Reference Data

Table 2. ^{13}C NMR data for neomenthyl halides

Carbon	1	2	3
1	28.6 (−)	26.7 (−)	25.9 (−)
2	45.3 (+)	43.9 (+)	43.4 (+)
3	46.6 (−)	60.5 (−)	63.2 (−)
4	49.3 (−)	49.2 (−)	49.1 (−)
5	26.7 (+)	25.0 (+)	24.3 (+)
6	34.8 (+)	34.8 (+)	34.9 (+)
7	21.6 (−)	21.7 (−)	21.9 (−)
8	33.8 (−)	31.3 (−)	30.1 (−)
9	20.4 (−)[a]	20.6 (−)[a]	20.8 (−)[a]
10	20.0 (−)[a]	20.0 (−)[a]	20.0 (−)[a]

[a] Assignments in the same column may be interchanged.

tive to the iodine atom, i.e. the protons are β-antiperiplanar to the halogen. In **1**, H-2α is also antiperiplanar to the iodine atom, but it is secondary and does not experience an unusual upfield shift. Hence it would appear that the proton must be tertiary to exhibit this effect (H-4 in **1** and H-10 in **4** are both tertiary). A previous report raised the question of whether it was necessary for the bromide or iodide to be tertiary to cause these shifts.[5] The present study shows that the halides may also be secondary. Both previous reports[5,6] discussed a number of the factors that should be considered in attempting to explain these unusual upfield shifts, but at this point the reasons are not obvious.

The ^{13}C NMR spectra of **1–3** were obtained to see if they might be of use in explaining the unusual proton shifts observed and the data are recorded in Table 2. The ^{13}C NMR spectra of **1** and **2** are reported here for the first time whereas that of **3** has been reported previously.[7] There is good agreement between our values for **3** and those reported, but our data are included in Table 2 for comparison with the other halides. C-3 becomes progressively more deshielded on going from **1** to **3**, as expected, but the C-4 resonances in the three compounds are remarkably similar and provide no clue as to the reason for the unusual shifts of H-4 in **1** and **2**. Possibly when more compounds which exhibit these shifts are discovered, the reasons for this interesting phenomenon will become more apparent.

EXPERIMENTAL

The iodide **1**,[1] bromide **2**[8] and chloride **3**[9] were prepared using procedures reported previously.

The ^1H and ^{13}C NMR spectra were obtained on a Bruker WH-400 spectrometer operating at 400 and 100.6 MHz, respectively. The probe temperature was maintained at 298 K and the samples (concentration *ca.* 100 mg ml^{-1}) were analysed in 5 mm o.d. tubes with $CDCl_3$ as solvent and TMS as internal standard ($\delta = 0.00$). In Table 1 the proton multiplicities and coupling constants in hertz are given in parentheses. Typical parameters for the ^{13}C NMR spectra were sweep width 29412 Hz, 16K data points, pulse width 9.6 μs (90° pulse) or 19.6 μs (180° pulse), delay 3.0 s, acquisition time 0.28 s, 3.59 Hz per point and line broadening 4.0 Hz. The multiplicities were established by *J* modulation C(H)–APT tests.[10] For these tests the usual $(90\text{–}\tau\text{–}180\text{–}\tau\text{–acquisition–delay})_n$ sequence was used, with $\tau = 0.01$ s and a delay of 3.0 s. This value of τ produced positive quaternary carbon and CH_2 signals and negative CH and CH_3 signals.

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^{13}C NMR Spectra of (*E*)-2-Pyridinecarbaldehyde Pyridin-2′-ylhydrazone and Eight Analogues

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The total assignment of the ^{13}C NMR spectra of (*E*)-2-pyridinecarbaldehyde pyridin-2′-ylhydrazone and eight analogues is reported. The assignment of the spectra was achieved by comparison with data from the hydrazone precursors and other similar compounds.

