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GUAIANOLIDES FROM *ACROPTILON REPENS**

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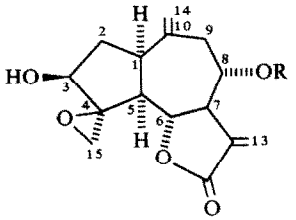
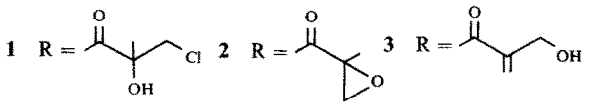
Key Word Index—*Acroptilon repens*; Compositae; Cynareae; sesquiterpene lactones; guaianolides.

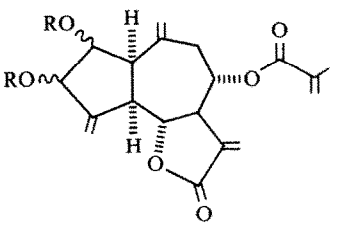
Abstract—Two new guaianolides have been isolated from the aerial parts of *Acroptilon repens*.

The aerial part of *A. repens* DC (*Centaurea picris*) has been investigated several times [1]. Two guaianolides were isolated, chlorohyssopifolin C (**1**) [1] and repin (**2**) [2]. A reinvestigation afforded, in addition to these lactones, janerin (**3**) [3], chlorohyssopifolin A (**4**) [4] and two other lactones, which are the closely related guaianolides **5** and **7**. The structures followed from the ^{1}H NMR data (Table 1), especially if compared with those of **2**–**4**. Acetylation of **5** gave the diacetate **6**, its ^{1}H NMR data (Table 1) showed that the stereochemistry at C-5 through C-8 was the same as that of **1**–**4**, while the presence of a C-4 methylene group was indicated by two broadened signals at δ 5.68 and 5.43 in the spectrum of **5**. Spin decoupling showed that the two hydroxyls were at C-2 and C-3. However, the stereochemistry could not be assigned with certainty. Inspection of models showed that the observed coupling $J_{2,3}$ would be in agreement with *cis* and *trans* positioned hydroxyls. The large coupling $J_{1,2}$ may be an indication of a 2α-hydroxy group. The ^{1}H NMR data of **7** again showed identical stereochemistry at C-5 through C-8, while the orientation of the hydroxyls at C-3 and C-4 again could not be determined with certainty. The downfield shift of the H-6 signal may indicate a 4β-hydroxyl. The presence of a hydroxymethacrylate followed from the ^{1}H NMR data. Due to the small amounts of material no further transformations were possible. We have named compound **7** acrorepiolide. Obviously all guaianolides present in this plant are closely related. Probably 8α-methacryloyloxydehydrocostuslactone is the common precursor. The different stereochemistry at C-3 and C-4 reported for **1**–**4**, however, is surprising.

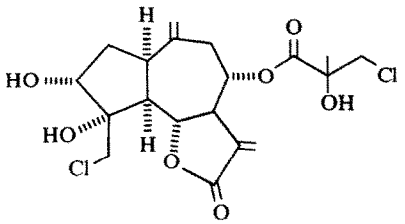




1 R = **2** R = **3** R =



5 R = H
6 R = Ac



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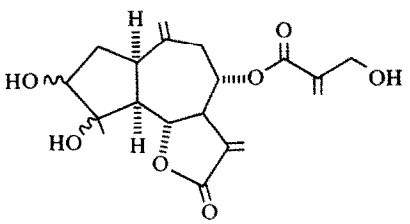

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* Part 329 in the series "Naturally Occurring Terpene Derivatives". For Part 328 see Bohlmann, F., Müller, L., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 1149.

Table 1. ^{1}H NMR spectral data of compounds **2**–**7** (TMS as int. stand., $CDCl_3$)

