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VELLOZONE, A TETRACYCLIC TRITERPENE FROM *VELLOZIA STIPITATA**

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Key Word Index—*Vellozia stipitata*; *V. aloifolia*; Velloziaceae; tetracyclic triterpene; (20*R*)-20-hydroxy-24-methylenedammar-3-one.

Abstract—The isolation of (20*R*)-20-hydroxy-24-methylenedammar-3-one from *Vellozia stipitata* is described.

INTRODUCTION

Previous papers [1, 2] have dealt with the chemical study of the hexane extract of *Vellozia stipitata* L. B. Smith & Ayensu which led to the isolation of a naphthalenic norditerpene, lupeol, lupenone and 22-hydroxy-21βH-hopan-3-one. Subsequent work has resulted in the isolation of oleanolic acid and a new triterpene named vellozone (**1**) from the same extract. Vellozone, isolated in 0.6% yield of the dry plant, had previously been obtained from *V. aloifolia* Martius [3].

RESULTS AND DISCUSSION

The molecular formula of vellozone (**1**), $C_{31}H_{52}O_2$, mp 141°, was determined by high resolution MS [M^+ observed at *m/e* 456.395020, requires 456.396484]. Vellozone gave a positive test with tetranitromethane [4]. The IR spectrum presented absorption bands for hydroxyl, carbonyl, terminal methylene (1640 and 880 cm^{-1}) and *gem*-dimethyl groups (1380 cm^{-1}).

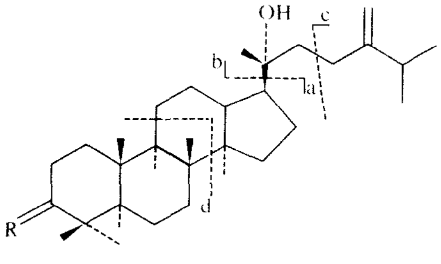
The ^{1}H NMR spectrum of **1** showed, *inter alia*, signals for five quaternary methyl groups between δ 0.9 and 1.1, a signal at 1.18 for a methyl on the same carbon as an oxygen, and a doublet at 1.02 (6H, $J = 7$ Hz) assigned to an isopropyl group. Two broad singlets at 4.7 and 4.76 and a signal at 1.38, which disappeared upon the addition of deuterium oxide, provided further evidence for a terminal methylene and hydroxyl group, respectively.

A detailed study of the ^{13}C NMR spectrum of this tetracyclic triterpene showed a signal at δ 75.6, attributed to C-20 which bears a tertiary hydroxyl group [5]. Signals at 106.8 (*t*) and 157.4 (*s*) confirmed the presence of a terminal methylene group. The signals at 50.6, 47.6, 40.4 and 37.0 for four quaternary carbons, and a singlet at 219.3 suggested that vellozone had a dammarane skeleton with a carbonyl group at C-3 [6]. The signals at 22.1 (*q*) and 34.1 (*d*) can be attributed to an isopropyl group α to a double bond, thus characterizing the nature of the side chain [7].

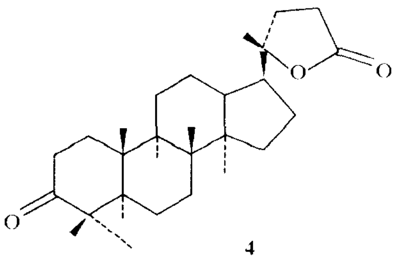
Reduction of vellozone with sodium borohydride gave a diol (**2**). This, upon acetylation with acetic anhydride and pyridine, gave a monoacetate (**3**) which presented absorption bands in the IR for a hydroxyl group as well as the terminal methylene and acetate groups.

The ^{1}H NMR of **3** showed signals for six quaternary C-Me groups, an isopropyl group and one acetyl Me. The double doublet at δ 4.5 ($J = 10$ and 6 Hz) is characteristic of an acetyl carbinolic proton α-oriented in a cyclohexane ring, and supported the presence of a 3-keto group in vellozone.

Analysis of the MS of **1** and its derivatives (Table 1) determined the nature of the tetracyclic skeleton.



1 R = O
2 R = βOH
3 R = βOAc



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* Part IX in the series "The Chemistry of S. American Velloziaceae". For Part VIII see Barreiro, E. J. Barreira, M. D. and Pinto, A. C. (1980) *An. Acad. Bras. Ciênc.* (in press).

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Table 1. Mass spectral fragmentation of compounds **1**, **2** and **3**

Fragment	**1**	**2**	**3**
a	315 (4.0)*	317 (5.0)	359 (2.0)
b	141 (71.0)	141 (53.0)	141 (83.0)
c	83 (53.0)	83 (44.0)	83 (55.0)
b − 18†	123 (100.0)	123 (100.0)	123 (100.0)
d	205 (23.0)	207 (24.0)	249 (9.0)

* Relative intensities are given in parentheses.

