¹³C-Nuclear Magnetic Resonance Study of 1,2- and 1,4-Naphthoquinones and their Derivatives

F.W. Ribeiro, M.C.F.R. Pinto and A.V. Pinto*

Núcleo de Pesquisas de Produtos Naturais-UFRJ, 21941 Rio de Janeiro, RJ, Brasil

C.G.T. de Oliveira and V. F. Ferreira

Instituto de Química-UFF, Valonguinho, 24000 Niterói, RJ, Brasil

Received: August 22,1989; November 20,1989

Foram registrados os espectros de ¹³C-NMR de 21 diferentes derivados de naftoquinonas substituídas possuindo anéis de furano, diidrofurano e pirano ligados à estrutura de 1,2 ou 1,4-naftoquinonas. A análise dos espectros mostra que o deslocamento químico do C-3 (séries 1,4) e C-1 (séries 1,2) dependem do tamanho do anel heterocíclico. Esses sinais podem ser usados para distinguirmos entre *orto* de paraquinonas e diidrofurano de piranonaftoquinonas.

The ¹³C NMR spectra of 21 differently substituted naphthoquinone derivatives having furan, dihydrofuran and pyran rings attached to a 1,2 or 1,4-naphthoquinone skeleton have been recorded. Analysis of these spectra has shown that the chemical shift of C-3 (1,4 series) and C-1 (1,2 series) depends on the size of the heterocyclic ring. These signals can be used as a probe distinguishing between *ortho* and *para*-quinones and of dihydrofuran from pyranonaphthoquinones.

Key Words: naphthoquinones, naphthopyrandiones, naphthofurandiones.

Introduction

During previous work dealing with a program of synthesis of biologically active naphthoquinones¹ and ¹³C NMR spectroscopy of numerous compounds of this class², we undertook a ¹³C NMR study of 1,2- and 1,4-naphthofurandiones and 1,2- and 1,4-naphtopyrandiones (Fig. and Table 1). Although some reports³⁻⁵ on the ¹³C NMR spectra of naphthoquinones have appeared, to our knowledge there is no exclusive report of such studies on naphthofurandiones and naphthopyrandiones. The information derived from the spectral analysis of compounds 1-21 can be used to differentiate between *ortho* and *para*-substituted isomers and establish the size of the heterocyclic ring attached on the naphthoquinone moieties.

Experimental

The preparation of the compounds studied in this work has been reported elsewhere^{1,2}. All spectra were obtained with the use of pulsed Fourier transform techniques. The carbon chemical shifts were measured downfield from TMS, in CDC ℓ_3 solution in 5mm tubes (100 mg/m ℓ). The pulse width was 20 μ s, corresponding to a field angle of 45 degrees, and the spectra were recorded at 25.5 MHz on a Varian XL-100 spectrometer. The numbering systems utilized are shown in compounds 1, 12 and 14 (Fig. 1).

Results and Conclusions

In order to use ¹³C NMR analysis to determine posi-

tion and size of the attached ring, it is necessary to find a probe which can be easily located in the ¹³C NMR spectra, has an unambiguous assignment and is distant from other functional groups. The carbon C-13 in furan or pyran of the 1,4-series, corresponding to C-1 in the 1,2-series, proved to be the most satisfactory for this purpose. A deshielding effect of ca. 7 ppm in the 1,2-naphthoquinones series (e.g., 13) as compared to the 1,4-series (e.g., 15) was observed. This increase in the δ value may be due to better conjugation with the carbonyl in the 1,2-series. The size of the heterocyclic ring also affects these carbons and a smaller deshielding effect of ca. 5 ppm in 1,4-naphthopyrandiones compared with 1,4-naphthofurandiones (e.g. 9 and 12) was observed. The same effect was present in the 1,2-series. The orientation of the methyl group attached to C-15 is syn to the group in C-12 (compounds 10, 12, 15, and 16) due to a γ -effect.

The magnitude of the observed effect for these two carbons is sufficiently large to make it useful for distinguishing between *ortho* and *para*-naphthoquinones with a furan or pyran ring attached to them.

Acknowledgement

This work is part of the MSc Thesis of C.G.T. de Oliveira and of V.F. Ferreira submitted to the NPPN-UFRJ; it was supported by the CNPq, CEPG-UFRJ and FINEP. The authors are grateful to Prof. A.J.R. da Silva, Central Analítica/NPPN-UFRJ, for the ¹³C NMR spectra.

