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A PSEUDOGUAIANOLIDE AND A HYDROXYGERANYLNEROL FROM *KINGIANTHUS PARADOXUS**

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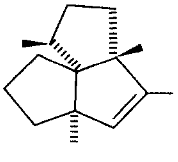
Key Word Index—*Kingianthus paradoxus*; Compositae; Heliantheae; sesquiterpene lactones; pseudoguaianolide; kingiolide; 20-hydroxygeranylnerol.

Abstract—Examination of *Kingianthus paradoxus* yielded kingiolide, a new pseudoguaianolide, and 20-hydroxygeranylnerol.

So far nothing is known about the chemistry of the new genus *Kingianthus* [1, 2] which is placed in the tribe Heliantheae (Compositae). To see whether the chemistry gives any indication of relationships to other parts of this large tribe, we have investigated *K. paradoxus* H. Robins. The aerial parts, collected in Ecuador, afforded α-pinene, germacrene D, germacrene B, α-humulene, phytol, isocomene (**1**), β-isocomene (**2**), lupenone, lupeol, lupeyl acetate and its isomer **3**, carabrone (**4**) [3] as the main constituent, helenalin (**5**) [4] and two further compounds, namely **6**, the hydroxymethacrylate of **5** and the diterpene diol **8**. The structure of **6** was deduced from the ^{1}H NMR data and those of the corresponding acetate **7**, obtained by heating with acetic anhydride (Table 1). The presence of a pseudoguaianolide structure, closely related to helenalin (**5**), was clear from the similarity of the ^{1}H NMR signals, except for the expected downfield shift of H-6. The similarity of the couplings of H-6 through H-9 further indicated the presence of an 8,12-lactone. In the ^{1}H NMR spectrum of **7** first-order interpretations of all signals were possible. We have named compound **6** kingiolide. The structure of the diterpene **8** also followed from the ^{1}H NMR data and those of the corresponding diacetate **9**, obtained by mild acetylation, as well as from those of the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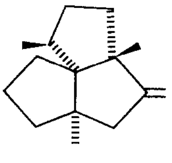
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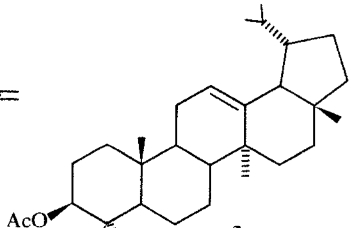

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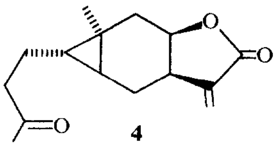
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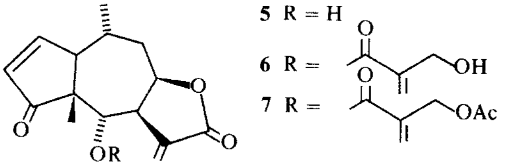
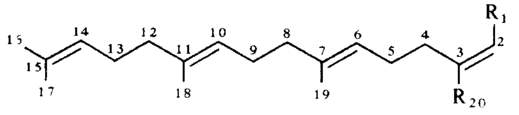


5 R = H
6 R =
7 R =



8 R = CH_2OH
9 R = CH_2OAc
10 R = CHO

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* Part 327 in series "Naturally Occurring Terpene Derivatives". For Part 326 see Bohlmann, F., Dhar, A. K., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 1144.

Table 1. ^1H NMR spectral data of compounds **6** and **7** (270 MHz, TMS as internal standard, $CDCl_3$)

	6	**7**
H-1	3.04 *ddd*	3.02 *ddd*
H-2	6.08 *dd*	6.08 *dd*
H-3	7.69 *dd*	7.68 *dd*
H-6	5.46 *br. d*	5.46 *br. d*
H-7	3.59 *dddd*	3.59 *dddd*
H-8	4.90 *ddd*	4.90 *ddd*
H-9	2.41 *ddd*	2.42 *ddd*
H-9′	1.75 *ddd*	1.74 *ddd*
H-10	2.19 *m*	2.19 *dddq*
H-13	6.42 *d*	6.48 *d*
H-13′	6.16 *d*	6.18 *d*
H-14	1.29 *d*	1.28 *d*
H-15	1.04 *s*	1.05 *s*
OCOR	6.05 *dt*	6.25 *dt*
	5.84 *q*	5.85 *q*
	4.27 *br. d*	4.70 *br. s*
OAc	—	2.08 *s*

J (Hz): 1, 2 = 2.7; 1, 3 = 1.8; 1, 10 = 11.5; 2, 3 = 6; 6, 7 = 1; 7, 8 = 7.5; 7, 13 = 3; 7, 13′ = 2.7; 8, 9 = 7.5; 8, 9′ = 2.5; 9, 9′ = 15; 9, 10 = 3.5; 9′, 10 = 8; 10, 14 = 7; 3′, 3′ = 3′, 4′ ~ 1; 4′, OH = 5.

dialdehyde **10**, obtained by manganese dioxide oxidation (Table 2). The stereochemistry of the 2,3-double bond was deduced from the shift differences of the signals for H-2 and H-4 in the spectra of **8** and **10** and the chemical shifts of H-1 and H-20 in the spectrum of **10**. Compound **8** has also been isolated from a *Disynaphia* species [5].

