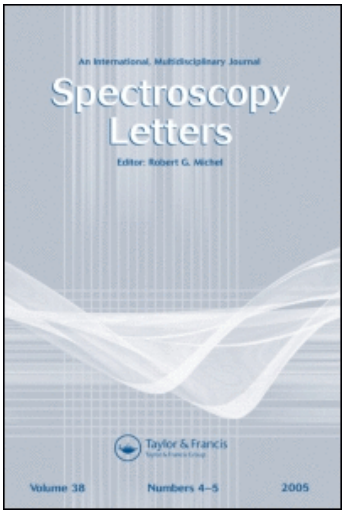

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Complete Carton-13 Assignments of the Sesquiterpene Lactone 11,13,-Dihydroparthenolide Using 2D-Inadequate

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COMPLETE CARBON-13 ASSIGNMENTS OF THE SESQUITERPENE LACTONE 11,13 - DIHYDROPARTHENOLIDE USING 2D-INADEQUATE

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Key Words: 11,13-dihydroparthenolide, sesquiterpene lactone, germacrolide, NMR, 2D-INADEQUATE.

ABSTRACT: The complete ^{13}C NMR resonances for the sesquiterpene lactone 11,13-dihydroparthenolide were established by the application of 2D-INADEQUATE.

INTRODUCTION

Sesquiterpene lactones are a major class of terpenoids which commonly occur in the Asteraceae (Compositae) as well as some angiosperm and gymnosperm families[1,2]. The allelopathic germacrolide-4-epoxide, 11,13-dihydroparthenolide, was isolated from Ambrosia artemisiifolia (common ragweed)[3,4]. It lacks the common α-methylene moiety in the γ-lactone ring which is the proposed receptor site for biological nucleophiles and is therefore responsible for a wide spectrum of biological activities[5,6].

Unambigeous ^{13}C NMR spectral assignments of germacrolides have in the past been difficult due to of the proximity of the methylene resonances in the ^{13}C NMR spectrum and the complexity of the ^{1}H NMR absorptions. Carbon-carbon shift correlation spectroscopy (2D-INADEQUATE), although a non-sensitive technique, has been possible using high field NMR instruments, providing direct information on the molecular framework and allowing unambiguous assignment of all ^{13}C NMR resonances[7,8]. The interpretation of a 2D-INADEQUATE spectrum and complete ^{13}C NMR spectral assignments for 11,13-dihydroparthenolide are described below.

^{13}C NMR SPECTRAL ASSIGNMENTS OF 11,13 DIHYDROPARTHENOLIDE (1)

Unequivocal assignments for all skeletal carbon resonances of 11,13-dihydroparthenolide (**1**) were made by the application of two-dimensional carbon-carbon chemical shift correlation 2D-INADEQUATE (Incredible Natural Abundance DoubIE Quantum Transfer Experiment)[7,8]. The 2D-Inadequate experiment, when applicable, provides direct information about the molecular framework.

Figure 1 shows a "carbon-carbon connectivity plot" of **1**, in which the vertical axis is the "f_1" dimension (double quantum frequency) and the horizontal axis gives the "f_2" dimension (chemical shift). In practice, if two carbon sites are directly bonded, they will both show the same double quantum frequency in f_1, and will appear equally spaced on both sides of the line $f_1 = -2\ f_2$[7]. By this method all carbon-carbon connectivities of the molecular framework of a molecule can be established.

Of course, a complete structural determination requires knowledge of the stereochemistry. This can be done by the use of 2D homo and heteronuclear shift correlation spectroscopy, nuclear Overhauser effect studies as well as determination of coupling constants using modern nmr techniques[7-10].

