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CARBON-13 NMR SPECTRA OF SOME FURANOSESQUITERPENES, MAJOR COMPONENTS OF *LINDERA STRYCHNIFOLIA*

Kazuo Tori*, Masako Ueyama, Isao Horibe, Youko Tamura and Ken'ichi Takeda

Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, 553 Japan

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The problem of ^{13}C signal assignments in ^{13}C NMR spectroscopy has been very important from the viewpoint of chemical[1] and biosynthetic[2] studies of organic compounds from natural sources. Residual ^{13}C, ^{1}H splittings due to indirect ^{13}C, ^{1}H spin couplings observed in a ^{13}C NMR spectrum with ^{1}H single-frequency off-resonance decoupling (SFORD)[1] have been known to be useful for assigning quaternary carbon signals.[3] However, it seems necessary to accumulate more data on a variety of indirect $J_{C,H}$ values until enough knowledge of its magnitudes is available as for $J_{H,H}$ values.

We present here ^{13}C signal assignments in several furanosesquiterpenes, major components isolated from *Lindera strychnifolia Vill*.[4] It also appears of practical value to report that the magnitudes of residual splittings of quaternary carbon signals in the furan rings showed behaviour different from the usual type.[†] This behaviour will be useful for assigning ^{13}C signals in a number of natural furan-containing compounds.

The natural-abundance ^{13}C FT NMR spectra of lindenenol (**1**), lindenenyl acetate (**2**), their dihydroderivatives (**3**-**5**), linderalactone (**6**), linderane (**7**), and isolinderalactone (**8**) in $CDCl_3$ were measured with ^{1}H noise decoupling, noise off-resonance decoupling (NORD),[6] and SFORD techniques.

The ^{13}C signals for compounds **1** through **5** were assigned using known chemical-shift rules[1] and by examining their SFORD spectra in detail with reference to their ^{1}H NMR spectra in which ^{1}H signal assignments were known.[7] The results are listed in the TABLE. The acetylation shifts observed for C-5, C-6, and C-7 were respectively -3.6, +0.8, and -3.2 ppm from **1** to **2**, and -3.2, +1.7, and -3.0 ppm from **4** to **5**. These shifts allowed differentiation between the C-5 and C-6 and between the C-7 and C-11 signals. The

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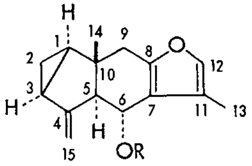
[†] Furans are one of a few heteroaromatic compounds in which $^{2}J_{C,H}$ is greater than $^{3}J_{C,H}$.[5a]

TABLE. ^{13}C Chemical Shift (δ_C) Data in $CDCl_3$[a]

Carbon No.	1	2	3	4	5	6[b]	7[b]	8
C-1	27.4	27.2	28.3	29.1	29.1	130.3 (2.5)	130.0 (1.6)	143.6
C-2	16.6	16.7	16.7	10.9	11.0	25.8 (2.8)	23.0 (1.8)	114.8
C-3	23.1	23.1	26.8	24.5	24.6	26.8 (4.5)	26.6 (2.9)	123.7
C-4	150.0	149.0	39.5	31.9	32.0	135.1 (2.6)	61.3 (6.2)	136.6
C-5	68.4	64.8	71.1	66.1	62.9	151.7 (4.9)	65.6 (4.6)	46.8
C-6	65.1	65.9	67.6	64.2	65.9	74.2 (4.2)	73.2 (2.7)	72.2
C-7	120.9	117.7	121.4	121.3	118.3	115.4 (2.3)	113.7 (1.2)	113.6
C-8	152.5	153.7	152.9	153.1	154.3	152.8 (2.2)	153.2 (1.1)	152.6
C-9	38.4	38.3	39.1	40.8	40.9	40.7 (1.8)	40.4 (0.9)	34.9
C-10	41.3	41.6	43.6	43.6	44.0	130.8 (4.0)	131.6 (1.4)	40.9
C-11	120.1	119.2	119.8	120.1	119.2	122.2 (1.3)	122.2 (0.6)	119.8
C-12	138.5	138.8	138.4	138.2	138.6	137.2 (1.0)	137.1 (0.4)	138.6
C-13	9.1	8.7	9.2	9.1	8.6	8.4 (0.4)	8.3 (0.2)	8.2
C-14	18.2	18.3	20.4	19.8	20.0	15.7 (2.9)	15.8 (1.4)	18.7
C-15	108.0	107.9	17.7	13.6	13.9	173.4 (8.7)	171.5 (5.0)	170.9
$\underline{C}O-CH_3$	-	171.0	-	-	170.7	-	-	-
$CO-\underline{C}H_3$	-	21.1	-	-	21.0	-	-	-

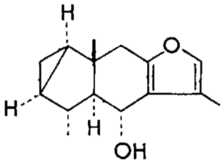
[a] ^{13}C NMR spectra were taken with a Varian NV-14 FT NMR spectrometer (15.087 MHz) in $CDCl_3$ containing TMS as an internal reference at 35° using 8-mm tubes; errors of δ_C are ±0.1. FT measurement conditions are as follows: spectral width, 3923 Hz; pulse flipping angle, 16°; acquisition time, 0.6 sec; number of data points, 4820; number of transients, ca. 5,000 for noise decouplings and ca. 20,000 for SFORD.

