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# TWO DITERPENES WITH A CLEISTANTHANE SKELETON FROM *VELLOZIA NIVEA*

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**Key Word Index**—*Vellozia nivea*; Velloziaceae; diterpenes; cleistanthane.

**Abstract**—Two new cleistanthane diterpenes have been isolated from *Vellozia nivea*. Their structures were established by spectroscopic data and chemical interconversion.

## INTRODUCTION

Cleistanthane diterpenes are secondary metabolites uncommon in nature. The members of this series were isolated from species of the family Euphorbiaceae, Compositae and Velloziaceae [1]. All these diterpenes isolated from Euphorbiaceae and Compositae possess the (5*R*, 10*R*)-absolute configuration while the cleistanthane diterpenes isolated from Velloziaceae belong the normal series (5*S*, 10*S*).

As part of our systematic phytochemical investigation of Brazilian Velloziaceae we wish to report on the study of *Vellozia nivea* L. B. Smith & Ayensu, a perennial species widely distributed in the State of Minas Gerais, Brazil. The present paper describes the structural elucidation of two new diterpenoids isolated from the hexane extract of the stem, roots and leaf sheaths of this plant.

## RESULTS

11-Hydroxycleistantha-8,11,13-trien-7-one (**1**) [$C_{20}H_{28}O_2$] revealed in the IR spectrum the presence of a conjugated ketone (1655 $cm^{-1}$), an hydroxy group (3185 $cm^{-1}$) and of a pentasubstituted aromatic ring (870 $cm^{-1}$) [2].

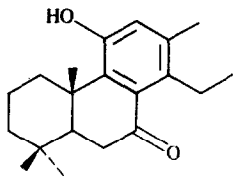
The UV spectrum presented three maxima at 232, 267 and 333 nm. The latter one was shifted to $\lambda_{max}^{EtOH}$ 383 nm after addition of one drop a aqueous sodium hydroxide solution, characterizing a *meta*-hydroxylated acetophenone system [3]. The $^1$H NMR spectrum of **1**, in $CDCl_3$, showed signals for five methyl groups, three of which were on quaternary saturated carbons ($\delta$ 0.94, 0.98 and 1.35). one on the aromatic ring ($\delta$ 2.27) and the fifth being part of an ethyl group attached to the aromatic nucleus ($\delta$ 1.20, *t*, $J = 7$ Hz and 2.81 *q*, $J = 7$ Hz) and one singlet, for one aromatic proton at $\delta$ 6.66 *ortho* to the phenolic hydroxyl. The $^1$H NMR spectrum also showed adjacent to the ketone, a methylene group ($\delta$ 2.65, *d*, $J = 9$ Hz), a which in turn, was adjacent to a methine ($\delta$ 1.84, *t*, $J = 9$ Hz). The fragments at *m/z* 285 $[M-15]^+$ (44%), 215 $[M-85]^+$ (82%), 203 $[M-97]^+$ (54%) and 189 $[M-111]^+$ (43%) in the mass spectrum are characteristic for tricyclic diterpenes with an aromatic C-ring [4]. Structure **1** was thus proposed for this new natural diterpene. The $^{13}$C NMR data were found consistent with the proposed structure. The chemical shifts of the carbon atoms of the A-ring showed the A/B ring junction to be *trans* [5]. The localization of the phenolic hydroxyl at C-11 was confirmed by the high field position of the angular methyl carbon ($\delta$ 19.0) [6]. The absolute configuration of **1** was deduced by comparison of chiroptical properties.

Thus, the optical rotation of **1** showed a positive value akin to that displayed by other cleistanthane diterpenes, with aromatic ring-C of known absolute configuration such as **3**, isolated from Velloziaceae [1]. Since the ketone cleistanthane is strongly dextrorotatory [$[\alpha]_D + 70°$, $CHCl_3$; *c* 0.50], it can be proposed that this diterpene also belongs to the normal series (5*S*, 10*S*).

