11,12-Dehydrovelloziolone, a Minor Constituent of Vellozia caput-ardeae

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Abstract: A new seco-diterpenoid, isolated from Vellozia caput-ardeae, is characterized by spectral analysis and chemical synthesis from a known compound.

A careful investigation of the mother liquors from the isolation of the major diterpenoid constituents of <u>Vellozia</u> caput-ardeae

L. B. Smith & Ayensu<sup>1-3</sup> indicated the presence of a minor amount of a new seco-diterpene, 11,12-dehydrovelloziolone (1).

The molecular formula of  $\frac{1}{2}$  [( $^{\text{C}}_{20}\text{H}_{30}^{\text{O}}_{2}$ ), colorless oil,  $[\alpha]_{D}^{25}$  =-16.1 (c=0.77 CHCl $_{3}$ )] was inferred from low-resolution MS data. The IR spectrum of  $\frac{1}{2}$  showed absorptions for hydroxyl (3509 cm $^{-1}$ ), enone (1675 cm $^{-1}$ ) and vinylidene (885 cm $^{-1}$ ) moieties. The UV data ( $^{\text{MeOH}}_{\text{max}}$  227 nm) pinpointed the pattern of the enone function (only one  $^{\beta}$  residue).

The  $^1$ H n.m.r. spectrum (CDCl $_3$ , 100 MHz) showed three methyl singlets at 0.76, 0.92 and 1.22 ppm and two methine signals, a doublet ( $\underline{J}$ = 9Hz) at 5.86 ppm and a double doublet ( $\underline{J}$ = 9 and 2Hz) at 7.14 ppm, related to the  $\alpha$ - and  $\beta$ - protons of the enone moiety, respectively. Irradiation of the signal at 7.14 ppm caused a broad methine multiplet at 3.40 ppm to collapse into a double doublet, showing that the  $\beta$ -proton of the enone moiety is spincoupled to a methine, on its turn neighboured by two protons. Two doublets at 4.81 ppm ( $\underline{J}$ = 2Hz) and 5.04 ppm ( $\underline{J}$ = 2Hz) are assigned to the vinylidene protons.

The similarity between the spectral data of the new diterpenoid and velloziolone (3), previously isolated from the same botanical source<sup>2</sup>, gave support for postulation of structure  $\underline{1}$ . In order to confirm unequivocally our assignments the conversion of  $\underline{3}$  into  $\underline{1}$  was undertaken.

Thus, reaction of  $\underline{3}$  with LDA and phenylselenyl bromide in dry THF at  $-78^{\circ}$ C afforded ketoalcohol  $\underline{2}$  which, on treatment with hydrogen peroxide at room temperature, furnished a product whose spectral and chromatographic properties were identical in all aspects with those shown by seco-diterpenoid  $\underline{1}$ .

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## REFERENCES

- A.C. Pinto S.K. do Prado and R. Pinchin, Phytochemistry, <u>20</u>, 520 (1981).
- A.C. Pinto, S.K. do Prado, R.B. Filho,
   W.E. Hull, A. Neszmelyi and G. Lukacs,
   Tetrahedron Letters, 5267 (1982).
- A.C. Pinto, S.K. do Prado and R.Pinchin, Phytochemistry, in press.
- H.J. Reich, J.M. Renga and I.L. Reich, J. Amer. Chem. Soc., 97, 5434 (1975).