[b] Values in parentheses are those for $Eu(fod)_3$-induced shifts at a 0.5 molar ratio of shift reagent to substrate.



1, R = H

2, R = $COCH_3$



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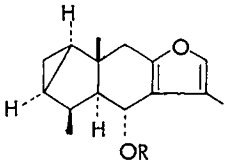
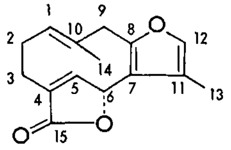


4, R = H

5, R = $COCH_3$



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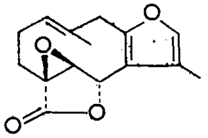

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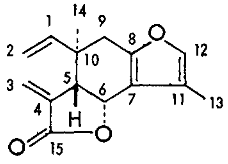

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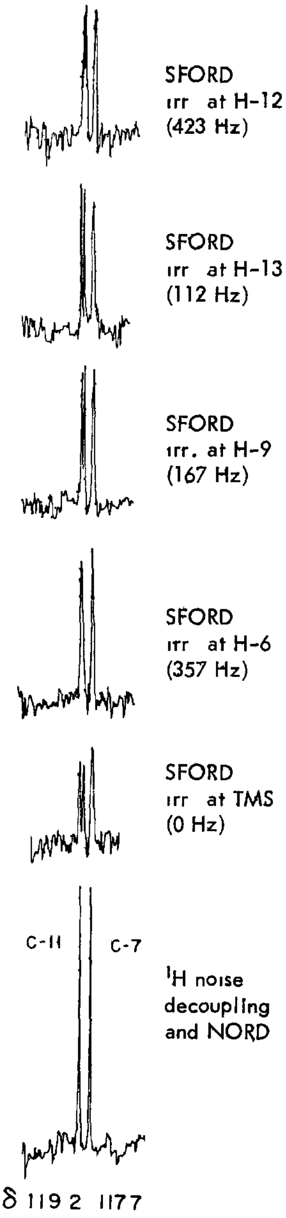
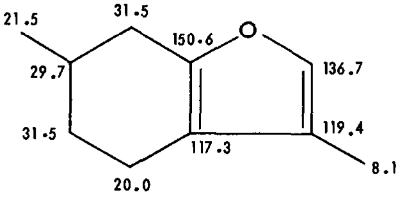


FIGURE. ^{13}C NMR signals due to C-7 and C-11 in 2 with various ^{1}H decouplings.

upfield shifts due to steric γ effects[1] observed for C-2 and C-6 were -5.8 and -3.4 ppm, respectively, on changing from 3 to 4.

The variable-temperature ^{13}C NMR spectra of 6 showed no significant change down to -90° in CD_2Cl_2 and up to +100° in $CDCl_3$, this implies that the ten-membered ring of 6 (and probably of 7) in solution exists as one fixed conformer at the temperatures as suggested earlier by ^{1}H NMR spectroscopy [8,9] The ^{13}C signals in 6 and 7 were assigned on the bases of known chemical-shift rules,[1] detailed SFORD experiments with reference to their ^{1}H NMR spectra,[8,10] and $Eu(fod)_3$-induced shifts.[11] The last method was powerful for differentiating between the C-2 and C-3 and between the C-7 and C-11 signals as the molecular conformations for 6 and 7 had already been revealed [8,10] The assignments as well as the $Eu(fod)_3$-induced shifts are also listed in the TABLE

During the present study, we found in the SFORD spectra of all the compounds examined that the magnitudes of residual splittings due to indirect $J_{C,H}$ are somewhat puzzling in the furan ring signals. Thus, we examined several SFORD spectra of each compound irradiated at $(CH_3)_4Si$, H-6, H-9, H-12, and H-13 signals (for example, see the FIGURE). Initially, the reverse assignments were attempted for the C-7 and C-11 signals closely positioned next to each other, since $^3J_{C,H}$ is generally greater than $^2J_{C,H}$ [1,3] However, it is known that $^2J_{C,H}$ values (ca. 13 Hz) are larger than $^3J_{C,H}$ values (ca. 6 Hz) for furan rings,[5] and also that $^2J_{CCH_3}$ values are considerably larger in olefinic methyl groups [12] By keeping these facts in mind, residual splittings in SFORD spectra of furan derivatives become useful in assigning furan-ring quaternary-carbon signals. For example, we assigned ^{13}C signals of menthofuran (9) and 3,6-dimethyl-5-hydroxybenzofuran (10) Finally, the ^{13}C signals of 8 were assigned as listed in the TABLE, this was quite straightforward



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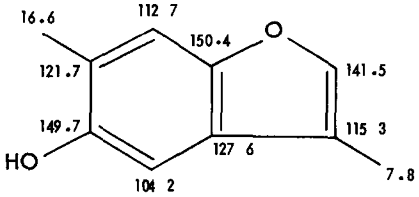

10

δC values

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