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THE FIRST ACETYLENIC MONOTERPENE AND OTHER CONSTITUENTS FROM *SENECIO CLEVELANDII**

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Key Word Index—*Senecio clevelandii*; Compositae; monoterpenes; acetylenes; acetylenic monoterpene lactone; tetrahydroquinol ester.

Abstract—The aerial parts of *Senecio clevelandii* afforded three new monoterpene lactones, one of them being the first acetylenic monoterpene to be isolated, a C-14 acetylenic angelate, a tetrahydroquinol ester and several known compounds, among them the tricyclic precursor of the polycyclopentanoide sesquiterpenes.

INTRODUCTION

In continuation of our investigation of the large genus *Senecio* [1], we have studied the constituents of *Senecio clevelandii* Greene. In addition to several known compounds, 3 new monoterpene lactones, an acetylenic angelate and the tetrahydro derivative of a widespread quinol ester were isolated. No furanoeremophilanes, however, were detected.

RESULTS AND DISCUSSION

The aerial parts of *S. clevelandii*, collected in California, afforded caryophyllene, α- and γ-humulene, sitosterol, the quinol ester **1** [2] and the corresponding tetrahydro derivative **3**, the structure of which followed from the ^1H NMR data (Table 1), especially when it was compared with those of **4** (obtained by hydrogenation of **2**) [2]. The main constituent was the precursor of the tricyclic sesquiterpene hydrocarbons, the alcohol **5** [3]. Furthermore, the dienyne **6** was isolated. Its structure followed from the UV and the ^1H NMR data (Table 2). Spin decoupling allowed the assignment of all signals, those of H-5 and H-6, however, were overlapped as usual. The stereochemistry of the double bonds was deduced from the couplings, only the configuration of the 5,6-double bond was assigned from the missing out-of-plane vibration of a *trans*-double bond and by the splitting pattern in the ^1H NMR spectrum, which was identical with that of similar authentic compounds. Furthermore, although H-5 and H-6 gave a still complex signal after irradiation of H-4, a 10-Hz coupling was visible. The fragmentation pattern in the MS of **6** also supported the structure. As usual, no elimination of angelic acid was visible. Instead of this *m/z* 218, formed by elimination of the corresponding ketene, was present. Also $M - {}^{\cdot}CH_2CHO$ and $-{}^{\cdot}CH_2CH_2CHO$ fragments were detected, as was the ion C_4H_7O (*m/z* 71). Chemical ionization led to formation of *m/z* 210 as the base peak, obviously formed from M + 1 by loss of angelic acid leading to a stable allylic ion. The polar fractions afforded three lactones, the monoterpenes **7**–**9**. While **7** and **8** could not be separated, **9**, the first acetylenic monoterpene to be

Table 1. ^1H NMR spectral data of compounds **3** and **4** ($CDCl_3$, 400 MHz, TMS as internal standard)

	3	4
H-2a, 6a	2.78 *ddd*	2.79 *ddd*
H-2e, 6e	2.24 *dddd*	2.23 *dddd*
H-3e, 5e	2.11 *dddd*	2.10 *dddd*
H-3a, 5a	1.75 *ddd*	1.77 *ddd*
H-7	2.50 *s*	2.56 *s*
OR	3.74 *s*	4.20 *q*
		1.29 *t*
OH	3.83 *s*	3.93 *s*

J (Hz): 2a,2e = 14; 2a,3a = 14; 2a,3e = 6; 2e,3a = 4.5; 2e,5e = 3e,6e = 2.5; 2e,3e = 2.5; 3a,3e = 13.

