **1** and **2** (400 MHz, $CDCl_3$, TMS as internal standard)

	1	**2**
H-1	3.20 *m*	2.06 *m*
H-2	4.73 *d br*	4.83 *s br*
H-3	5.72 *s br*	5.75 *s br*
H-5	2.67 *dd br*	2.66 *dd br*
H-6	4.65 *dd*	4.75 *dd*
H-7	3.20 *m*	3.22 *dddd*
H-8	5.53 *ddd*	5.57 *ddd*
H-9	2.86 *dd br*	2.94 *dd br*
H-9′	2.75 *dd br*	2.06 *m*
H-13	6.29 *d*	6.34 *d*
H-13′	5.50 *d*	5.55 *d*
H-14	5.12 *s br*	2.80 *d*
H-14′	5.10 *s br*	2.75 *dd*
H-15	1.99 *s br*	2.02 *s br*
OCOR	6.70 *tq*	6.71 *tq*
	4.32 *d br*	4.34 *d br*
	1.76 *dt*	1.78 *dt*

J (Hz): Compound **1**: 1, 2 = 6; 1, 5 = 8; 5, 6 = 10.5; 6, 7 = 9; 7, 8 = 4; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 7; 8, 9′ = 7.5; 9, 9′ = 14; compound **2**: 1, 2 = 6; 1, 5 = 8.5; 5, 6 = 10.5; 6, 7 = 8.5; 7, 8 = 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 8; 9, 9′ = 14; 9, 14 = 1; 14, 14′ = 5; OCOR: 3′, 4′ = 6; 3′, 5′ = 4′, 5′ = 1.



1



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A GERMACRANOLIDE FROM *CYATHOCLINE LUTEA*

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Key Word Index—*Cyathocline lutea*; *C. lyrata*; Compositae; Astereae; sesquiterpene lactones; germacranolides; 5β-hydroxy-4,9-oxidogermacr-11-en-6,12-olide.

Abstract—While *Cyathocline lyrata* only afforded known compounds, the aerial parts of *C. lutea* gave a new sesquiterpene lactone, 5β-hydroxy-4,9-oxidogermacr-11-en-6,12-olide.

Two species of the small genus *Cyathocline* have been investigated chemically. While only the volatile compounds from *C. lyrata* D. Don have been studied so far [1, 2], *C. purpurea* Kuntze afforded a eudesmanolide and a guaianolide [3]. We have now studied again the aerial parts of *C. lyrata*. In addition to thymohydroquinone dimethyl ether, 10-isobutyryloxy-8,9-epoxythymol isobutyrate, parthenolide [4] and balchanin [5] were isolated.

The polar fractions of the aerial parts of *C. lutea* Cass. afforded a crystalline compound of molecular formula $C_{15}H_{22}O_4$; its IR and ^1H NMR spectra clearly showed the presence of a methylene lactone. Furthermore, a hydroxyl group was indicated by the IR band, as well as by the result of acetylation and oxidation, which led to the formation of a monoacetate and a ketone, respectively. Catalytic hydrogenation gave a dihydro derivative. While the signals at 60 and 90 MHz could only be partly