Note

Two-dimensional NMR Investigation of Solanascone

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Solanascone **1** was first isolated from *Nicotiana tabacum* cv. Burley¹⁾ and later obtained as a stress compound of tobacco.²⁾ The structure of **1** has been determined by X-ray analyses of its oxime to be (2*R*,6*S*,7*S*)-trimethyltetracyclo-[6.2.1.1^{5,7}.0^{1,6}]-dodecan-4-one. The present paper describes the assignments of the proton and carbon signals of **1** by 2-D NMR techniques and discusses its conformation.

In the 500 MHz resolution enhanced ¹H NMR spectrum of **1**, each signal of 22 protons was numbered in accordance with the conjugating carbon number. The coupling effects between these signals have been established with 2-D correlated spectroscopy (COSY).³⁾ The contour plot (Fig. 1) shows the correlated spectrum of **1**, which was symmetrized with respect to the diagonal. It clearly shows the spin coupling effects. The spin systems of

1 were classified into three groups. The first spin system (C5~C12) was observed as cross peaks (5, 12), (5, 12') and (12, 12'). The cross peak (12, 15) shows the 4-bond W-coupling between H-12 and H-15 (methyl). The second spin system (C3~C2~C13) was proved by the cross peaks (3, 3'), (2, 3), (2, 3') and (2, 13). The cross peak (3, 13), which shows the 4-bond W-coupling between H-3 and H-13, gives the precise assignment of H-3 (δ 2.09). The remained spin system (C11~C8~C9~C10) was observed as the cross peaks (11, 11'), (11, 8), (11', 8), (8, 9), (9, 10), (11', 10'), (11', 9'), (8, 14) and (11, 14). The signal of H-11', which was strongly deshielded by the carbonyl group at C4 (discussed later), was weakly coupled with H-10'. Although the signal of H-9' was not distinguishable from H-9 by their overlapping, the cross peak (11', 9') suggests the presence of a 4-bond W-coupling between H-11' and H-9'. The remaining cross peaks (8, 14) and (11, 14) show a 5-bond coupling between each proton. The 5-bond coupling between H-8 and H-14 was also clarified by a decoupling experiment using conventional ¹H NMR, but coupling between H-11 and H-14 was not observed. Table I shows the complete assignment of the ¹H NMR spectrum of **1**. Homonuclear spin coupling constants can be most accurately obtained by a cross section through the f1 axis (slices) of a 2-D J spectrum.⁴⁾ In contrast to the normal spectrum, in which some of the long range couplings shown in Fig. 1 could not be observed, those couplings were observed in the slices by the enhanced resolution of these spectra.

The heteronuclear shift-correlated spectrum displays a carbon chemical shift in the horizontal axis and a proton chemical shift in the vertical axis.⁵⁾ The cross peaks show the directly bonded carbon-proton relationships. Extraction of cross sections through each axis allows the

FIG. 1. Correlated Spectrum of **1**.

^1H and ^{13}C spectra to be correlated. The assignment of the carbon signals is summarized in Table II.

In the ^1H NMR spectrum of **1**, two signals of the bridge methylene (H-11, 11') were observed at δ 1.06 and 2.02, respectively. The former appeared as a doublet of doublets

and the latter as a broad doublet due to long range spin couplings which correspond to the cross peaks (10', 11') and (9', 11') in Fig. 1. This type of long range coupling has also been observed in norbornane **2**⁶⁾ and norbornene **3**,⁷⁾ which have a similar bridge ring system to **1**. In **2**, the

TABLE I. PROTON CHEMICAL SHIFTS OF SOLANASCONC

H-No.	Chemical shifts (ppm)	Coupling constants (Hz)
H-2	2.42 (m)	
H-3	2.09 (d,d,d)	$J_{2,3}=6.8$, $J_{3,3'}=11.6$, $J_{3,13}=0.6^a$
H-3'	2.45 (d,d)	$J_{2,3'}=8.4$
H-5	2.53 (d,d)	$J_{5,12}=6.0$, $J_{5,12'}=12.0$
H-8	1.68 (m)	
H-9,9'	1.45 (m)	
H-10	1.25 (m)	$J_{10,10'}=11.9$
H-10'	1.57 (m)	
H-11	1.06 (d,d)	$J_{11,11'}=11.4$, $J_{11,8}=1.3$
H-11'	2.02 (m)	
H-12	2.11 (d,d)	$J_{12,12'}=13.1$, $J_{12,15}=0.5^a$
H-12'	1.89 (d,d)	
H-13 (Me)	1.12 (d)	$J_{13,2}=6.9$
H-14 (Me)	1.30 (d)	$J_{14,8}=1.0^a$
H-15 (Me)	1.03 (s)	

^a Assigned by a 2-D *J*-resolved spectrum.

TABLE II. CARBON CHEMICAL SHIFTS OF SOLANASCONC

Chemical shifts (ppm)	Carbon number
219.3	4
50.8	^a
50.1	^a
49.1	5
46.7	3
46.2	^a
44.5	8
43.0	11
37.3	2
34.8	12
26.6	10
23.7	9
20.5	13
18.2	14
17.8	15

^a Carbon numbers 1, 6 and 7 could not be assigned.

couplings between 7s and 5endo, and 7s and 6endo were observed to be 2~3 Hz, whereas no coupling was observed between 7a and 5endo, and 7a and 6endo. In the ¹H NMR spectrum of **1**, no coupling was observed between H-11 and H-9', and H-11 and H-10'. H-11 and H-11' were observed at δ 1.06 and 2.02, respectively. The shielding of the former and the deshielding of the latter compared to the corresponding proton signal of **2** (H-7 1.2 ppm) can be explained in terms of anisotropy by the C=O group. In their papers on the anisotropic effect of the C=C and C=O functions, ApSimon *et al.*^{8,10)} invoked a modification of the conventional shielding "cone" around the C=O

group that is generally presented in most textbooks.¹¹⁾ The use of ApSimon's model allowed us to explain the strongly deshielded nature of H-11' relative to H-11, and the somewhat deshielded nature of H-3 relative to H-3'. (If the conventional model had been used, these protons would have been shielded.) In addition to the strong deshielding of H-11', the coupling constants between H-2 and H-3, and H-2 and H-3' ($J_{2,3}=6.8$ Hz, $J_{2,3'}=8.4$ Hz) suggest that the conformation of the cyclohexane ring system (C1-C6) was an almost twist boat form (⁴S₆). The 1, 3 diaxial interaction between the 13 and 14 methyl groups is reduced by taking this twist boat conformation.

EXPERIMENTAL

The 500 MHz ¹H NMR spectra were recorded with a Bruker AM 500 spectrometer.

The data size of the time-domain of the correlated spectrum was a 512 × 2K data matrix. To improve the spectral resolution, these data were multiplied in both the f1 and f2 directions with the sinebell function. Fourier transformation was performed with zero filling in both directions.

Hetero nuclear shift correlated spectrum was processed in a similar way. The data size of the time-domain was a 128 × 4K data matrix.

The data size of time-domain of 2D *J* spectrum was 256 × 2K data matrix. To improve the spectral resolution, Fourier transformation was performed with zero filling in both directions.

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