

CARBON-13 NMR SPECTRA OF JUGLONE, NAPHTHAZARIN AND THEIR DERIVATIVES

Masaaki Kobayashi, Yoshihiro Terui, Kazuo Tori and Naoki Tsuji\*

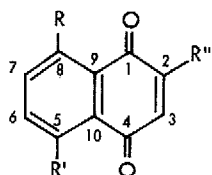
Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, 553 Japan

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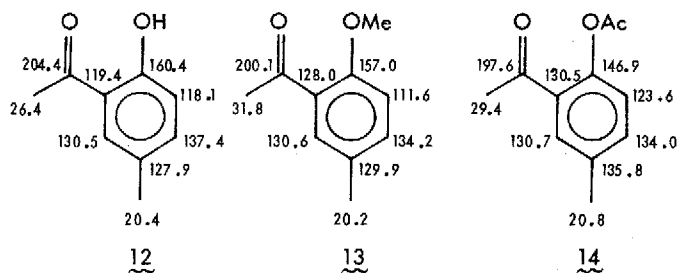
A number of naturally occurring quinones have been reported.<sup>1,2</sup> In the course of our chemical studies of microbial quinone antibiotics,<sup>2</sup> we have frequently encountered peri-hydroxy-p-naphthoquinone moieties. Carbon-13 NMR spectroscopy<sup>3</sup> promises to be a powerful tool for determining structures and studying biosyntheses of this kind of antibiotic, if some fundamental <sup>13</sup>C chemical-shift  $\delta_C$  data on peri-hydroxy-p-naphthoquinones are available together with values for the methylation and acetylation shifts.

We report here  $\delta_C$  data for 1,4-naphthoquinone (1), vitamin K<sub>3</sub> (2), juglone (3), naphthazarin (6), and their methyl ethers and acetates (4, 5, 7-11). The <sup>13</sup>C signals were assigned by using <sup>1</sup>H-noise,<sup>3</sup> noise off-resonance,<sup>4</sup> and single-frequency off-resonance<sup>3</sup> decoupling techniques, with known chemical-shift rules including hydrogen bonding shift for a carbonyl group,<sup>3</sup> by comparison of  $\delta_C$  values from compound to compound, and by employing an NMR shift reagent,<sup>5</sup> Yb(fod)<sub>3</sub>, for 3 and 4, and deuteration effects<sup>6</sup> of peri-OH by an addition of D<sub>2</sub>O for 7 and 9.

Chemical-shift comparisons with those of o-hydroxyacetophenone derivatives (12-14) were extremely useful. TABLE 1 summarizes the  $\delta_C$  data thus obtained. The additivity of substituent chemical-shifts (see



- 1: R = R' = R'' = H
- 2: R = R' = H, R'' = Me
- 3: R = OH, R' = R'' = H
- 4: R = OMe, R' = R'' = H
- 5: R = OAc, R' = R'' = H
- 6: R = R' = OH, R'' = H
- 7: R = OMe, R' = OH, R'' = H
- 8: R = R' = OMe, R'' = H
- 9: R = OAc, R' = OH, R'' = H
- 10: R = R' = OAc, R'' = H
- 11: R = OMe, R' = OAc, R'' = H



$\delta_C$  values

TABLE 1.  $^{13}\text{C}$  Chemical Shift Data,  $^a \delta_{\text{C}}$ 

Carbon No.	1	2	3	4	5	6	7	8	9	10	11
1	184.6	184.9	190.0	184.0	184.0 <sup>c</sup>	172.9	183.3	184.8	182.9	183.1	184.1
2	138.5	147.8	138.4	136.2	137.2	134.6	136.4	138.4	137.5	138.5	137.2
3	138.5	135.4	139.3	140.9	139.7	134.6	141.7	138.4	140.6	138.5	139.5
4	184.6	184.3	183.9	185.0	183.5 <sup>c</sup>	172.9	190.5	184.8	190.0	183.1	183.8
5	126.2	125.8 <sup>c</sup>	118.9	118.3 <sup>c</sup>	124.9	172.9	156.6 <sup>b</sup>	153.7	160.2 <sup>b</sup>	147.6	142.7
6	133.6	133.3	136.4	134.8	134.7	134.6	126.8	120.5	126.2	130.9	131.0
7	133.6	133.3	124.2	119.3 <sup>c</sup>	129.6	134.6	123.6	120.5	133.3	130.9	119.3
8	126.2	126.2 <sup>c</sup>	161.2	159.9	149.2	172.9	154.0	153.7	142.9	147.6	157.8
9	131.7	131.9	114.8	120.3	123.3	111.9	117.5 <sup>c</sup>	120.9	121.8	124.4	120.4
10	131.7	131.9	131.5	134.4	133.4	111.9	114.8 <sup>c</sup>	120.9	114.8	124.4	124.5
OMe		16.3(2-Me)		56.6			56.9	57.0			56.8
COMe					21.0				21.0	21.0	21.0
COMe					169.2				169.4	169.2	169.9

<sup>a</sup> Natural-abundance  $^{13}\text{C}$  FT NMR spectra were recorded on a Varian NV-14 FT NMR spectrometer at 15.087 MHz using about 0.2–0.5 mmol  $\text{cm}^{-3}$  solutions in  $\text{CDCl}_3$  and 8-mm spinning tubes; errors of  $\delta_{\text{C}}$  (from internal TMS) are about  $\pm 0.1$ . FT measurement conditions are as follows: spectral width, 3923 Hz; pulse flipping angle,  $8^\circ$ ; acquisition time, 0.6 sec; number of data points, 4820. <sup>b</sup> An upfield shift of about -0.4 ppm was observed when  $\text{D}_2\text{O}$  was added to the  $\text{CDCl}_3$  solution. <sup>c</sup> These assignments may be reversed in each column.

TABLE 2.  $^{13}\text{C}$  Substituent Chemical Shifts,  $\Delta\delta$  in ppm<sup>a</sup>, for 1

Substituent	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
8-OH	+5.4	-0.1	+0.8	-0.7	-7.3	+2.8	-9.4	+35.0	-16.9	-0.2
8-OMe	+0.6	-2.3	+2.4	+0.4	-7.9 <sup>c</sup>	+1.2	-14.3 <sup>c</sup>	+33.7	-11.4	+2.7
	(-6.0)	-2.2	+1.6	+1.1	-0.6 <sup>c</sup>	-1.6	-4.9 <sup>c</sup>	-1.3	+5.5	+2.5) <sup>b</sup>
8-OAc	-0.6 <sup>c</sup>	-1.3	+1.2	-1.1 <sup>c</sup>	-1.3	+1.1	-4.0	+23.0	-8.4	+1.7
	(-6.0 <sup>c</sup> )	-1.2	+0.4	-0.4 <sup>c</sup>	+6.0	-1.7	+5.4	-12.0	+8.5	+1.9) <sup>b</sup>

<sup>a</sup> Plus sign denotes a downfield shift. <sup>b</sup> Values in parentheses are the methylation or acetylation shifts. <sup>c</sup> These values should be changed if the signal assignments are reversed.

TABLE 2) holds fairly well except for 6, where a delocalized-electronic structure is dominant.<sup>7</sup> It should be noted that the shift reagent complexed preferentially to the 4-CO rather than the 1-CO in 3.

Some applications of the present results will be published later.

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