The second compound described is 7,11-diketo-14$\alpha$-hydroxy-cleistantha-8,12-diene (**2**). The molecular formula of **2** [$C_{20}H_{28}O_3$] was obtained by high resolution mass spectrometry. The IR spectrum showed the presence of hydroxyl (3420 $cm^{-1}$) and two carbonyl groups (broad band at 1650 $cm^{-1}$). The UV spectrum was indicative of an enedione transoid moiety with a double bond cross conjugation ($\lambda_{max}$ 248 nm; $\varepsilon = 6000$)

The $^{13}$C NMR spectrum revealed an unsubstituted A-ring, the presence of two keto groups at C-7 and C-11 [$\delta$ 203.8 (C-7, *s*) and 185.5 (C-11, *s*)] and two double bonds between C(8)–C(9) and C(12)–C(13), with the latter one trisubstituted [$\delta$ 141.9 (C-8, *s*), 157.6 (C-9, *s*), 127.7 (C-12, *d*) and 159.3 (C-13, *s*)].

The $^1$H NMR spectrum of **2** presented signals for three methyl groups on quaternary saturated carbons ($\delta$ 0.90, 0.93 and 1.44), one methyl group attached to the double bond ($\delta$ 2.10, *d*, $J = 2$ Hz) which coupled with one olefinic proton at $\delta$ 6.08 (*br*, *q*, $J = 2$ Hz) and another methyl group being part of an ethyl group ($\delta$ 0.45, *t*, $J = 7$ Hz). The upfield shift of the latter allowed assignment of the configuration of the ethyl group at C-14. Indeed, the strong shielding suffered by this methyl group can be attributed, by analysis of a Dreiding model, to its spatial orientation, the methyl group laying over the diamagnetic anisotropy region of the enedione chromophore [7]. The $^1$H NMR spectrum also showed a multiplet signal centred at $\delta$ 2.75 (1H) that was attributed to the 1$\beta$-H which is deshielded due to the (Rabbit-ear) effect of the



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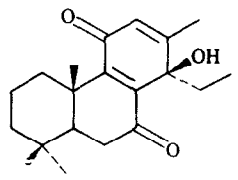

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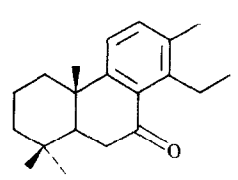

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oxygenated C-11 also observed in the cleistanthane diterpene **1**. [8].

The proposed structure was confirmed by conversion of **2** to **1**. Treatment, of **2** with zinc dust in acetic acid [8] yielded, as the sole product of the reaction, a compound (**1**) identical in all respects with the natural diterpene.

The fact that compound **1** occurs in the same plant with **2** allows us to consider **2** as a possible biogenetic precursor for the former diterpenoid.

## EXPERIMENTAL

All the equipment used for this work has been previously described [1].

