

## NORDITERPENOIDS FROM *VELLOZIA PUSILLA*

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**Key Word Index**—*Vellozia pusilla*; Velloziaceae; norpimarane-type diterpenes.

**Abstract**—New norditerpenoids and a series of known di- and triterpenoids were isolated from *Vellozia pusilla* and their structures were elucidated by spectroscopic methods and chemical transformations.

### INTRODUCTION

In the course of a continuing phytochemical survey of Brazilian Velloziaceae, we have examined a sample of *Vellozia pusilla* Pohl, a species occurring in the subtropical regions of the South America, specially in the State of Minas Gerais.

From the hexane and ethyl acetate extracts of roots, stem and leaf sheaths of this plant we have isolated a mixture of  $\beta$ -sitosterol and stigmasterol (identified by comparing their spectral data and chromatographic properties with authentic samples), lupeol, 20-hydroxylupan-3-one [1], 12  $\beta$ -hydroxy-8 (9),15-isopimaradien-7-one [2, 3], 7,16-epoxy-20-nor-5,7,9,11,13-cleistanthapentaen-3-one [4, 5], 7,16-epoxy-20-nor-1,5,7,9,11,13-cleistanthahexaen-3-one [4, 5], (5*R*,7*S*,10*S*)-7 $\alpha$ ,16, 7 $\beta$ ,20-diepoxy-1,8,11,13-tetraen-3-one, (5*R*,7*S*,10*S*)-7 $\alpha$ ,16, 7 $\beta$ ,20-diepoxy-1,8,11,13-trien-3-one [5–7], 20-hydroxy-8,11,13-cleistanthatrien-7-one (**1**) [8], known from other Brazilian Velloziaceae, and two new pimarane diterpenes, **2** and **3**, which we have named 11 $\beta$ -hydroxy-20-nor-8 (9),15-isopimaradien-7-one and 20-nor-8(9),15-isopimaradien-7,11-dione respectively. This paper describes the structure elucidation of these two norditerpenes.

### RESULTS AND DISCUSSION

The molecular formula of 11 $\beta$ -hydroxy-20-nor-8 (9),15-isopimaradien-7-one (**2**), C<sub>19</sub>H<sub>28</sub>O<sub>2</sub>, was determined by HRMS [ $M^+$  obs. 288.2085 (25%) req. 288.2089]. The IR spectrum revealed the presence of hydroxyl (3460 cm<sup>-1</sup>),  $\alpha,\beta$ -unsaturated carbonyl (1650 and 1605 cm<sup>-1</sup>) and vinyl groups (907 cm<sup>-1</sup>). The UV spectrum showed  $\lambda_{\max}^{\text{EtOH}}$  249 nm (log  $\epsilon$  = 3.93) indicative of a carbonyl group conjugated to a tetrasubstituted double bond. The <sup>1</sup>H NMR spectrum, in CDCl<sub>3</sub>, showed signals for three methyl groups ( $\delta$  0.91, 0.94 and 1.11) and one vinyl group linked to quaternary carbon atoms [ $\delta$  4.85 (1H, *dd*, *J* = 18 and 2 Hz), 4.93 (1H, *dd*, *J* = 11 and 2 Hz) and 5.67 (1H, *dd*, *J* = 18 and 11 Hz)] and one carbinolic proton ( $\delta$  4.42, *m*), which was shifted downfield to  $\delta$  5.48 upon acetylation of **2** to **2a**. The downfield position of the carbinolic proton suggested that the  $\text{CHOH}$  proton might be allylic. The

interrelation between the secondary hydroxyl group and the ethylenic linkage was derived by oxidation of **2** with PCC which afforded a transoid enedione [ $\nu_{\max}^{\text{KBr}}$  1670 cm<sup>-1</sup>;  $\lambda_{\max}^{\text{EtOH}}$  266 nm (log  $\epsilon$  = 3.90)] identical with diketone **3** isolated from the same plant.

These data, in combination with comparative analysis of the proton noise decoupled and single frequency off-resonance decoupled <sup>13</sup>C NMR spectra (Table 1), allowed identification of the sequence (C)<sub>2</sub> (C=O) (■-C=C-■) (■-CH=CH<sub>2</sub>) (CHOH) (CH)<sub>2</sub> (CH<sub>2</sub>)<sub>6</sub> (Me)<sub>3</sub>.

These results together with biogenetic considerations and the previous isolation of pimarane diterpenoids from the plants of this family revealed the substance to have a norpimarane skeleton [2, 3].

