Spectroscopic Study of Grilactone

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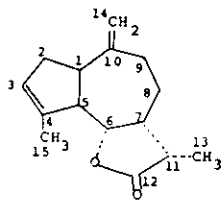
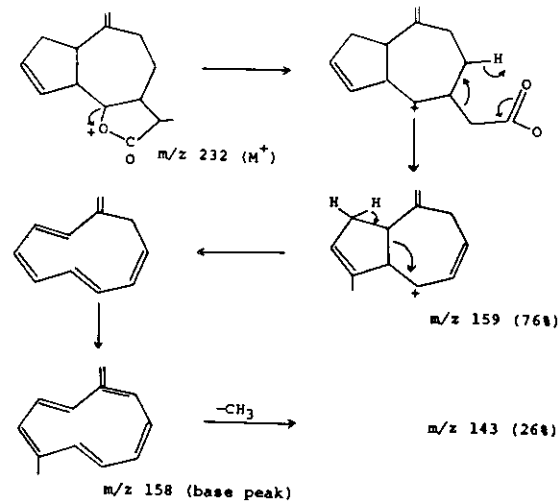
The guaianolide grilactone was first isolated by Kir'yalov from Ferula grigoriewii but the structures proposed by him [1,2] were erroneous. The correct structure (1) of this sesquiterpene lactone, isolated from Ferula oopoda was established by Malone and co-workers [3] through X-ray diffraction studies.



(1)

Grilactone has a very unusual stereochemical configuration of the lactone ring at C-7. Since the ^{13}C-nmr spectral data of very few guianolides, particularly of those with a methyl rather than an exocyclic methylene attached to C-11, have been recorded, we isolated this lactone from F.oopoda and scanned the ^{13}C-nmr of grilactone in $CDCl_3$ with MW 400 (Bruker) spectrometer at 100 MHz. The chemical shifts and the assignment are produced in table I. The assignments were made from the known chemical shifts of similar compounds for example pachydictyol A [4] and dihydrocostus lactone [5] as well as from the gated spin echo (GASPE) spectrum, in which the primary (CH_3) and tertiary (CH) carbon peaks are upright, whereas the secondary (CH_2) and quarternary (C=O, -C = and -C-) carbon peaks are inverted.

The PMR data are partly available in literature [2,3]. Table II reproduces full proton nmr data. The



assignments have been made with the help of spin decoupling and ^{1}H shift correlated 2D nmr (COSY) experiments (fig.1).

Table-I: ^{13}C-NMR data of Grilactone (25.1 MHz) in $CHCl_3$

Carbon number	Chemical shift	Carbon number	Chemical shift
1	47.67	9	33.78*
2	34.60*	10	147.67
3	125.44	11	38.91
4	142.44	12	179.28
5	51.94	13	10.99
6	84.38	14	111.91
7	37.97	15	17.27
8	19.37		

*Assignments may be reversed.