KEY WORDS ^{13}C NMR *N*-Heterocyclic hydrazones

INTRODUCTION

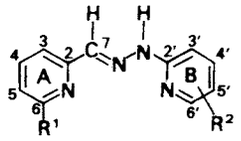
The equilibrium and thermochemical properties of a number of *N*-heterocyclic hydrazones containing the diazapropene moiety (RCH=NNHR, R = pyridyl or substituted pyridyl) have recently been investigated.[1] Accordingly, a number of these hydrazones have been synthesized and their ^{13}C NMR spectra recorded. The hydrazones studied (**1–9**) are listed in Table 1 and the corresponding ^{13}C chemical shifts (δ, ppm) in Table 2; the majority of these spectra are, to our knowledge, the first reported for this class of hydrazone.

EXPERIMENTAL

All proton decoupled ^{13}C NMR spectra were recorded at 25.2 MHz on a JEOL FX100 spectrometer operating in the FT mode. Spectra were measured under the following conditions: 50–100 mg cm^{-3} solution in $CDCl_3$–TMS, probe temperature 25 °C, 5 mm tubes, 8K data points and aquisition time 0.7 s. Compounds **1–9** are in the *E*-isomeric form and were prepared from the appropriately substituted 2-pyridinecarbaldehyde and the appropriately substituted 2-hydrazinopyridine as reported.[2,3]

Reference Data

Table 1. *N*-Heterocyclic hydrazones used



Compound	R^1	R^2	Compound	R^1	R^2
1	H	H	**6**	H	4-CH_3
2	CH_3	H	**7**	H	3-CH_3
3	CH_3	6-CH_3	**8**	H	6-Cl
4	H	6-CH_3	**9**	CH_3	6-Cl
5	H	5-CH_3			

Table 2. ^{13}C NMR chemical shift assignments for (*E*)-2-pyridinecarbaldehyde pyridin-2′-ylhydrazone and analogues (ppm relative to internal TMS in $CDCl_3$ solution)[a]

Compound	C-2 C-2′	C-3 C-3′	C-4 C-4′	C-5 C-5′	C-6 C-6′	C-7	Me Me′
1	*156.7*	119.8	136.3	122.9	149.3	139.2	—
	154.3	107.7	138.3	116.2	147.4	—	—
2	*156.6*	116.8	136.5	122.6	*158.0*	139.7	24.3
	153.6	107.7	138.2	115.8	147.5	—	—
3	*156.6*	116.8	136.5	122.6	*158.0*	139.5	24.4
	153.6	104.4	138.4	115.7	*155.7*	—	24.1
4	*156.7*	119.8	136.3	122.9	149.2	139.1	—
	154.2	104.4	138.5	115.8	*155.7*	—	24.0
5	*154.9*	119.6	136.2	122.7	149.2	139.2	—
	154.6	107.4	138.4	*125.2*	146.8	—	17.7
6	*156.9*	119.8	136.2	122.9	149.6	139.0	—
	154.5	107.9	*149.6*	117.8	149.3	—	21.5
7	*154.0*	120.5	136.4	123.0	149.1	139.2	—
	153.2	*118.1*	140.6	116.2	145.3	—	16.8
8	*156.0*	120.0	136.4	123.4	149.5	140.5	—
	153.6	105.5	140.8	115.7	*149.2*	—	—
9	*156.3*	117.0	136.6	123.0	*158.2*	140.4	24.4
	153.1	105.6	141.3	115.6	*149.2*	—	—

[a] Shifts in italics refer to quaternary carbon atoms.

RESULTS AND DISCUSSION

The ^{13}C NMR spectrum of the parent compound (**1**) has been previously published.[4,5] The results of those studies together with the assignment strategy outlined by Stothers[6] were used to assign the spectra of the parent and analogous (**2–9**) compounds. Each resonance in the spectrum of **1** was assigned by comparison with spectra of the precursors, 2-pyridinecarbaldehyde and 2-hydrazinopyridine, which have been published[6,7] and the results are reproduced in Table 3. This strategy resulted in the assignment of all resonances; however, two resonances which can be initially assigned to the quaternary carbons (italic type in Table 2) C-2 (154.3 ppm) and C-2′ (156.7 ppm) on the same basis require further consideration. An earlier study[5] has reported the ^{13}C NMR spectra of similar types of compounds. In that study, the pyridyl ring B was replaced with a series of substituted non-heterocyclic aromatic rings. As an example, the ^{13}C NMR spectrum of 2-acetylpyridine phenylhydrazone contains a resonance at 156.26 ppm and has been assigned[5] to the substituted carbon on the pyridine ring which is the equivalent of C-2 in **1**. Therefore, the resonances at 156.7 and 154.3 ppm in **1** must be reassigned to C-2 (ring A) and C-2′ (ring B), respectively.

