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TWO KAURENES FROM *VELLOZIA CAPUT-ARDEAE**

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Key Word Index—*Vellozia caput-ardeae*; Velloziaceae; kaurenes; 12β-hydroxy-9,11-dehydrokaurene; 12-oxo-9,11-dehydrokaurene.

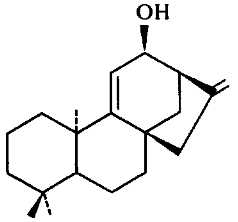
INTRODUCTION

During the course of a continuing phytochemical survey of Brazilian Velloziaceae, we have examined a sample of *Vellozia caput-ardeae* L. B. Smith & Ayensu, a species occurring in Diamantina, State of Minas Gerais, Brazil.

Chromatographic fractionation on silica gel of the hexane extract of the stem, roots and leaf sheaths of *V. caput-ardeae* afforded two crystalline compounds, which were shown to be two new kaurenes.

RESULTS AND DISCUSSION

The molecular formula of 12β-hydroxy-9,11-dehydrokaurene (**1**) $C_{20}H_{30}O$, was determined by MS [M^+ observed 286.2232 (68%), requires 286.2296]. The IR spectrum revealed the presence of hydroxyl (3 300 cm^{-1}) and terminal methylene (870 cm^{-1}) groups. The ^1H NMR spectrum showed signals for three tertiary methyl groups (δ 1.10, 0.92, 0.84), a carbinolic proton (3.95, 1H, *dd*, $J = 4.0$ and 3.5 Hz), a terminal methylene (5.05, 1H, *br s*) and (4.90, 1H, *br s*) and trisubstituted double bond (δ 5.30, 1H, *br d*). These data suggested a kaurene-type diterpene structure for compound **1**.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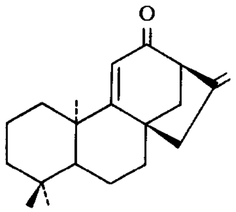
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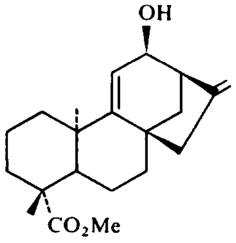
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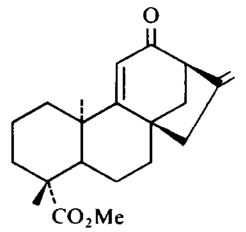
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Substance **1** was oxidized with pyridinium chlorochromate which yielded an α,β-unsaturated ketone (ν_{max}^{EtOH} 1660 cm^{-1}; λ_{max}^{EtOH} 248 nm, log ε 3.92) identical with ketone **2** isolated from the plant. Analysis of the ^1H NMR spectrum of **2** showed downfield shifts for the protons of the terminal methylene group and for the proton on the trisubstituted double bond relative to the values observed for substance **1** (Table 1).

The positions of the trisubstituted double bond and hydroxyl group, located at C-9, 11 and C-12, respectively, were deduced by comparison of the chemical shifts in the ^1H NMR spectra of **1** and **2** (Table 1) with the data recorded for the other kaurene-type diterpenes **3** and **4** [1].

EXPERIMENTAL

Mps are uncorr. The UV spectrum was measured in 95% EtOH. ^1H NMR spectra were recorded at 100 MHz, in $CDCl_3$ and chemical shifts (δ ppm) measured from TMS as internal standard. Optical rotations were determined in $CHCl_3$.

Isolation of 12β-*hydroxy*-9,11-*dehydrokaurene* (**1**) *and* 12-*oxo*-9,11-*dehydrokaurene* (**2**). Chromatography of the hexane extract (51 g) of roots, stem, and leaf sheaths of *Vellozia caput-ardeae*, collected in Diamantina, State of Minas Gerais, Brazil, yielded 12β-hydroxy-9,11-dehydrokaurene (**1**), mp 143–144°, 0.5% of dry plant wt; IR ν_{max}^{KBr} cm^{-1}: 3300, 1640, 1020 and 870. ^1H NMR (100 MHz, $CDCl_3$): δ 0.84 (3H, *s*), 0.92 (3H, *s*), 1.10 (3H, *s*), 1.82 (1H, *br s*, exchangeable with D_2O), 2.85 (1H, *br s*), 3.95 (1H, *dd*, $J = 4$ and 3.5 Hz), 4.90 (1H, *br s*), 5.05 (1H, *br s*) and 5.30 (1H, *br d*). MS *m/e* (rel. int.): 286 M^+ (68), 271 (81), 201 (19), 175 (22), 123 (25), 105 (35), 43 (100) and 41 (49).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365}{+103.7 \quad +108.5 \quad +124.6 \quad +225.6 \quad +385.7} \quad (c = 0.91).$$

Also isolated was 12-oxo-9,11-dehydrokaurene (**2**), mp 131–132°, 0.06% of dry plant wt; IR ν_{max}^{KBr} cm^{-1}: 2980, 1660 and 880. UV λ_{max}^{EtOH} nm (log ε) 248 (3.92), ^1H NMR (100 MHz, $CDCl_3$): δ 0.88 (3H, *s*), 0.97 (3H, *s*), 1.18 (3H, *s*), 3.38 (1H, *br s*), 4.98 (1H, *br s*), 5.24 (1H, *br s*) and 5.71 (1H, *br s*). MS *m/e* (rel. int.): 284 M^+ (100), 269 (32), 160 (19), 105 (15) and 41 (31).

Oxidation of 12β-*hydroxy*-9,11-*dehydrokaurene* (**1**). Pyridinium chlorochromate [2] (124 mg, 0.57 mmol) was added with stirring to a soln of 12β-hydroxy-9,11-dehydrokaurene (100 mg; 0.34 mmol) in dry CH_2Cl_2 (2 ml). After 1.5 hr dry Et_2O (10 ml) was added and the supernatant decanted from a black gum. The insoluble residue was washed thoroughly with dry Et_2O (3 × 5 ml) whereupon it became a black granular solid. The

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*Part 12 in the series 'The Chemistry of S. American Velloziaceae'. For Part 11 see Pinto, A. C., Valente, L. M. M., da Silva, R. S., Garcez, W. S. and Queiroz, P. P. da S. (1980) *An. Acad. Bras. Ciênc.* (in press).

Table 1. ^{1}H NMR chemical shifts for compounds **1**, **2**, **3** and **4** (100 MHz, TMS internal standard, $CDCl_3$)

	1	**2**	**3**	**4**
11-H	5.30 *br d*	5.71 *br s*	5.36 *br d*	5.76 *br s*
12α-H	3.95 *dd*	—	3.95 *dd*	—
13-H	2.85 *br s*	3.38 *br d*	2.84 *br s*	3.39 *br d*
17-H	5.05 *br s*	5.24 *br s*	5.05 *br s*	5.26 *br s*
17-H	4.90 *br s*	4.98 *br s*	4.90 *br s*	5.00 *br s*

J (Hz): 11, 12α = 4.0; 12α, 13 = 3.5.

Et_2O solns were combined and filtered through a pad of florisil. The solvent was removed at red. pres. and crystals of **2**, mp 131–132° (70 mg, 70 %), were obtained.

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