^{13}C NMR OF ISOPIMARANE DITERPENES. PART 4[1] DITERPENES FROM Vellozia patens

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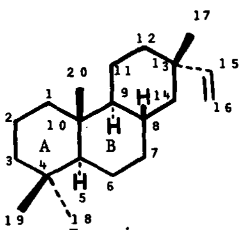
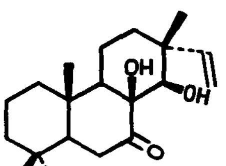
Abstract. The ^{13}C nmr data of six oxygenated diterpenes isolated from Vellozia patens L.B. Smith & Ayensu are reported and the main points useful for their structural assignment are discussed.

As a further contribution in the series "^{13}C nmr of Isopimarane Diterpenes" we analyze the carbon chemical shifts of six isopimarane diterpenoids (1-6) isolated from Vellozia patens[2].



Isopimarane

The chemical shift data of the A ring carbons of these diterpenes are in perfect agreement with those described for analogous compounds in the literature[3].



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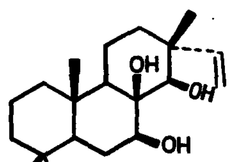

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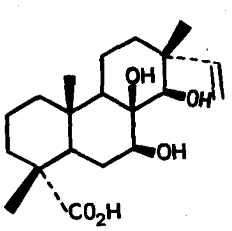

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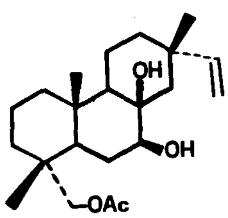

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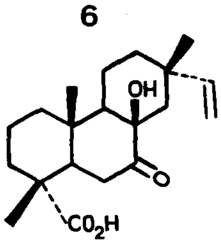

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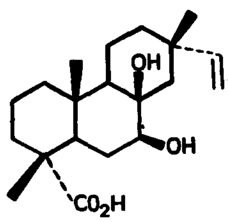

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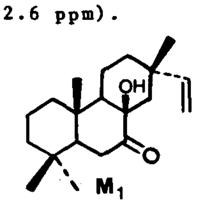
The localization at C-4α of the acetoxymethylene group in 3 as well as of the carboxylic acid function in 4-6 follows, first from the chemical shifts of C-3, C-19 and C-5 which are all, in compounds 3-6, shielded due to a kind of "γ-oxi" shielding effect originated by the oxygenated functions at C-18, and second from the deshielding observed for C-4 due to a net β-effect (Table 1).

Table 1 - ^{13}C nmr chemical shifts of isopimarane diterpenes (1-6)

C/Cpd.	1	2	3	4	5	6
C-1	39.7	39.6	38.8	39.0	38.8	39.1
C-2	18.3	18.3	17.5	17.8	17.9	18.1
C-3	41.7	41.8	35.6	38.0	38.1	37.1*
C-4	33.9	33.0	36.0	47.4	47.2	47.1
C-5	56.5*	53.0	46.7	50.2	47.4	47.5
C-6	35.5	26.0	26.9	37.4*	29.8	29.8
C-7	214.2	79.1	77.2	209.2	77.0	79.4
C-8	76.9	74.3	73.9	76.4	74.2	75.1
C-9	57.3*	55.0	55.1	58.9	55.9	55.1
C-10	36.5	36.9	36.3	36.5	36.3	36.7
C-11	15.7	16.1	16.0	16.7	16.9	16.4
C-12	37.5	37.3	37.2	37.2*	37.2	37.2*
C-13	40.7	42.4	36.7	36.9	36.3	42.2
C-14	74.7	82.1	47.0	42.7	47.4	82.4
C-15	148.0	148.2	151.3	151.4	151.7	142.5
C-16	111.0	113.0	108.3	108.6	108.2	110.6
C-17	17.5	16.1	24.4	24.7	24.4	17.1
C-18	32.9	33.3	72.5	180.0	181.4	180.8
C-19	21.2	21.4	17.5	16.5	16.7	17.0
C-20	15.3	15.1	15.9	15.7	16.0	16.4
CO	-	-	171.0	-	-	-
CH_3	-	-	21.0	-	-	-

The δ values are in ppm downfield from TMS; the solvent was taken in $CDCl_3$ except for 4 and 5 in $CDCl_3/Pyd_5$ and 6 in $(CD_3)_2CO/Pyd_5$; values assigned with an asterisk are interchangeable.

It is worth noting also the deshielding effect observed at C-6 on substitution of the methyl group by carboxylic acid function at C-4α(compounds 1 and 4 (Δδ= + 1.9 ppm); 2 and 6 (Δδ= + 3.8 ppm)resulting most probably from some kind of δ-effect. The same trend is observed when one compares compactone (M_1) with 4 (Δδ= + 2.1 ppm) and compactol (M_2) with 5 (Δδ= + 2.6 ppm).



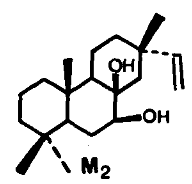


Table 2 - ^{13}C Chemical shifts of model compounds M_1 and M_2[a]

	M_1	M_2		M_1	M_2
C-1	39.8	39.4	C-11	17.1	16.8
C-2	18.6	18.4	C-12	38.3	37.8
C-3	42.0	41.9	C-13	36.7	36.0
C-4	33.8	33.1	C-14	43.0	47.1
C-5	56.2	53.1	C-15	151.7	151.2
C-6	35.3	27.2	C-16	108.7	108.5
C-7	190.9	78.2	C-17	24.9	24.3
C-8	76.5	74.1	C-18	33.0	33.4
C-9	59.1	55.7	C-19	21.3	21.6
C-10	37.7	36.9	C-20	15.5	15.5

[a]The δ values are in ppm downfield from TMS, The solvent was C_5D_5N for M_1 and $CDCl_3$ for M_2.

The most remarkable effects observed for these substances are correlated with the hydroxyl functionalization of C-14. The spatial orientation of this hydroxyl group is determined on basis of the chemical shifts of C-12.

Analysis of the Dreiding models for these diterpoids shows that a β(equatorial) orientation of the hydroxyl group at C-14 precludes the occurrence of a γ-gauche interaction with the hydrogens of C-12. Thus, the chemical shift of this carbon is not affected by the β-hydroxyl functionalization (compare 1 with M_1, 2 with M_2 and 5 with 6).

However, a γ-antiperiplanar effect between the β-hydroxyl group at C-14 and the hydrogen at C-7 would deshield the latter carbon and this is indeed observed (compare 2 with M_2 and 5 with 6). Most probably due to conformational constraints in the C-ring, it is not possible to observe this same effect at C-12. The stereochemistry at C-14 is further corroborated spectroscopically by the shielding effect observed for the C-17 methyl group due to the γ-gauche effect (Table 1) and chemically by the formation of the corresponding acetonide derivatives[2], thus proving the cis relationship between the hydroxyl groups at C-7 and C-14.

The C-7 carbonyl carbon is deshielded in the C-14 hydroxylated compounds, an effect that can be ascribed to an hydrogen bonding interaction between the hydroxyl and the oxygen carbonyl group.

Finally, the deshielding observed in the chemical shifts of C-13 on introduction of an hydroxyl function at C-14 is an effect of utmost importance in the localization of the hydroxyl in this diterpene class.

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References

1. Part III, see A.C. Pinto, W.S. Garcez, P.P.S. Queiroz and A.L. Pereira. An. Acad. brasil. Cienc., paper submitted.

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