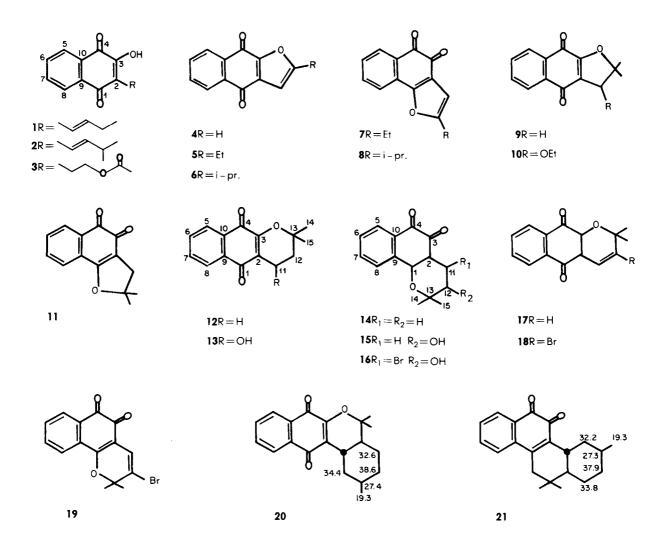


Table 1. ¹³C chemical shifts (δ) in ppm of naphthoquinones studied (ppm relative to internal TMS in CDCl₃ solution).

			-																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
C-1	184.0	184.0	184.0	180.2	180.5	180.4	159.2	159.5	182.1	182.2	168.5	183.4	185.3	161.7	159.9	161.6	181.3	180.1	160.4	183.7	161.2
C-2	118.6	118.6	119.8	130.3	131.5	131.2	122.3	122.2	123.2	123.2	114.8	119.8	120.2	112.4	111.0	113.4	117.6	117.8	112.3	123.4	116.4
C-3	151.1	151.1	154.1	152.5	151.4	151.2	174.1	174.1	158.6	160.0	175.3	154.1	154.4	178.8	177.7	178.5	152.1	150.5	174.1	153.8	178.0
C-4	181.1	181.1	180.9	178.3	178.2	178.2	181.0	181.0	177.9	178.6	180.9	179.1	179.6	179.3	178.8	178.8	179.3	178.8	178.6	179.6	179.8
C-5	125.7	125.7	126.6	126.4	126.6	126.4	135.1	135.1	125.9	126.0	134.4	125.8	126.2	134.6	134.7	135.0	125.9	126.0	135.0	125.6	134.6
C-6	132.8	132.8	132.8	133.7	133.6	133.5	130.1	130.0	132.6	132.7	132.1	132.5	133.1	130.4	130.6	131.9	132.9	133.8	131.6	132.5	132.5
C-7	134.6	134.6	134.6	133.7	133.3	133.2	129.6	129.6	133.9	134.2	128.9	133.5	133.9	127.9	127.6	128.9	133.7	133.4	128.9	133.5	127.8
C-8							121.8														
C-9	132.6	132.3	132.6	132.3	132.4	131.7	130.0	129.9	132.8	133.0	127.6	131.6	131.6	129.7	129.5	130.2	131.2	131.1	130.1	132.3	130.0
C-10	129.3	129.3	129.3	133.0	132.9	132.4	128.4	128.5	131.4	131.4	130.5	130.8	130.6	132.3	131.6	130.7	131.2	130.9	130.6	130.6	130.3
C-11	117.7	115.8	23.1	108.5	103.3	102.1	102.8	101.6	40.0	83.3	39.1	16.6	59.6	16.0	24.9	67.0	115.2	118.9	118.8	35.5	35.1
C-12	145.2	150.2	62.1	148.4	165.6	169.3	161.3	165.2	91.8	93.9	93.6	26.5	39.5	31.4	66.5	55.5	130.6	134.3	120.4	47.9	47.8
C-13	28.0	33.4	170.3		21.7	28.3	21.3	27.8	28.3	26.4	28.3	77.8	78.4	79.2	81.4	83.0	80.2	83.8	85.5	81.1	82.3
C-14	13.3	22.2	20.7	_	16.6	20.6	11.6	20.7	28.3	20.4	28.3	26.5	26.9	26.6	21.3	26.9	28.3	26.9	27.3	26.8	27.0
C-15	_	22.2		_	_	20.6	_	20.7	~	67.4	_	26.5	26.9	26.6	24.9	23.3	28.3	26.9	27.3	22.2	22.2
C-16	_		_	_	_	_	_	_		15.3	_	_	_		_		_	_			_

References

- A.V. Pinto, V.F. Ferreira, M.C.R. Pinto, R.S. Capella, B. Gilbert and J.S. da Silva; *Trans. Roy. Soc. Trop. Med. Hyg.* 81, 609 (1987).
- A.V. Pinto, V.F. Ferreira, M.C.R. Pinto, C.A.C. Ferreira, R.S. Lopes and A.J.R. da Silva, An. Acad. brasil. Ciênc. 59, 5 (1987).
- 3. G. Hofle, Tetrahedron, 33, 1963 (1970).
- 4. I.A. McDonald, T.J. Simpson and A.F. Sierakowiski, Aust. J. Chem. 30, 1727 (1977).
- 5 D.X.M. Donnelly and J.O. Reilly, *Phytochemistry* 19, 27 (1980).