Table 2. ^1H NMR spectral data of compound **6** ($CDCl_3$, 400 MHz, TMS as internal standard)

H-1	9.79 *t*	H-11	6.51 *dd*
H-2	2.46 *dt*	H-12	6.30 *dd* (*br*)
H-3	1.72 *tt*	H-13	5.83 *dt*
H-4	2.12 *dt*	H-14	4.18 *d* (*br*)
H-5 H-6	5.46 *m*	OAng	6.07 *qq* 1.98 *dq* 1.90 *dq*
H-7	3.06 *d* (*br*)		
H-10	5.60 *dt* (*br*)		

J (Hz): 1,2 = 1.5; 2,3 = 7.5; 3,4 = 7; 4,5 = 7; 6,7 = 6; 7,10 = 2; 10,11 = 15; 11,12 = 11; 12,13 = 15.5; 13,14 = 6; 3′,4′ = 7; 3′,5′ = 4′,5′ = 1.5.

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*Part 367 in the series "Naturally Occurring Terpene Derivatives". For Part 366 see Bohlmann, F., Borthakur, A., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20** (in press).

isolated, was obtained crystalline. Again the structures followed from the spectroscopic data. The ^1H NMR data (Table 3) clearly indicated the presence of unsaturated butyrolactones, while the stereochemistry of the 4,5-double bond was deduced from the couplings in the spectrum of **7** and **8**. The presence of an acetylenic bond in **9** followed from the characteristic IR band at 2200 cm^{-1}. The MS of **8** and **9** were characteristically different. Thus whilst **8**, after loss of methyl, showed elimination of CO_2 (m/z 105), **9**, most probably, was directly transformed to **10** by loss of CH_2OCO. **9** we have named cleviolide.

The roots also gave caryophhllene, γ-humulene and the alcohol **5**.

The compounds isolated from *S. clevelandii* may be an indication that this species also belongs to the Eusenecioid group [1], as from this group so far no furanoeremophilanes, but **1**, **2** and small amounts of acetylenic compounds have been isolated. The co-occurrence of **8** and **9** as well as an usual acetylenic compound is of biogenetic interest, as this may support the assumption that the triple bond is formed by dehydrogenation of a *cis*-double bond [4].

Table 3. ^1H NMR spectral data of compounds **7**–**9** (400 MHz, TMS as internal standard)

	7 (C_6D_6/ $CDCl_3$)	**8** (C_6D_6/ $CDCl_3$)	**8** ($CDCl_3$)	**9** ($CDCl_3$)
H-2	5.53 *s* (*br*)	5.70 *s* (*br*)	5.87 *s* (*br*)	6.10 *t*
H-4	5.83 *d* (*br*)	5.46 *d* (*br*)	5.87 *d* (*br*)	—
H-5	6.27 *dd*	6.28 *dd*	6.58 *dd*	—
H-6	5.70 *d* (*br*)	5.74 *d* (*br*)	5.98 *d* (*br*)	5.99 *s* (*br*)
H-8	1.64 *s* (*br*)	1.60 *s* (*br*)	1.92 *s* (*br*)	1.96 *s* (*br*)
H-9	1.54 *s* (*br*)	1.52 *s* (*br*)	1.87 *s* (*br*)	1.91 *s* (*br*)
H-10	4.29 *d* (*br*)	4.36 *d*	5.01 *d*	4.80 *d*

J (Hz): 2,10 = 1.5; 4,5 = 15 (compound **8**: 11.5); 5,6 = 11 (compound **8**: 11.5).

EXPERIMENTAL

The air-dried plant material (voucher RMK 8422) was extracted with Et_2O–petrol (1:2) and the resulting extracts were first separated by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparison of their IR and ^1H NMR spectra with those of authentic material. The aerial parts (500 g) afforded 50 mg caryophyllene, 5 mg α- and 5 mg γ-humulene, 3 mg sitosterol, 10 mg **1**, 2 mg **3** (Et_2O–petrol, 1:3), 50 mg **5**, 5 mg **6** (Et_2O–petrol, 1:1), 1 mg **7** and 3 mg **8** (Et_2O–petrol, 1:1, not sepd) and 3 mg **9** (Et_2O–petrol, 1:1), while the roots (130 g) gave 30 mg caryophyllene, 5 mg γ-humulene and 40 mg **5**.