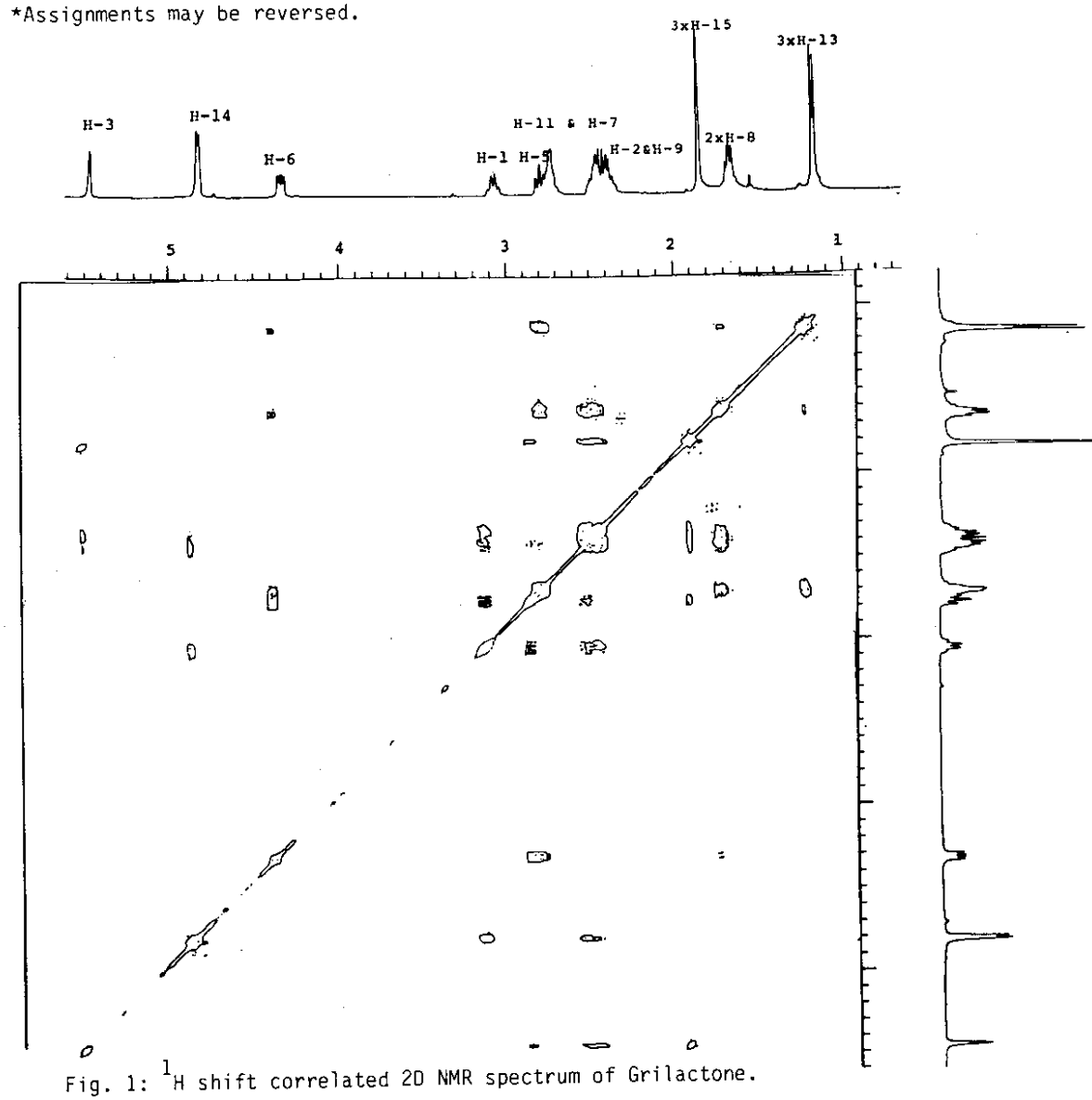


Fig. 1: ^{1}H shift correlated 2D NMR spectrum of Grilactone.

Table-II: ^{1}H-NMR data of Grilactone

Proton On Carbon No.	Chemical shift (ppm)	No. of Protons	Multiplicity	J in Hz
1	3.06	1H	dt	8.8,8.6
2	2.4	2H	m	
3	5.46	1H	br peak	
4	-	-	-	
5	2.77	1H	dd	11,8.8
6	4.325	1H	dd	11,6.1
7	2.72	1H	m	
8	1.85	2H	m	
9	2.40	2H	m	
10	-		-	
11	2.72	2H	m	
12	-		-	
13	1.14	3H	d	6.84
14	4.810	1H	br s	
	4.823	1H	br s	
15	1.830	3H	d	0.6

$J_{1,5}$=8.8 Hz, $J_{1,2}$=8.6 Hz, $J_{5,6}$=11.0 Hz, $J_{6,7}$=6.1 Hz, $J_{11,13}$=6.84 Hz, $J_{3,15}$=0.6 Hz.

The mass spectrum of grillactone, which has also not been reported so far, shows a molecular peak at m/z 232 (30%). Besides there were peaks at m/z 217 (M^{+}-CH_3,6%) 204 (92% M^{+}-CO) 188 (18%) 176 (16%) 159 (76%) 158 (100%), 143 (26%) 131 (36%) 120 (42%) 119 (42%), 106 (64%) 105 (86%) 93 (34%) 91 (68%) 80 (50%) 79 (58%) 67 (22%) 55 (46%). A possible route of fragmentation giving rise to very strong peaks at m/z and 158 could be as follows:-

References

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