*Isolation of* 11-*hydroxycleistantha*-8,11,13-*trien*-7-*one* (**1**). Chromatography of the $CHCl_3$ extract (36 g) of the trunk, roots and leaf sheaths of *Vellozia nivea* collected in Diamantina, Minas Gerais, Brazil, yielded **1**, mp 236–238°, 0.10% of plant dry wt; IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3185, 2882, 1655, 1580, 1440, 1410, 1370, 1285, 1230, 1170, 1110, 1070, 1020, 870 and 645. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 221 (3.92), 230 (3.95), 266 (3.67) and 332 (3.34). $^1H$ NMR (100 MHz, $CDCl_3$): $\delta$ 0.94 (3H, *s*), 0.98 (3H, *s*), 1.20 (3H, *t*, $J = 7$ Hz), 1.35 (3H, *s*), 1.84 (1H, *t*, $J = 9$ Hz), 2.27 (3H, *s*), 2.65 (2H, *d*, $J = 9$ Hz), 2.81 (2H, *q*, $J = 7$ Hz), 3.15 (1H, *m*), 5.18 (1H, *br s*, exchangeable with $D_2O$) and 6.66 (1H, *s*). $^{13}C$ NMR (25.2 MHz, $CDCl_3$): $\delta$ 15.0 (*q*, C-16), 18.2 (*q*, C-17), 19.0 (*q*, C-20), 19.2 (*t*, C-2), 21.5 (*q*, C-19), 23.6 (*t*, C-15), 32.9 (*q*, C-18), 33.4 (*s*, C-4), 37.0 (*t*, C-1), 37.8 (*t*, C-6), 40.5 (*s*, C-10), 41.3 (*t*, C-3), 49.5 (*d*, C-5), 123.3 (*d*, C-12), 133.6 (*s*, C-8), 134.9 (*s*, C-13), 135.7 (*s*, C-14), 138.9 (*s*, C-9), 152.8 (*s*, C-11) and 202.3 (*s*, C-7). MS *m/z* (rel. int.): 300 $[M]^+$ (100) 285 (44), 267 (15), 215 (82), 203 (54), 197 (21), 189 (43), 163 (14) and 69 (20).

$$[\alpha]_{25^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436}{+70.0 \quad +75.0 \quad +92.2 \quad +136.6} \text{ nm } (CHCl_3;\ c\ 0.50)$$

7,11-*Diketo*-14α-*hydroxycleistantha*-8,12-*diene* (**2**). Yellow crystals, mp 113–115°, 0.10% plant dry wt. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3420, 2970, 2900, 2840, 1650 (*br*), 1370, 1315, 1240, 1035, 970, 930, 870 and 740. UV $\lambda_{max}^{hexane}$ nm (log $\varepsilon$): 248 (3.77). $^1H$ NMR (100 MHz, $CDCl_3$): $\delta$ 0.45 (3H, *t*, $J = 7$ Hz), 0.90 (3H, *s*), 0.93 (3H, *s*), 1.44 (3H, *s*), 2.10 (3H, *d*, $J = 2$ Hz), 2.55 (2H, *m*), 2.75 (1H, *m*), 4.82 (1H, *br s*) and 6.08 (*br q*, $J = 2$ Hz). $^{13}C$ NMR (25.2 MHz, $CDCl_3$): $\delta$ 8.90 (*q*, C-16), 17.0 (*q*, C-17), 17.8 (*q*, C-20), 18.5 (*t*, C-2), 21.2 (*q*, C-19), 32.6 (*q*, C-18), 32.9 (*s*, C-4), 33.4 (*t*, C-15), 34.9 (*t*, C-1), 36.3 (*t*, C-6), 39.5 (*s*, C-10), 40.7 (*t*, C-3), 49.2 (*d*, C-5), 75.2 (*s*, C-14), 127.7 (*d*, C-12), 141.9 (*s*, C-8), 157.6 (*s*, C-9), 159.3 (*s*, C-13), 185.5 (*s*, C-11) and 203.8 (*s*, C-7). MS *m/z* (rel. int.): 316 $[M]^+$ (5) 287 (100), 245 (27), 219 (12), 217 (10), 203 (13), 191 (17), 175 (8), 165 (10) and 151 (14).

$$[\alpha]_{25^\circ}^{\lambda} = \frac{589 \quad 578 \quad 436}{-4.7 \quad -7.4 \quad -20.1} \text{ nm (MeOH; } c\ 0.85)$$

*Conversion of* **2** *to* **1**. To a soln of **2** (20 mg) in HOAc (2 ml) was added with stirring and heating powdered Zn (30 mg). After 2 hr the yellow colour of **2** had disappeared. The mixture was filtered and the filtrate diluted with $H_2O$ and extracted with $CHCl_3$. The washed and dried $CHCl_3$ extract was evapd and the residue (19 mg) was identical in all aspects with the natural diterpene **1**.

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