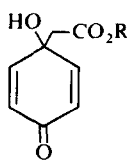
4-[*Carbomethoxymethyl*]-4-*hydroxycyclohexanone* (**3**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3510 (OH, hydrogen-bonded), 1720 (C=C, CO_2R); MS m/z (rel. int.): 186.089 (M^+, 6) ($C_9H_{14}O_4$), 168 ($M - H_2O$, 100), 154 (M − MeOH, 24), 140 (168 − CO, 30), 129 ($M - CH_2CH_2CHO$, 30), 126 (154 − CO, 27), 112 (154 − ketene, 80), 98 (126 − CO, 95).

Preparation of **4**. 30 mg **2** in 5 ml Et_2O were hydrogenated in the presence of 20 mg $Pd/BaSO_4$ (5 %) to give 30 mg **4**, colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3510 (OH), 1720 (C=O, CO_2R); MS m/z (rel. int.): 200.105 (M^+, 4), 182 ($M - H_2O$, 71), 154 (M − EtOH, 41), 143 ($M - CH_2CH_2CHO$, 63), 112 (154–ketene, 100).

14-*Angeloyloxy-tetradeca*-5c,10t,12t-*trien*-8-*yn*-1-*al* (**6**). Colourless oil, UV $\lambda_{max}^{Et_2O}$: 277, 266; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2200 (C≡C), 1730 ($C{=}CCO_2R$, CHO), 1630, 990 [*t*, *t*-$(CH{=}CH)_2$—]; MS m/z (rel. int): 300.173 (M^+, 2) ($C_{19}H_{24}O_3$), 257 ($M - CH_2CHO$, 1), 229 [$M - (CH_2)_3CHO$, 1], 218 [$M - O{=}C(Me){=}CH{-}CH{=}CO_2$, 5], 178 ($218 - CH_2O$, 6), 83 ($C_4H_7CO^+$, 100), 71 ($C_4H_7O$, 40), 55 (83 − CO, 71); CIMS (isobutane): 301 (M + 1, 4), 201 (M + 1 − AngOH, 100), 173 (201 − CO, 14).

4-Trans- *and* cis-4,5-*dihydrocleviolide* (**7** *and* **8**). Not sepd. Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1785, 1760 (γ-lactone), 1630, 1620 (C=C); MS m/z (rel. int.): 164.083 (M^+, 81) ($C_{10}H_{12}O_2$), 149 (M − Me, 8), 121 (149 − CO, 39), 105 ($149 - CO_2$, 100).

Cleviolide (**9**). Colourless crystals, mp 64° (petrol), UV $\lambda_{max}^{Et_2O}$ nm: 292; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2200 (C≡C), 1780, 1745 (γ-



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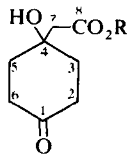
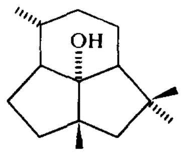
2 R = Et



3 R = Me

4 R = Et



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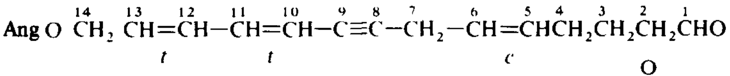
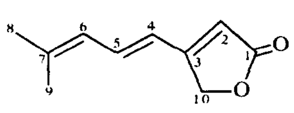


$$\mathrm{Ang\,O}\ \overset{14}{\mathrm{C}}\mathrm{H_2}\ \underset{t}{\overset{13}{\mathrm{C}}\mathrm{H}{=}\overset{12}{\mathrm{C}}\mathrm{H}}{-}\underset{t}{\overset{11}{\mathrm{C}}\mathrm{H}{=}\overset{10}{\mathrm{C}}\mathrm{H}}{-}\overset{9}{\mathrm{C}}{\equiv}\overset{8}{\mathrm{C}}{-}\overset{7}{\mathrm{C}}\mathrm{H_2}{-}\underset{c}{\overset{6}{\mathrm{C}}\mathrm{H}{=}\overset{5}{\mathrm{C}}\mathrm{H}}\overset{4}{\mathrm{C}}\mathrm{H_2}\overset{3}{\mathrm{C}}\mathrm{H_2}\overset{2}{\mathrm{C}}\mathrm{H_2}\overset{1}{\mathrm{C}}\mathrm{HO}$$