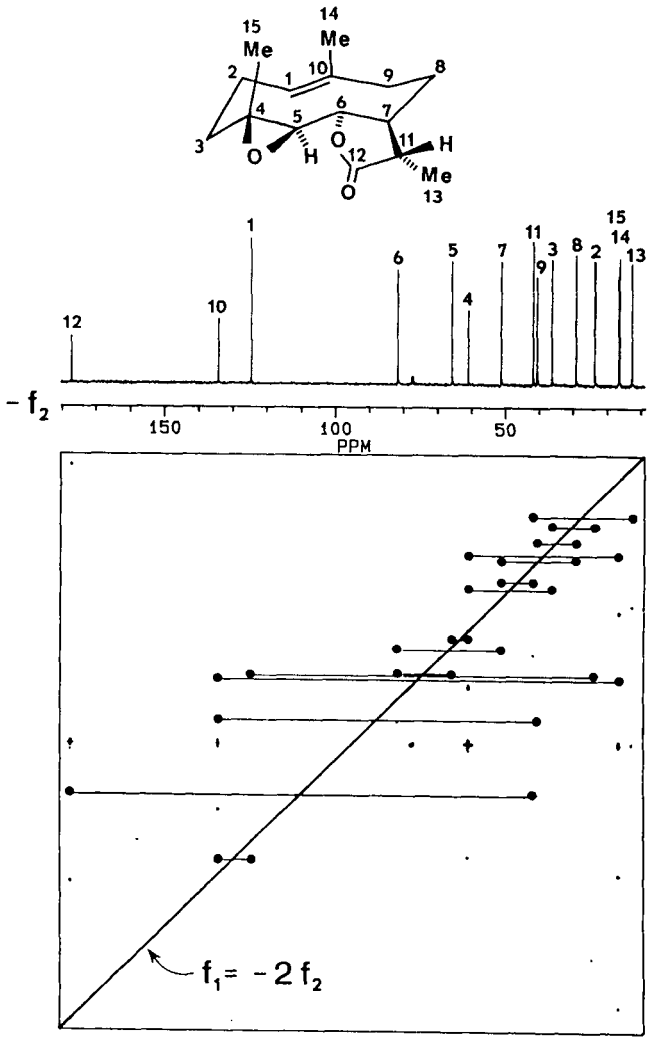

FIG 1. Accentuated Carbon-carbon connectivity plot of 11,13 Dihydroparthenolide 1.Carbons sharing the same quantum frequency f_1 appear equally spaced on both sides of the line $f_1 = -2f_2$.

TABLE

	^{13}C Assignment		
	δ^a	m^b	$T_1{}^c$
1	125.0	d	0.60
2	24.0	t	0.44
3	36.6	t	0.36
4	61.3	s	4.82
5	66.6	d	0.55
6	82.0	d	0.50
7	51.8	d	0.57
8	29.7	t	0.33
9	41.0	t	0.37
10	134.4	s	2.88
11	42.3	d	0.57
12	177.2	s	5.83
13	13.1	q	0.90
14	16.7	q	1.93
15	17.0	q	2.13

[a] δ ppm, relative to TMS.

[b] Based on DEPT method[10].

[c] Based on Inverse Recovery Technique[11]. Recycle delay 1 min.

EXPERIMENTAL

A 5 M $CDCl_3$ solution of 11,13-dihydroparthenolide was used in all experiments. The spectra were acquired at 298°K using a 5mm dual tuned $^1H/^{13}C$ probe with observation frequencies of 400.13 and 100.62 MHz, respectively on a BRUKER AM400 instrument. The 2D-INADEQUATE experiment was performed using a Ernst-type phase cycle with the following pulse sequence:[12]

D1-90-D2-180-D2-90-τ-120-FID

The data was acquired in 20h with D1=2 sec; IN=0.000029 sec; τ=0.000003 sec; D2=0.0035 sec; NE=504, NS=64. The recycle delay, D1, was based on T_1 values obtained from the INVRECX technique and D2=(2N+1)/4 J_{CC}; N=0 to avoid loss of sensitivity and long range effects, and J=72 based on carbon-carbon coupling constants of similar compounds derived from biosynthetic studies[13].

The data was processed with Gaussian multiplication in both dimensions (LB2=GB2=0, LB1=-20.0, GB1=0.5). Zero filling and magnitude calculation (MC) in the second dimension prior to the Fourier transformation resulted in a 1K x 1K real data point matrix used to establish the carbon-carbon connectivities.

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