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TWO NEW DITERPENES WITH A ROSANE SKELETON FROM VELLOZIACEAE.

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SUMMARY: Two new rosane diterpenes, epoxicorcovadin and epoxivellozin, have been isolated from Vellozia candida Mikan: their structures were stablished by spectroscopic data and chemical transformations.

Vellozia candida Mikan grows on the hillside of Corcovado mountain and on the rocky mountains of the coast of State of Rio de Janeiro. We have previously reported the isolation of velloziolide (1)[1] and of three rosane diterpenes[2] from the hexane extract of the stem, roots and leaf sheaths of this plant. The present paper describes the structural elucidation of two new diterpenoids, epoxicorcovadin (2a) and epoxivellozin (3a), isolated as minor components from the same plant.

Epoxicorcovadin (2a) was purified and characterized as its acetate derivative (2b). 2b [$C_{22}H_{30}O_4$; m.p. 168-69°C, $[\alpha]_D^{25} = 0.00$ (c = 1.00 $CHCl_3$)][3] possesses as a characteristic feature an α,β-unsaturated ketone moiety (νc= 0 at 1668cm^{-1} and λ_{max}^{EtOH} at 253 nm). The ^1H NMR spectrum, in $CDCl_3$, showed signals for four tertiary methyl groups (0.98, 1.10, 1.18 and 1.26 ppm), a methyl group of an acetate (2.09 ppm) and one tertiary vinyl group at 5.67 ppm (1H, dd, J=17 and 10 Hz). The multiplet signal (3H) between at 4.98 and 5.31 ppm (CH_2,m) corresponds to the methylene of the vinyl residue and the acetyl carbinolic proton. Two doublets at 5.9 (1H, J=9 Hz) and 7.45 ppm (1H, J=9 Hz) are due to the two olefinic protons α,β-conjugated to the carbonyl group, with the β carbon linked to a quaternary carbon. Double irradiation experiments demonstrated that these two protons are mutually spin coupled. The absence of absorptions in the IR spectrum for hydroxyl groups and the presence of two singlet signals at 64.3 and 68.4 ppm in ^{13}C NMR spectrum of 2b indicated that the remaining oxygen atom belongs to an epoxide function. These data, in combination with the comparative analysis of the proton noise decoupled and single frequence off-resonance decoupled ^{13}C NMR spectrum (Table 1), allowed expansion of the molecular formula $C_{22}H_{30}O_4$ to (CO-CH=CH-■) (CHOAc) (■-CH=CH_2) ($\blacksquare\!-\!\overset{O}{C\!-\!C}\!-\!\blacksquare$) $(C)_3(CH)(CH_2)_4(CH_3)_4$ and to deduce the structure 2b, which was confirmed by chemical transformation. Thus, epoxidation of 4[2] with m-CPBA at 10°C, in CH_2Cl_2, afforded the 5α,10α-epoxide 5 as the main product by attack of the bulky reagent from the less hindered α-face. Stereochemical assignment of the epoxy ring of 5 can be made by comparative ^{13}C NMR analysis of 2 and 4. Thus in 2b, C-8 appears at a more shielded position (32.7 ppm) than in 4 (37.7 ppm, Table 1). This can be explained by a shielding effect due to the "γ-gauche like" relationship between the C-8-H and the 5α,10α-oxirane ring in 2. Treatment of epoxide 5 with LDA and phenylselenyl bromide[4] in dry THF at -78°C followed by addition of hydrogen peroxide at room temp, furnished a product that upon acetylation was identical in all aspects with natural 2.

Epoxivellozin [3a; $C_{20}H_{28}O_4$; m.p. 142-4°C; $[\alpha]_D^{25}$ = + 14.9 (c= 0.77 $CHCl_3$)] revealed in the IR spectrum the presence of a conjugated ketone (1630 cm^{-1}, broad band), hydroxyl (3420cm^{-1}, broad band), and vinyl (900 cm^{-1}) groups. The UV spectrum presented bands at λ_{max}^{EtOH} 228 and 291 nm, which were shifted to λ_{max}^{EtOH} 229 and 338 nm after addition of one drop a NaOH solution, indicating the presence of a diosphenol chromophore.[5]

Table 2 lists the ^1H NMR spectral data of 3b assigned to the corresponding protons by integration, multiplicity and nuclear magnetic double resonance techniques. The smaller value of the coupling constant of one of the protons at C-14 (J= 2.5Hz) indicates its equatorial position (W-type coupling with Heq-12). The presence of two hydroxyl group was confirmed by acetylation of 3a (Ac_2O/DMAP) to yield a diacetyl derivative 3b showing two methyl singlets at 2.02 and 2.24 ppm (acetyl groups) and a double doublet at 5.24 ppm which corresponds to a carbinolic proton deshielded by acetylation (4.04 ppm in 3). The UV spectrum of 3b showed λ_{max}^{EtOH} at 252 nm. The hypsochromic shift observed in the conversion of 3a to 3b confirmed the presence of the diosphenol chromophore in 3a.[5]

The remaining oxygen atom in 3a was assigned to a tetrasubstituted epoxide moiety on the basis of ^{13}C NMR peaks observed at 66.9 (s) and 72.3 (s) ppm. Reduction of 3b with $NaBH_4$ in MeOH at room temp gave mono acetate (3c) (λ_{max}^{EtOH} 228 and 291 nm). The ^{13}C NMR spectral data of 3a and 3b (Table 2) in combination with biogenetic considerations allowed postulation of structure 3a for epoxivellozin.