6



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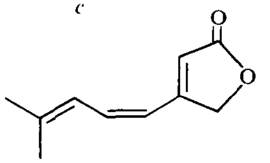

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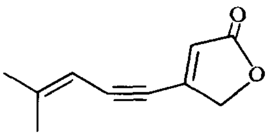

9

$$\mathbf{8}\quad m/z\ 164 \xrightarrow{-CO_2\ -Me} m/z\ 105$$

$$\mathbf{9}\quad m/z\ 162 \xrightarrow{-CH_2OCO} Me_2C{=}CH[C{\equiv}C]_2H^{+\cdot}$$

m/z 104 **10**

lactone), 1600 (C=C); MS m/z (rel. int.): 162.068 (M^+, 100) ($C_{10}H_{10}O_2$), 133 (M − CHO, 18), 104.060 (M − CH_2OCO, 68) (C_8H_8).

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A GUAIANOLIDE FROM *CENTAUREA BEHEN**

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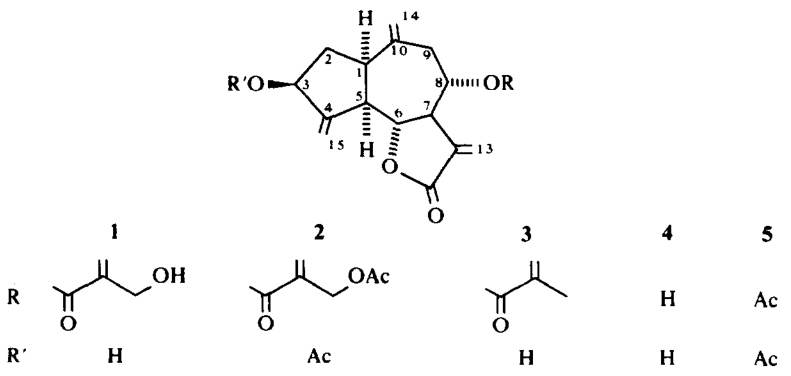
Key Word Index—*Centaurea behen*; Compositae; sesquiterpene lactones; guaianolides.

Abstract—The aerial parts of *Centaurea behen* afforded in addition to known lactones a new derivative of solstitialin A.



Centaurea behen L., native in Iran, had not been investigated chemically. The aerial parts of this plant afforded several sesquiterpene lactones, the guaianolides cynaropicrin (**1**) [1], arguerin B (**3**) [2], desacylcynaropicrin (**4**) [3], grosshemin (**6**) [4] and minor amounts of the ketone **8**, which is closely related to solstitialin A, the absolute configuration of which had been established [5]. **8** could only be isolated as its diacetate **9**, which still was mixed with the acetate of **6**. The latter, however, could be separated from **9** after transformation to the corresponding pyrazoline derivative. The structures of **1**, the corresponding diacetate **2**, **3**, **4** and **6** were elucidated by their ^1H NMR data, which are presented in part in Table 1, as good spectra are not available in the literature. The structure of **8** also followed from the ^1H NMR data of the corresponding diacetate **9** (Table 1). At 400 MHz in C_6D_6 all signals could be assigned by careful spin decoupling. Starting with the methyl doublet at δ 1.28 H-4 was assigned. H-4 was coupled with a signal at δ 2.12 which was assigned to H-5, as it also was coupled with the proton under the lactone oxygen. H-4 further showed a *W*-coupling with the three-fold doublet at δ 2.13, which obviously was the H-2 β-signal, as it was further coupled with a proton, which also was coupled with H-5. Finally, by further decoupling all signals could be assigned. The

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*Part 352 in the series "Naturally Occurring Terpene Derivatives". For Part 351 see Bohlmann, F., Zdero, C. and Gupta, R. K. (1981) *Phytochemistry* **20**, 2024.