	2	3	4	5	6	7
H-1	3.33 *ddd*	3.37 *ddd*	3.44 *ddd*	2.81 *dd*	3.01 *m*	3.34 *ddd*
H-2α	1.83 *ddd*	1.83 *ddd*	1.64 *ddd*	3.80 *dd*	5.37 *dd*	1.73 *ddd*
H-2β	2.47 *ddd*	2.47 *ddd*	2.48 *ddd*			2.79 *ddd*
H-3	3.95 *dd*	3.98 *dd*	4.16 *dd*	4.32 *brd*	5.66 *d*	4.19 *dd*
H-5	2.07 *dd*	2.08 *dd*	2.31 *dd*	3.01 *brdd*	3.01 *m*	2.01 *dd*
H-6	4.60 *dd*	4.65 *dd*	4.66 *dd*	4.22 *dd*	4.25 *dd*	4.59 *dd*
H-7	3.05 *dddd*	3.12 *dddd*	3.15 *dddd*	3.21 *dddd*	3.18 *dddd*	3.18 *dddd*
H-8	5.03 *ddd*	5.18 *ddd*	5.20 *ddd*	5.12 *ddd*	5.15 *ddd*	5.10 *dd*
H-9α	2.38 *dd*	2.44 *dd*	2.40 *dd*	2.50 *brs*	2.47 *dd*	2.34 *dd*
H-9β	2.78 *dd*	2.78 *dd*	2.75 *dd*		2.73 *dd*	2.79 *dd*
H-13	6.24 *d*	6.21 *d*	6.24 *d*	6.23 *d*	6.24 *d*	6.24 *d*
H-13′	5.73 *d*	5.61 *d*	5.63 *d*	5.62 *d*	5.63 *d*	5.67 *d*
H-14	5.19 *brs*	5.20 *brs*	5.17 *brs*	5.22 *brs*	5.14 *brs*	5.17 *brs*
H-14′	4.94 *brs*	4.97 *brs*	5.07 *brs*	5.03 *brs*	4.97 *brs*	4.96 *brs*
H-15	3.32 *d*	3.34 *d*	3.87 *d*	5.68 *brs*	5.63 *brs*	1.42 *s*
H-15′	3.05 *d*	3.07 *d*	3.64 *d*	5.43 *brs*	5.33 *brs*	
OCOR	3.17 *d*	6.34 *brs*	4.02 *d*	6.20 *brs*	6.13 *brs*	6.34 *brs*
	2.82 *d*	5.96 *brs*	3.98 *d*	5.69 *brs*	5.68 *brs*	5.97 *brs*
	1.61 *s*	4.39 *brs*	1.55 *s*	2.00 *brs*	2.00 *brs*	4.39 *brs*
OAc	—	—	—	—	2.13 *s*	
					2.02 *s*	

J (Hz): Compounds **2**/**3**: 1,2α = 7; 1,2β = 10; 1,5 = 8; 2α,2β = 15; 2α,3 = 7; 2β,3 = 4; 5,6 = 11; 6,7 = 9; 7,8 = 9; 7,13 = 3.5; 7,13′ = 3; 8,9α = 3.5; 8,9β = 5; 9α,9β = 15; 15,15′ = 4; 4′,4′ = 5; compound **4**: 1,2α = 9; 1,2β = 10; 1,5 = 9; 2α,2β = 14; 2α,3 = 6; 2β,3 = 3; 5,6 = 11; 6,7 = 9; 7,8 = 9; 7,13 = 3.5; 7,13′ = 3; 8,9α = 3.5; 8,9β = 5; 9α,9β = 15; 15,15′ = 11; 4′,4′ = 12; compounds **5**/**6**: 1,2α = 10; 1,5 = 10; 2,3 = 7.5; 5,6 = 10; 6,7 = 9; 7,8 = 9; 7,13 = 3.5; 7,13′ = 3; 8,9α = 3; 8,9β = 5; 9α,9β = 15; compound **7**: 1,2α = 7; 1,2β = 10; 1,5 = 8; 2α,2β = 15; 2α,3 = 7; 2β,3 = 4; 5,6 = 11; 6,7 = 9; 7,8 = 9; 7,13 = 3.5; 7,13′ = 3; 8,9α = 3; 8,9β = 5; 9α,9β = 15.

EXPERIMENTAL

The air dried aerial parts of *Acroptilon repens* (500 g) were collected north of Teheran and extracted with Et_2O. The resulting extract after removal of saturated hydrocarbons by treatment with MeOH was first separated by CC (Si gel) and further by repeated TLC (Si gel). With Et_2O–MeOH (20:1) **1**–**5** and **7** were eluted. Finally 120 mg **1**, 180 mg **2**, 30 mg **3**, 25 mg **4**, 25 mg **5** and 10 mg **7** were isolated. Compounds **1**–**4** had the same data as those reported in the lit. Their structures followed from the ^{1}H NMR data.

2,3-Dihydroxy-8α-methacryloyloxydehydrocostuslactone (**5**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1770 (γ-lactone), 1720 (C=CCO$_2$R); MS *m/z* (rel. int.): 346.143 (M$^+$, 8) ($C_{19}H_{22}O_6$), 328 (M − H_2O, 0.5), 260 (M − RCO_2H, 5), 242 (260 − H_2O, 9), 224 (242 − H_2O, 2), 69 ($C_3H_5CO^+$, 100). Compound **5** (10 mg) was heated for 4 hr with Ac_2O at 70°. TLC (Et_2O) afforded 10 mg **6**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1750 (OAc), 1715 (C=CCO$_2$R); MS *m/z* (rel. int.): 370 (M − AcOH, 2), 328 (370 − ketene, 22), 242 (328 − RCO_2H, 28), 69 ($C_3H_5CO^+$, 100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{+28 \quad +32 \quad +35 \quad +59} (c = 1.0, CHCl_3).$$

Acrorepiolide (**7**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1715 (C=CCO$_2$R); MS *m/z* (rel. int.): 364 (M$^+$, 0.5), 349.129 (M − Me, 16) ($C_{18}H_{21}O_7$), 332.126 (349 − OH, 12) ($C_{18}H_{20}O_6$), 265 (349 − $C_4H_4O_2$, 38), 85 (RCO$^+$, 100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{+16 \quad +19 \quad +25 \quad +29} (c = 1.0, CHCl_3).$$

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