The position of the carbonyl group at C-7 was deduced from the chemical shift of C-14 which suffered a net  $\gamma$  shielding effect (of *ca* 8.5 ppm) [9].

The methyl multiplicity in the <sup>1</sup>H NMR spectra of **2** and **3**, all singlets, revealed the absence of the C-20 methyl. This fact was confirmed by comparing the chemical shifts of C-2 and C-6 in **2** and **3** with those in the known pimarane diterpenes **4** and **5** [9]. In these compounds, the above mentioned carbons are shielded due to the  $\gamma$ -gauche effect of the C-20 methyl group.

Dehydration of **2** with TsOH yielded the  $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl compound **6**. The <sup>1</sup>H NMR spectrum of **6** showed signals for the olefinic protons of an AB system [ $\delta$  5.94 (1H, *d*, *J* = 9 Hz) and 6.25 (1H, *d*, *J* = 9 Hz)]. The UV spectrum of **6** contained a band at  $\lambda_{\max}^{\text{EtOH}}$  308 nm which confirmed an extended conjugation and, consequently, the position of the hydroxyl at C-11.

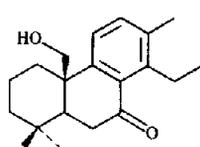
The stereochemistry of the hydroxyl group at C-11 was deduced by comparison of the chemical shifts of the sp<sup>3</sup> carbon atoms of the C-ring of **2** and its acetylated derivative **2a** with those of the pimarane models **4**, **4a** and **7**. This showed the hydroxyl group at C-11 to be  $\beta$ -oriented [5, 9].

The A/B *trans* junction was determined by the positive Cotton effect for the n- $\pi^*$  transition in the CD spectrum similar to that observed for model compound **4** [10].

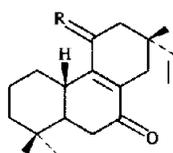
The configuration at C-13 was established by the chemical shift of the C-17 methyl (29.4 ppm) since it is known that axial methyl groups are usually more shielded than equatorial ones [9].

Table 1.  $^{13}\text{C}$  NMR data of compounds 2-5 ( $\text{CDCl}_3$ )

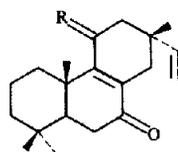
C	2	2a	3	4	4a	5
1	30.2	29.7	30.3	35.3 <sup>a</sup>	35.3	35.2
2	22.4	22.2	22.2	18.5	18.5	18.5
3	40.9	40.6	40.9	41.0	41.0	40.8
4	32.9	32.7	32.7	33.2	33.4	32.8
5	48.9	48.7	47.4	51.0	50.9	49.7
6	38.2	38.2	38.1	35.0 <sup>a</sup>	35.3	35.0
7	200.9	199.6	200.9	201.6	200.5	200.4
8	131.4	133.5	144.2	130.2	132.8	141.5
9	158.1	152.8	149.8	163.4	158.7	154.9
10	38.2	37.9	36.5	40.1	39.7	39.0
11	66.1	69.1	201.6	67.1	69.1	201.6
12	44.1	39.0	49.3	44.8	39.7	50.5
13	35.6	35.2	37.8	35.3	34.6	37.6
14	33.9	33.5	34.8	34.1 <sup>a</sup>	34.1	34.8
15	143.6	143.4	142.3	144.5	145.6	144.5
16	112.1	112.2	112.9	111.6	111.7	112.3
17	29.4	28.8	27.2	28.1	26.8	26.4
18	30.2	29.7	30.1	32.8	32.7	32.8
19	20.1	19.0	19.8	21.6	21.7	21.2
20	---	---	---	19.0	19.3	17.3
(OAc)CO	---	169.9	---	---	169.7	---
(OAc)Me	---	21.1	---	---	21.6	---

<sup>a</sup>Interchangeable values.

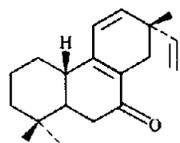
1



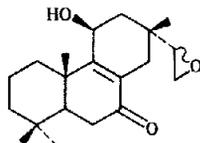
2 R = βOH,H  
 2a R = βOAc,H  
 3 R = O



4 R = βOH,H  
 4a R = βOAc,H  
 5 R = O



6



7

## EXPERIMENTAL

The equipment used for this work was identical to that described in ref. [5].

