The 2-Dimensional INADEQUATE N.M.R. Experiment for Carbon Connectivity Pattern Determination of a New Bis-nor-diterpene

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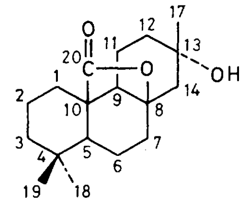
A new bis-nor-diterpene has been isolated from *Vellozia bicolor*; its structure has been established with the help of natural abundance ^{13}C–^{13}C coupling constants observed *via* double quantum coherence.

A phytochemical survey of Brazilian Velloziaceae has permitted recently the isolation, from *Vellozia bicolor* L. B. Smith, of a new bis-nor-diterpene whose structural elucidation and natural abundance one-bond ^{13}C–^{13}C coupling constants are reported here, determined with the help of 'INADEQUATE' n.m.r. experiments.[1,2]

The molecular formula of the bis-nor-diterpene (**1**), m.p. 179—181 °C, $[\alpha]_D^{22}$ $-16.5°$ (*c* 1.08, $CHCl_3$), $C_{18}H_{28}O_3$, was established by microanalysis and by mass spectrometry [m/z 292 ($M^{\cdot+}$)]. Its 400 MHz ^1H n.m.r. spectrum ($CDCl_3$) displayed three methyl singlets at δ 0.92, 0.92, and 1.33, and a number of complex multiplet signals. Carbon-13 n.m.r. spectral analysis of (**1**) was accomplished at 100.62 MHz with a Bruker WM-400 spectrometer using Freeman's 2-dimensional[2] and 1-dimensional[1], 'INADEQUATE' techniques. A solution of (**1**) was prepared in [$^2H_5$]pyridine [470 mg of (**1**) in 2 ml of solvent] and the spectrum, optimized for the 2-dimensional experiment at $^1J_{CC} = 40$ Hz ($J\tau = 1/4$), was accumulated at 60 °C overnight using a relaxation delay of 3.0 s. Quadrature detection in both directions was employed. The spectral width for F_1 was ± 7353 Hz and for F_2 was 7353 Hz. This spectrum has afforded, except for the C-10–C-20 linkage, an unambiguous carbon connectivity pattern as well as precise carbon-13 signal assignments for (**1**) (Table 1).



(**1**)

Table 1. ^{13}C N.m.r. spectral data for (**1**).[a]

Carbon	Chemical shifts/ p.p.m. ($Me_4Si=0$)	Coupled with carbon	One-bond coupling constant/Hz
C-1	28.8	C-2	33.2
		C-10	37.5
C-2	19.0	C-3	33.2
C-3	42.1		
C-4	34.0	C-3	34.2
		C-5	34.2
C-5	50.1		
C-6	21.6	C-5	33.2
C-7	37.2	C-6	33.0
C-8	83.7	C-7	37.3
		C-9	32.5
		C-14	39.4
C-9	54.1	C-11	33.9
C-10	51.0	C-5	29.8
		C-9	31.5
C-11	22.5		
C-12	38.8	C-11	32.4
		C-13	38.3
C-13	68.4		
C-14	47.4	C-13	37.6
C-17	28 0	C-13	38.7
C-18	32.2	C-4	36.0
C-19	20.6	C-4	35.6
C-20	179.7	C-10	not measured

[a] Chemical shifts were measured at 60 °C with respect to the low-field triplet of [$^2H_5$]pyridine (149.9 p.p.m.) and are given for $Me_4Si = 0$. The one-bond coupling constants are shown only once for all coupling pairs at that nucleus where the $^1J_{CC}$ values could be determined more precisely from the 1-dimensional 'INADEQUATE' experiment.

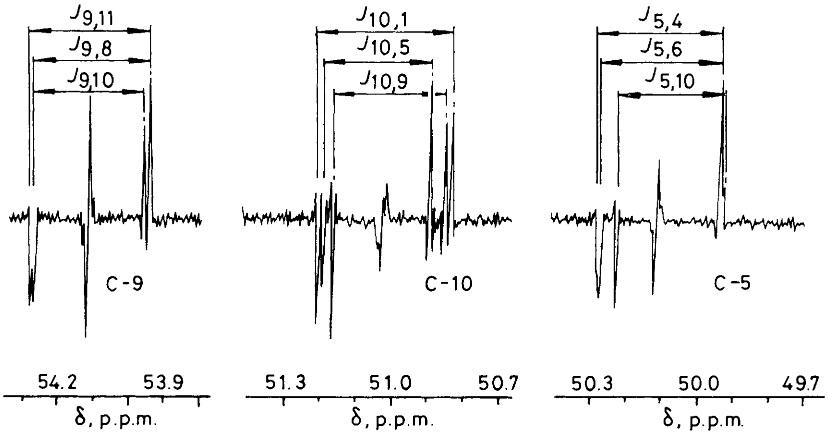


Figure 1. Section of the C-5, C-10, and C-9 signals from the 100.62 MHz 'INADEQUATE' ^{13}C n.m.r. spectrum of (**1**). Satellites due to $J_{5,10}$ and $J_{10,5}$ and those due to $J_{10,9}$ and $J_{9,10}$ exhibit, respectively, strong ($J/\Delta\nu = 0.33$) and weak ($J/\Delta\nu = 0.11$) AB systems. Satellites due to $J_{10,20}$ cannot be detected (see text).

In order to obtain accurate one-bond $^{13}C-^{13}C$ coupling constants, the 1-dimensional 'INADEQUATE' spectrum of (**1**) was also recorded, at 60 °C, overnight, on the sample used in the 2-dimensional experiment. Maximum signal intensity was selected for $^1J_{CC} = 40$ Hz ($J\tau = 1/4$). A frequency range of 7353 Hz was used with a digital resolution of 0.22 Hz/point. Resolution enhancement with the Gaussian multiplication procedure was applied.[3] As a result of the good digital resolution and the assigned carbon-13 resonances *via* the 2-dimensional spectrum, this experiment has permitted the determination of precise one-bond $^{13}C-^{13}C$ coupling constants for all linkages of (**1**) except for C-10–C-20 (Table 1 and Figure 1). The absence of satellite lines corresponding to the C-10–C-20 bond is the consequence of three factors: (a) the expected $^1J_{CC}$ value is considerably larger than 40 Hz for which the pulse sequence was optimized,[1] (b) both carbons involved in this linkage have relatively long T_1 values,[4] (c) the transmitter offset is about 140 p.p.m. away from the carbonyl signal, inducing a reduction of the efficiency of the spin-echo pulse sequence.

Based on these carbon-13 n.m.r. results structure (**1**) should be attributed to the new naturally occurring bis-nor-diterpene. The axial configuration of C-17 of (**1**) was assigned from its 28.0 p.p.m. chemical shift. Taking into account the deshielding *syn*-axial δ-effect[5] on the signal position of C-17 of (**1**), originating from the C-8–oxygen bond, the 28.0 p.p.m. δ-value is consistent with the 25.3 p.p.m. chemical shift of the 1-methyl resonance in *trans*-1-methyl-4-t-butylcyclohexanol.[6]

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