Carabrone (**4**) has been isolated from a *Monactis* species (F. Bohlmann *et al.*, unpublished results) indicating a relationship of this genus to *Kingianthus*. These groups are also taxonomically very close to each other [2]. However, the pseudoguaianolides are typical for the genera *Helenium*, *Gaillardia*, *Ambrosia*, *Arnica* and *Parthenium* [6], while these lactones have not so far been isolated from members of the subtribe Verbesininae. Relationships to *Zaluzania*, where *Kingianthus* was placed earlier [1], are not apparent.

EXPERIMENTAL

The air-dried plant material (voucher RMK 7813) was extracted with Et_2O–petrol (1:2) and the resulting extract was first separated by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the IR and ^1H NMR spectra with those of authentic material.

The hydrocarbons were identified by GC/MS. Compounds obtained were 1 mg α-pinene, 20 mg germacrene D, 30 mg germacrene B, 10 mg α-humulene, 50 mg lupenone, 2· mg lupeol, 50 mg lupeyl acetate, 20 mg phytol, 1 mg **1**, 1 mg **2**, 50 mg **3**, 250 mg **4**, 1 mg **5**, 65 mg **6** and 190 mg **8**.

Kingiolide (**6**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1760 (γ-lactone), 1715 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 346.142 (M^+, 1), 328 ($M - H_2O$, 0.5), 262 ($M - C_3H_4O_2$, 32), 244 ($M - RCO_2H$, 38), 85 (RCO^+, 100).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546\,\text{nm}}{-70.1 \quad -78.8 \quad -87.4} (c = 6.5).$$

Compound **6** (10 mg) in 0.1 ml Ac_2O was heated for 1 hr at 70°. TLC (Et_2O–petrol, 1:1) afforded 8 mg **7**, colourless gum; IR $\nu_{max}^{CCl_3}$ cm^{-1}: 1785 (γ-lactone), 1750, 1235 (OAc), 1720 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 388 (M^+, 3), 346 (M − ketene, 1), 329 (M − OAc, 1), 244 ($M - RCO_2H$, 24), 125 ($C_6H_5O_3$, 100).

20-*Hydroxygeranylnerol* (**8**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1630 (C=C); MS *m/z* (rel. int.): 306 (M^+, 0.5), 238.193 (M − isoprene, 6) ($C_{15}H_{26}O_2$), 220 ($238 - H_2O$, 15), 69 ($C_5H_9^+$, 100). Compound **8** (5 mg) in 0.1 ml Ac_2O was heated for

Table 2. ^1H NMR spectral data of compounds **8**–**10** (270 MHz, TMS as internal standard, $CDCl_3$)

	8	**9**	**9** (C_6D_6)	**10**
H-1	4.22 *br. d*	4.64 *br. d*	4.67 *br. d*	10.22 *d*
H-2	5.70 *br. t*	5.63 *br. t*	5.67 *br. t*	6.51 *d*
H-4, 5	2.07 *m*	2.15 *m*	2.22 *m*	2.73 *br. t* 2.22 *dt*
H-6	5.12 *br. t*	5.11 *br. t*	5.32 *tq*	5.10 *br. t*
H-8, 9	2.07 *m*	2.00 *m*	2.11 *m*	2.02 *m*
H-10	5.10 *br. t*	5.11 *br. t*	5.29 *tq*	5.10 *br. t*
H-12, 13	2.07 *m*	2.00 *m*	2.11 *m*	2.02 *m*
H-14	5.10 *br. t*	5.11 *br. t*	5.20 *tq*	5.10 *br. t*
H-16*	1.68 *br. s*	1.69 *br. s*	1.73 *br. s*	1.69 *br. s*
H-17 to H-19*	1.60 *br. s*	1.61 *br. s*	1.67 *br. s* 1.63 *br. s* 1.61 *br. s*	1.61 *br. s* 1.61 *br. s* 1.54 *br. s*
H-20	4.10 *br. s*	4.55 *br. s*	4.56 *br. s*	9.67 *s*
OAc	—	2.10 *s*	1.72 *s*	—
	—	2.08 *s*	1.70 *s*	—

*In C_6D_6: 1.73 *br. s*, 1.65 *br. s*, 1.61 *br. s*, 1.59 *br s*.

J (Hz): 1, 2 = 7; (**9**: 7.5); 5, 6 = 9, 10 = 13, 14 ~ 6.5.

1 hr at 70°. TLC (Et_2O–petrol, 3:1) afforded 5 mg **9**, colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 and 1240 (OAc); MS (CI, isobutane) *m/z* (rel. int.): 391 (M + 1, 1), 331 (391 − HOAc, 15), 271 (331 − HOAc, 100). Compound **8** (5 mg) in 2 ml Et_2O was stirred for 2 hr with 50 mg MnO_2. TLC (Et_2O–petrol, 3:1) afforded 2 mg **10**, colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1695 and 1685 (C=CCHO); MS *m/z* (rel. int.): 302 (M^+, 4), 136 ($C_{10}H_{16}^+$, 17), 81 ($C_6H_9^+$, 40), 69 ($C_5H_9^+$, 100).

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