Rotenone NMR Assignments

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Complete and unambiguous ^{13}C nmr assignments for rotenone have been determined and are presented along with proton nmr data.

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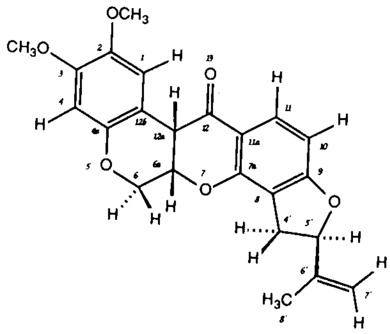
Rotenone, **1**, is increasingly used in many laboratories to demonstrate [1,2] 2D nmr pulse experiments.



However, conflicting ^{13}C nmr assignments appear in the literature [3,4]. In reference [4], the list of carbon shifts for rotenone [4, Table 1] even differs from the assignments on the spectrum [4, Figure 2]. Complete proton assignments have not, to our knowledge, been previously published.

During our investigations of new (and established) 2D nmr sequences, it became essential to have accurate assignments for all carbon and proton resonances. We found the assignments in reference [3] to be correct although two resonances (for carbons 7a and 11a) differed by more than the usual ±0.1 ppm from our own data - this may simply be due to concentration differences. Additionally, we assigned the 2-methoxyl and 3-methoxyl proton

Table 1

^{13}C NMR Data for Rotenone, **1**

Carbon	Chemical Shift [a]	[b]	[c]	[d]	Long rang correlations observed [e]
1	110.1	110.4	110.4	**110.3**	
2	*157.4*	143.4	143.9	**143.8**	2-OMe (3), 4 (3), 1 (2)
3	*166.8*	*147.0*	149.5	**149.4**	3-OMe (3), 1 (3)
4	100.6	100.6	100.9	**100.8**	
4a	*143.4*	*149.0*	147.4	**147.3**	6β (3), 4 (2), 1 (3)
6	65.9	65.9	66.3	**66.2**	
6a	71.8	71.8	72.2	**72.1**	6β (2)
7a	*147.0*	157.4	156.1	**157.9**	11 (3)
8	112.9	112.9	113.0	**112.9**	10 (3), 4'β (2), 4'α (2)
9	*149.0*	166.8	167.4	**167.3**	11 (3)
10	104.4	104.4	104.7	**104.8**	
11	129.4	129.4	130.0	**129.9**	
11a	113.1	113.1	114.7	**113.3**	10 (3)
12	188.3	188.9	188.9	**188.9**	12a (2)
12a	44.1	44.1	44.6	**44.5**	
12b	104.5	104.5	104.7	**104.8**	12a (2), 6a (3), 4 (3)
4'	30.9	30.9	31.3	**31.2**	
5'	87.3	87.3	87.8	**87.8**	8' (3), 7'*syn* (3), 7'*anti* (3)
6'	142.6	142.6	143.0	**143.0**	8' (2)
7'	112.5	112.5	112.6	**112.5**	8' (3)
8'	16.7	16.7	17.2	**17.1**	7'*syn* (3), 7'*anti* (3)
2-OMe	*55.3*	*53.3*	55.8}	**56.2**	
3-OMe	*55.9*	*55.9*	56.3}	**55.8**	

[a] Reference [4], Table 1. [b] Reference [4], Figure 2. [c] Reference [3]. [d] Our assignments. [e] Correlations from the carbon to the proton(s) indicated; coupling through the number of bonds indicated in brackets, (2) or (3).

Note: Table entries in italics type are at variance with our assignments.

Table 2

^{1}H NMR Data for Rotenone, **1**

Proton	δ	mult [a]	J's
1	1.72	d	1.0 (12a)
4	6.40	s	
6α	4.13	ddd	12.1 (6β), 1.0 (6a), 1.0 (12a)
6β	4.56	dd	12.1 (6α), 3.1 (6a)
6a	4.89	d+	unresolved from 7'*syn* [b]
10	6.46	d	8.6 (11)
11	7.79	dt	8.6 (10), 0.7 (4'α), 0.7 (4'β)
12a	3.79	ddd	4.1 (6a), 1.0 (1), 1.0 (6α)
4'α	2.91	ddd+	15.8 (4'β), 8.1 (5'), 0.7 (11) [b]
4'β	3.27	ddd+	15.8 (4'α), 9.8 (5'), 0.7 (11) [b]
5'	5.19	dd+	9.8 (4'β), 8.1 (4'α) [b]
7'*syn*	4.89	m	unresolved from 6a [b]
7'*anti*	5.03	m	[b]
8'	1.72	dd	1.5 (7'*anti*), 0.9 (7'*syn*)
2-OMe	3.72	s	
3-OMe	3.76	s	

[a] Multiplicity assignments s, d, t, m, *etc.* have normal meanings; + signifies additional small couplings were present but not assigned. [b] Unresolved couplings or other couplings < 1 Hz present.

resonances unequivocally by proton-proton 2D nOe (the 2-methoxyl protons correlated with proton 1, and the 3-methoxyl protons with proton 4). 2D C-H correlation lead to the corresponding ^{13}C assignments. NOESY (2D nOe) also suggested the proton assignments for 4'α *vs* 4'β, 6α *vs* 6β, and 7'*syn* (*syn* to the methyl) *vs* 7'*anti*: 4'α correlated with 8', 7'*syn* with 8', 7'*anti* with 5', 6α with 12a and 6a.

Table 1 lists the carbon assignments from previous literature along with our own (which were substantiated with evidence from 2D experiments). Table 2 lists the proton assignments.

EXPERIMENTAL

Rotenone, **1** was obtained commercially (Aldrich) and used without purification. For ^{13}C nmr experiments (proton-decoupled carbon, 2D C-H (1-bond) correlation, and a variety of 2D long-range C-H (2- and 3-bond) correlation experiments, 70 mg, and for proton experiments (COSY, NOESY) 5 mg, was dissolved in about 500 μl of deuteriochloroform. Both samples were degassed by several freeze-pump-thaw cycles and sealed to assure reproducible results.

Spectra were obtained on both a home-built 300 MHz instrument and a Bruker AM-500 instrument at ambient probe temperature (*ca.* 22°). The ^{13}C spectra were referenced to the central deuteriochloroform peak (δ 77.04 ppm) and ^{1}H spectra to residual chloroform (δ 7.24 ppm).

REFERENCES AND NOTES

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