The spectra for the substituted analogues **2–9** are similar to that of the parent compound **1** and were also easily assigned by comparative means. In all cases in which a hydrogen has been replaced with a methyl group, the expected downfield shift[6] of the resonance occurred. The spectra of the chloro-substituted analogues indicate that the resonance of C-6′ has shifted slightly downfield as expected.[6] These observations provide further support for the correct assignment of the resonances in the spectrum of **1**.

Reference Data

Table 3. Literature ^{13}C NMR chemical shift data for 2-pyridinecarbaldehyde and 2-hydrazinopyridine (ppm relative to internal TMS in $CDCl_3$ solution)[a]

Compound	C-2	C-3	C-4	C-5	C-6	Ref.
2-Pyridinecarbaldehyde	*153.3*	121.8	137.7	128.3	150.5	6
2-Hydrazinopyridine	*161.3*	107.1	137.5	114.3	147.5	7

[a] Shifts in italics refer to quaternary carbon atoms.

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Characterization of Cyclonerodiol Isolated from Corn Infested by *Fusarium Moniliforme* Sheld.: One- and Two-Dimensional ^1H and ^{13}C NMR Study

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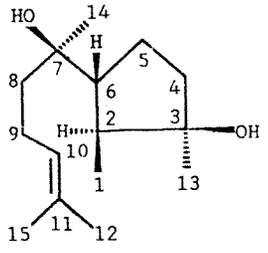
A metabolite extracted from maize culture was identified as cyclonerodiol. Its ^1H and ^{13}C NMR spectra have been fully analysed, and some literature assignments have been reversed.

KEY WORDS Cyclonerodiol ^1H and ^{13}C NMR

INTRODUCTION

During the course of our investigations to identify the mycotoxin(s) of *Fusarium moniliforme* Sheld., involved in the aetiology of equine leukoencephalomalacia (LEM),[1] we have isolated two metabolites.[2] Macrofusin, which is lethal to rats when administered per os, has the same structure as fumonisin B_1,[3] which recently induced LEM in a horse treated intravenously.[4,5] The second metabolite, non-toxic for rats but active on the sodium channel of the frog muscle,[2] was purified from an aqueous extract of a maize culture inoculated with microconidia of *Fusarium moniliforme* (strain 68). In this paper we report the identification of this metabolite as cyclonerodiol[6–9] (**1**), and the complete analysis of the ^1H and ^{13}C NMR spectra of this compound via one- and two-dimensional methods. Some of the previous partial data are revised.



The relative configurations of the asymmetric carbons in the five-membered ring, as established by the present spectroscopic study, are in agreement with those previously postulated on the basis of the biosynthetic pathway.[8]

RESULTS

The ^1H NMR signals cannot be directly assigned, even from a spectrum recorded at 500 MHz, due to extensive overlap. However, the signals corresponding to a double bond bearing two geminal methyl groups and a methylene group are easily recognized. The ^{13}C signals of the corresponding carbons are identified on the basis of their chemical shifts and/or through heteronuclear 2D correlation.[10] The relaxation time, T_1, for the methyl group in the *syn* position vs the methylene group is significantly greater than those of the other methyl groups. Apart from the ethylenic carbons, the complete network of the carbon skeleton was deduced from a 2D INADEQUATE NMR experiment.[11] Connections between pairs of coupled carbons, starting from the easily assigned signal of the 1-methyl carbon, are shown in Fig. 1. To double check the assignments it was ascertained that the mid-points of the lines connecting correlated spins have coordinates $F_1 = 2F_2$. For the pairs C-2, C-6 and C-7, C-14 the double quantum frequencies are fortuitously coincident. The two quaternary aliphatic carbons which show only three connections to other carbon atoms must clearly be linked to heteroatoms.

The resonances of the attached protons were identified by heteronuclear 2D correlation without, at this point, more precise assignment of the signals of the geminal protons at C-4 and C-5. The results are given in Table 1.

When the ^1H NMR spectrum was recorded using dimethyl-d_6 sulphoxide as solvent the signals of the protons were found to