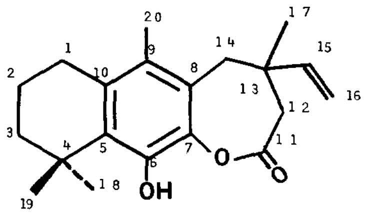
The fact that compound 3a occurs in the same plant with velloziolide 1 allows us to consider 3a as a possible biogenetic precursor for the former diterpenoid.

Table 1. ^{13}C n.m.r. spectral data(δ) for compounds 2b, 3a, 3b, 4 and 5, (TMS as internal standard, in $CDCl_3$)

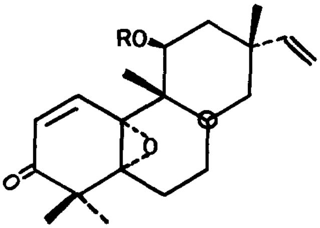
Carbon	2b	3a	3b	4	5
1	145.4	28.1	28.2	25.1	22.4
2	128.4	17.9	17.7	37.1	33.7
3	201.0	37.7	36.7	216.0	213.0
4	48.2	31.8	31.9	47.6	48.9
5	64.3	72.3	70.4	133.1	66.9
6	23.0	189.7	186.9	24.9	22.4
7	23.5	140.2	138.7	27.4	23.1
8	32.7	128.9	143.8	37.7	31.8
9	39.9	45.3	45.4	42.9	42.0
10	68.4	66.9	68.5	136.4	68.9
11	74.7	70.9	72.5	72.9	70.8
12	40.2	44.0	39.0	43.6	43.4
13	38.0	38.0	37.5	37.3	37.4
14	37.0	33.3	33.3	40.5	40.1
15	146.5	143.6	142.5	146.6	145.9
16	113.5	112.9	113.9	112.1	112.3
17	31.1	30.0	29.9	31.1	30.9
18	17.3	23.9	23.4	25.8	18.7
19	24.3	26.2	26.0	23.0	22.4
20	11.2	17.3	19.3	11.6	8.9
COO	169.7	-	169.1 167.8	-	..
CH_3	21.6	-	20.2 21.5	-	..

Table 2. ^1H n.m.r. spectral data (δ) including decoupling experiments for vellozioepoxi 3b (400MHz, TMS as internal standard, in $CDCl_3$)

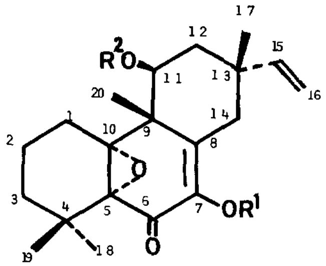
Heq-1: 2.60 (dt, J= 15 and 4Hz)
Hax-1: 1.97 (ddd, J= 15,11 and 5Hz)
2H-2 1.70-1.20
2H-3
Hax-11: 4.05 (dd, J= 11 and 4.4Hz)
Heq-12: 1.78 (ddd, J= 13, 4.4 and 2.5Hz)
Hax-12: 1.68 (dd, J= 13 and 11Hz)
Heq-14: 3.02 (dd, J= 15 and 2.5Hz)
Hax-14: 1.92 (d, J= 15Hz)
H-15: 5.60 (dd, J= 18.0 and 11.3Hz)
H-16: 5.02 (d, J= 18Hz)
H-16: 4.98 (d, J= 11.3Hz)
CH_3-17 1.09 (s)
CH_3-18 1.30 (s)
CH_3-19 1.22 (s)
CH_3-20 1.34 (s)



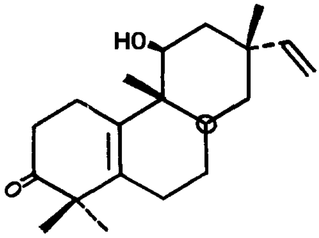
1



2a=H
2b=Ac



3a=R^1=R^2=H
3b=R^1=R^2=Ac
3c=R^1=H, R^2=Ac



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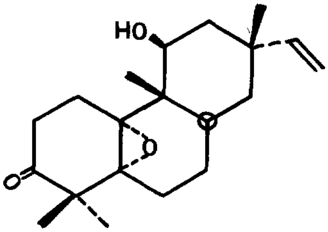

5

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3. $[\alpha]^{\lambda}_{25^{\circ}} = \begin{array}{ccccc} 589 & 578 & 546 & 436 & 365 \\ \hline 0.00 & 0.002 & 0.011 & 0.21 & 1.69 \end{array}$ (c= 1,0 $CHCl_3$)

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