Chromatography of the hexane extract (39 g) of roots, stem and leaf sheaths of *Vellozia pusilla* Pohl collected in the Serra do Cipó, Minas Gerais, Brazil, yielded 11β-hydroxy-20-nor-8(9),15-isopimaradien-7-one (2), mp 158–160° from hexane and EtOAc (4:1). IR  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 3460, 1650, 1605 and 907; UV  $\lambda_{\text{max}}^{\text{EtOH}}$  249 nm (log  $\epsilon$  = 3.93);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.91 (3H, s), 0.94 (3H, s), 1.11 (3H, s), 4.42 (1H, m), 4.85 (1H, dd,  $J$  = 18 and 2 Hz), 4.93 (1H, dd,  $J$  = 11 and 2 Hz) and 5.67 (1H, dd,  $J$  = 18 and 11 Hz);  $^{13}\text{C}$  NMR: Table 1; MS  $m/z$  (rel. int.): 288 [ $\text{M}$ ]<sup>+</sup> (25), 273 (2), 260 (7), 245 (10) and 231 (16). Found,  $m/z$  288.2085 ( $\text{C}_{19}\text{H}_{28}\text{O}_2$  requires 288.2089).

$$[\alpha]_{\text{D}}^{24} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365}{+116.1 \quad -122.1 \quad +136.7 \quad +248.0 \quad +468.6} \text{ nm}$$

( $\text{CHCl}_3$ ;  $c$  0.58)

**Acetylation of (2).** Compound 2 (47 mg) was dissolved in  $\text{Ac}_2\text{O}$  (10 ml) and a catalytic amount of DMAP was added. The mixture was left for 4 hr at room temp. and the usual work-up yielded 2a as a colourless oil. IR  $\nu_{\text{max}}^{\text{CHCl}_3}$   $\text{cm}^{-1}$ : 1720, 1650, 1610 and 1205;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.90 (3H, s), 0.92 (3H, s), 1.06 (3H, s), 2.10 (3H, s), 4.90 (1H, dd,  $J$  = 18 and 2 Hz), 4.94 (1H, dd,  $J$  = 11 and 2 Hz), 5.48 (1H, t,  $J$  = 6 Hz) and 5.70 (1H, dd,  $J$  = 18 and 11 Hz);  $^{13}\text{C}$  NMR: Table 1; MS  $m/z$  (rel. int.): 330 [ $\text{M}$ ]<sup>+</sup> (1), 288 (18), 270 (67), 255 (42) and 41 (100).

**20-nor-8(9),15-Isopimaradien-7,11-dione (3).** Colourless crystals from hexane, mp 80–82°; IR  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 1670 and 917; UV  $\nu_{\text{max}}^{\text{EtOH}}$  266 nm (log  $\epsilon$  = 3.90);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.92 (3H, s) 0.95 (3H, s), 1.13 (3H, s), 4.88 (1H, d,  $J$  = 18 Hz), 5.03 (1H, d,  $J$  = 11 Hz) and 5.94 (1H, dd,  $J$  = 18 and 11 Hz);  $^{13}\text{C}$  NMR: Table 1; MS  $m/z$  (rel. int.): 286 [ $\text{M}$ ]<sup>+</sup> (96), 271 (21), 258 (64), 244 (43), 243 (43), 218 (94) and 41 (100).

**Oxidation of (2).** Compound 2 (40 mg) was treated with pyridinium chlorochromate (45 mg) in dry  $\text{CH}_2\text{Cl}_2$  (2 ml) at room temp. After 2 hr, dry  $\text{Et}_2\text{O}$  (10 ml) was added and the supernatant decanted from a brown gum. The insoluble residue was washed thoroughly with dry  $\text{Et}_2\text{O}$  ( $3 \times 5$  ml) whereupon it

gave a brown granular solid. The Et<sub>2</sub>O solns were combined and filtered through a pad of Florisil. The solvent was removed at red. pres. and crystals of 3 mp 80–82° were obtained.

*Dehydration of 2.* Compound 2 (20 mg) was refluxed for 4 hr with C<sub>6</sub>H<sub>6</sub> (3 ml) and TsOH (10 mg) under N<sub>2</sub>. After cooling, the mixture was washed with 5% aq. NaHCO<sub>3</sub> (3 × 10 ml), H<sub>2</sub>O (3 × 10 ml), dried and concd *in vacuo* to give a yellow oil 6. UV λ<sub>max</sub><sup>MeOH</sup> 309 nm; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.94 (1H, *d*, *J*=9 Hz) and 6.25 (1H, *d*, *J*=9 Hz).

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