

Table 1. The ^{13}C -NMR and APT spectra of 2 indicated the presence of a carbonyl, five quaternary carbons, eight methines, four methylenes and three methyls. The HETCOR and selective INEPT [3] spectra of 2 permitted the unambiguous assignment of the ^{13}C -NMR signals of 2 as shown in Table 1.

Table 1. ^1H - and ^{13}C -NMR Chemical Shifts Assignments of 1 and 2^a

Carbon	1	2	1	2
	^1H	^1H	^{13}C	^{13}C
2	----	----	181.59	181.80
3	4.73 (m)	4.68 (m)	79.47	79.69
5	3.99 (dd, 6.0, 9.3)	3.97 (dd, 5.2, 9.3)	54.06	54.69
6 α	2.47 (m)	2.43 (m)	32.79	32.68
6 β	1.86 (m)	1.86 (m)		
7	----	----	61.06	60.49
8	----	----	124.81	117.28
9	7.28 (dd, 1.5, 8.1)	7.06 (d, 7.8)	113.56	99.64
10	6.87 (dt, 1.5, 8.1)	6.38 (dd, 1.8, 7.8)	120.43	105.03
11	7.24 (dt, 1.5, 8.1)	----	128.36	160.04
12	7.17 (dd, 1.5, 8.1)	6.87 (d, 1.8)	127.17	128.24
13	----	----	147.59	148.98
14 α	2.58 (d, 12)	2.55 (d, 12.3)	31.50	31.56
14 β	2.37 (dd, 4.5, 12)	2.31 (dd, 5.4, 12.3)		
15	2.25 (m)	2.25 (m)	36.59	36.51
16	2.48 (m)	2.49 (m)	37.24	37.22
17 α	4.20 (dd, 1.8, 9.6)	4.19 (dd, 2.7, 10.5)	68.17	68.18
17 β	3.86 (dd, 1.8, 9.6)	3.85 (dd, 2.7, 10.5)		
18	1.57 (d, 6.9)	1.56 (d, 6.9)	12.72	12.68
19	5.35 (q, 6.9)	5.35 (q, 6.9)	119.18	119.12
20 α	----	----	140.66	140.69
21 β	4.76 (dd, 2.4, 12.3)	4.76 (d, 15.6)	42.14	42.06
21	3.53 (dd, 2.4, 12.6)	3.51 (dd, 3.3, 15.6)		
NOMe	3.56 (s)	3.51 (s)	2.11	62.19
Ar-OMe	----	3.80 (s)	----	55.18
N-H	9.61 (s)	9.68 (s)	----	----

a: Recorded in CDCl_3 , chemical shift values are reported as values (ppm) from internal TMS at 300 MHz, signal multiplicity and coupling constants (Hz) are shown in parentheses.

The presence of an NOE between H_{18} (δ 1.56) and $H_{21\alpha}$ (δ 4.76) or $H_{21\beta}$ (δ 3.53) distinguished the H_{21} signals from those of H_{17} (δ 4.19, 3.85), which are unusually upfield from H_{21} and also established the Z-configuration for the 19,20-double bond. Similarly, the nOe enhancements of H_6 and H_{16} on the irradiation of H_5 and H_{17} , respectively, permitted the assignment of those protons, the signals of which are close to several other proton resonances. Magnetization transfer [3,5] via irradiation of H_9 (δ 7.06) resulted in enhancement to carbons at δ 147.98, 160.04 and 60.49, which could be assigned as C_{13} , C_{11} and C_7 , respectively. Similarly, irradiation of H_{12} (δ 6.87) enhanced the aromatic quaternary carbon at δ 117.28 which should be C_8 , and the aromatic tertiary carbon at δ 128.24 which is C_{10} .

The molecular ion of gelsemamide (1) at m/z 340 ($C_{20}H_{24}N_2O_4$) was 30 amu less than that of 2. Furthermore, 1 showed nearly identical characteristics (UV, MS, CD, 1H - and ^{13}C -NMR) as 2, except that 1 has no aromatic methoxy group at C_{11} , therefore, 1 should be the parent compound of 2. The 1H -NMR, COSY, ^{13}C -NMR, CSDM 1D [4,5] results of 1 led to assignments for the 1H and ^{13}C signals as shown in Table 1.

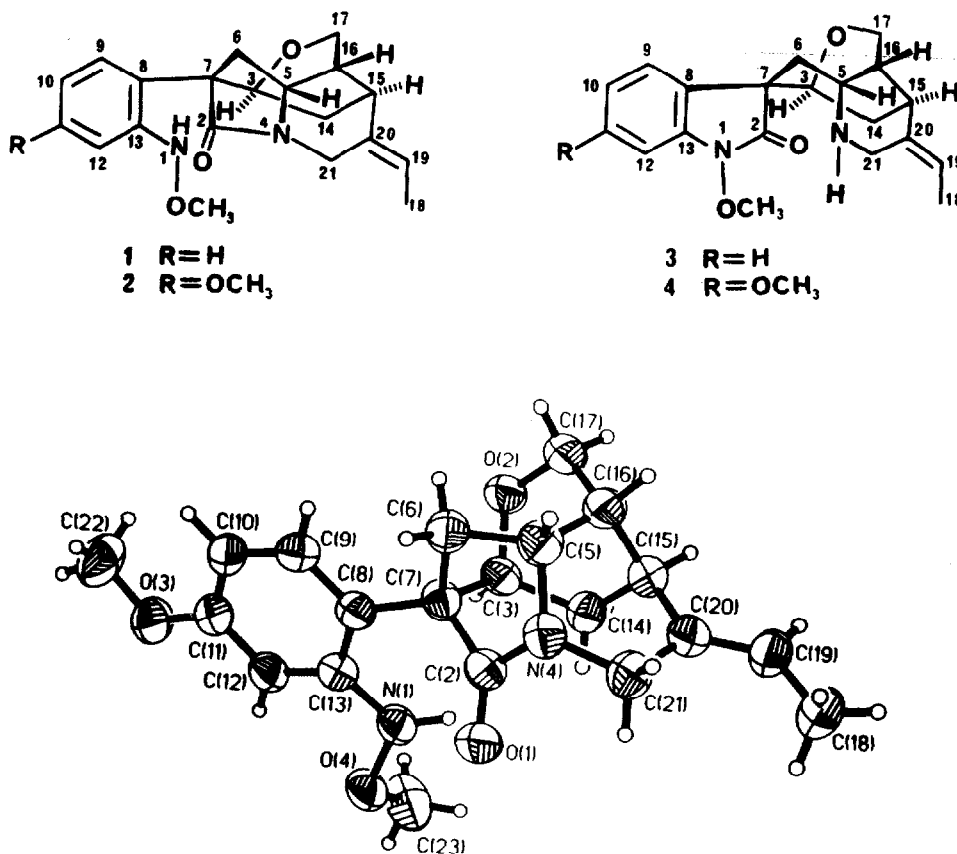


Figure 1. Molecular structure for 2.