† \|b → (b − 18)\|, M* 107.4, observed; 107.3 calculated.

Cleavage of ring C of **1**, **2**, and **3**, gave peaks at *m/e* 205, 207, and 249, respectively, which limited the choice of skeletons to the dammarane group and excluded the euphane and lanostane type skeletons [8, 9]. Rupture of the bond between C-17 and C-20 gave peaks at *m/e* 315, 317 and 359 for the cyclic part of the three compounds [10] and another at *m/e* 141, which in turn loses water (m* at *m/e* 107.3 corresponds to 141–123), for the side chain.

The CD curve of **1** gave a weakly negative Cotton effect, similar to (20*R*)-20-hydroxydammar-24-en-3-one [11], which made it possible to postulate the A and B-rings as being *trans*-anti-*trans* with the C-5 hydrogen α-oriented.

Care had to be taken when working with vellozone to avoid epimerization at C-20 (from *R* to *S*). This was observed to occur if, during the chromatographic purification of the extracts, the compound remained in contact with the Si gel for several days. Ozonolysis, in CH_2Cl_2 at 0°, of the epimer gave Mills' trisnorlactone (**4**) [12, 13], thus proving the *R* configuration at C-20 in vellozone. Thus vellozone is assigned the structure (20*R*)-20-hydroxy-24-methylenedammar-3-one.

EXPERIMENTAL

Mps are uncorr. IR spectra in KBr disc. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 100 and 25.2 MHz, respectively, and chemical shifts (δ ppm) measured from TMS as internal standard. Column chromatography was on Merck Si gel (0.05–0.20 mm), TLC on Merck Si gel H, G or $PF_{254+366}$.

Isolation of vellozone (**1**). Chromatography of the hexane extract (90 g) of the trunk, roots and leaf sheaths of *Vellozia stipitata*, collected in the Serra do Cipó, Minas Gerais, Brazil, yielded vellozone (**1**) as white needles, mp 141°; UV λ_{max}^{EtOH} nm: 288 ($\varepsilon = 24$). IR ν_{max}^{KBr} cm^{-1}: 3340, 1700, 1640 and 880. ^1H NMR (100 MHz, $CDCl_3$): δ 0.90 (3 H, *s*), 0.92 (3 H, *s*), 0.94 (3 H, *s*), 1.02 (6 H, *d*, $J = 7$ Hz), 1.05 (3 H, *s*), 1.1 (3 H, *s*), 1.18 (3 H, *s*), 1.38 (1 H, *br s*, exchangeable with D_2O), 2.5 (2 H, *m*), 4.7 (1 H, *br s*) and 4.76 (1 H, *br s*). MS *m/e* (rel. int.): 456 (M^+, 3), 441 (2), 438 (7), 413 (4), 359 (16), 316 (48), 315 (4), 205 (23), 141 (71), 123 (100), 83 (53), and 81 (51).

Reduction of vellozone (**1**). Compound **1** (50 mg) was reduced with $NaBH_4$ in MeOH for 10 min at room temp. The product was recrystallized from a mixture of hexane and EtOAc to give needles of the diol **2**, (42 mg), mp 102–3°.

Acetylation of diol **2**. Ac_2O (2 ml) was added to a soln of **2** (30 mg) in C_6H_5N (2 ml). The mixture was left overnight at room temp., extracted with $CHCl_3$ (5 × 20 ml), washed with 1 M HCl, neutralized and dried. Evapn of the solvent *in vacuo* gave a colourless oil (32 mg). IR ν_{max} cm^{-1}: 1735, 1250 (OAc), 1640 and 880 ($C{=}CH_2$).

Ozonolysis of the epimer of vellozone. The (20*S*)-epimer of vellozone (200 mg) in CH_2Cl_2 (30 ml) was ozonized for 3 hr at 0°. The ozonide was decomposed with conc KI soln, and extracted with CH_2Cl_2 (5 × 20 ml). The combined extracts were washed with H_2O, dried and concd. Purification by chromatography gave colourless crystals (90 mg), mp 181–182°, as the principle product. The spectral data were identical to those reported for Mills' trisnorlactone [12, 13], mp 181–183° (lit. 181–183°); ν_{max}^{KBr} cm^{-1}: 1760 and 1700. The MS showed significant peaks at *m/e* (rel. int.): 414 (M^+, 75), 399 ($M^+ - 15$, 10), 205 (78) and 99 (100).

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