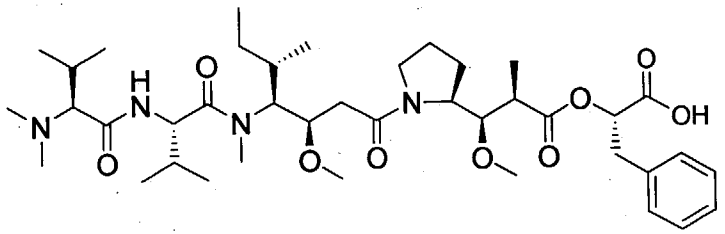
500 MHz ^{1}H NMR Spectrum of Symplostatin 3 (1) in MeOH-d_3



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125 MHz ^{13}C NMR Spectrum of Symplostatin 3 (1) in MeOH-d_3

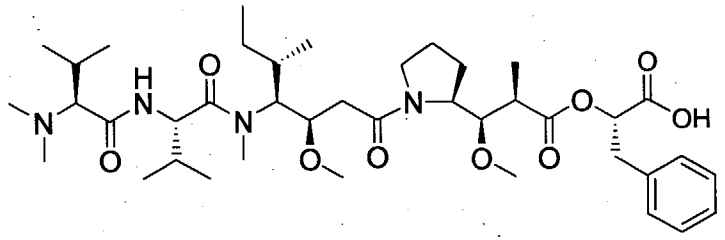

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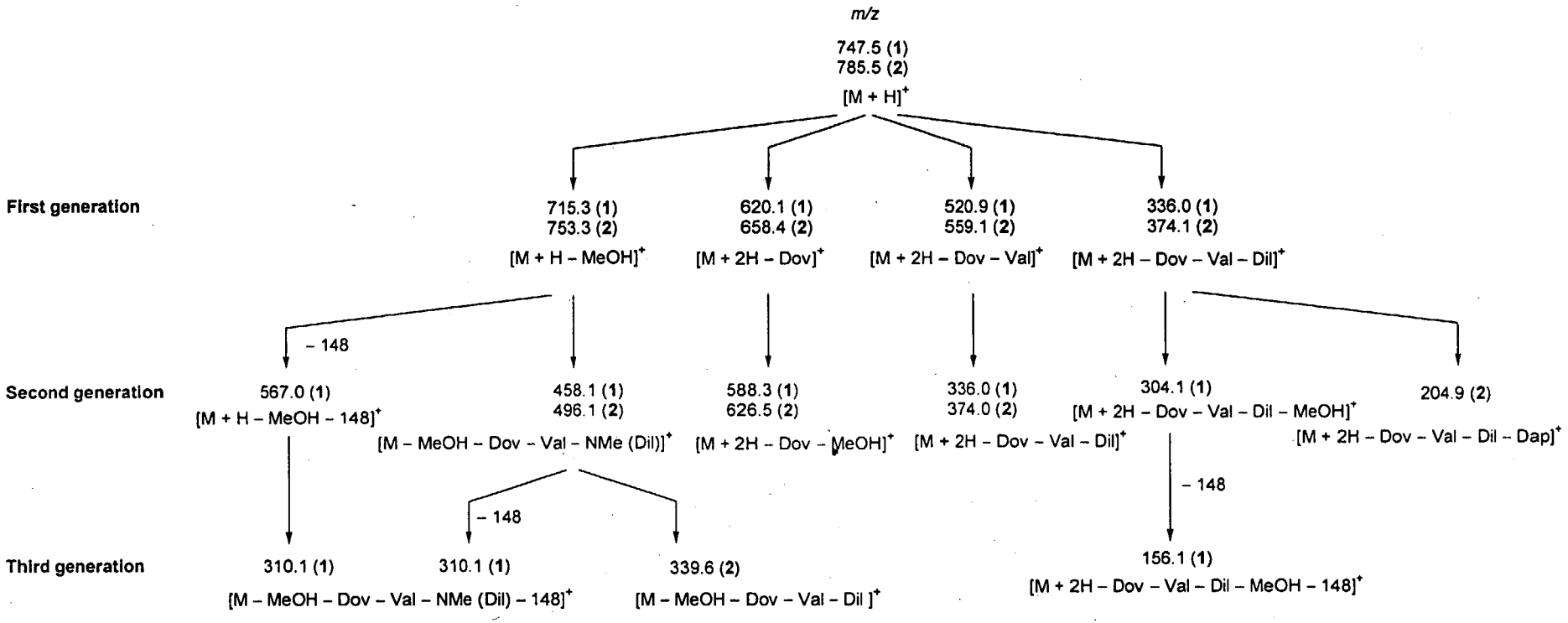
Table 3. NMR Spectral Data for Both Conformers of Dolastatin 10 (**2**) in MeOH-d_3 (Ratio 3:2) at 500 MHz (^{1}H) and 125 MHz (^{13}C)

		major conformer		minor conformer	
unit	C/H no.[a]	δ_H (J in Hz)	δ_C[b]	δ_H (J in Hz)	δ_C[b]
Doe	2		174.9, s		175.1, s
	4	7.79, d (3.2)	143.7, d	7.76, d (3.4)	143.5, d
	5	7.53, d (3.2)	120.6, d	7.50, d (3.4)	120.5, d
	6	5.68, ddd (12.1, 8.7, 4.2)	52.6, d	5.60, ddd (11.7, 8.1, 4.4)	53.6, d
	6a	3.00, dd (−14.6, 12.1), 3.60, dd (−14.6, 4.2)	41.1, t	3.02, dd (−14.4, 11.7), 3.50, dd (−14.4, 4.4)	41.4, t
	6b1		138.9, s		138.8, s
	6b2/6b6	7.29, m	129.9, d × 2	7.30, m	130.2, d × 2
	6b3/6b5	7.28, m	129.8, d × 2	7.25, m	129.6, d × 2
	6b4	7.19, m	127.9, d	7.16, m	127.7, d
	7	8.90, d (8.7)		8.75, d (8.1)	
Dap	8		176.2, s		176.5, s
	9	2.22, m	45.4, d	2.28, m	45.5, d
	9a	1.21, d (7.1)	15.7, q	1.14, d (6.7)	15.0, q
	10	3.42, br d (10.4)	86.5, d	3.84, dd (9.1, 2.0)	83.2, d
	10ab	3.33, s	62.1, q	3.27, s	61.5, q
	11	3.23, m	60.5, d	3.51, m	60.6, d
	12	1.19, m, 1.74, m	26.4, t	1.58, m, 1.87, m	25.9, t
	13	1.52, m, 1.85, m	24.5, t	1.31, m, 1.68, m	25.5, t
	14	3.16, m, 3.66, m	48.0, t	3.32, m, 3.51, m	49.0, t
Dil	16		172.1, s		171.6, s
	17	2.45, m, 2H	36.7, t	2.37, m, 2.46, m	38.1, t
	18	4.13, br dd (8.9, 4.9)	79.0, d	4.04, br	79.6, d
	18ab	3.34, s	58.5, q	3.26, s	58.3, q
	19	4.82, dd (11.0, 5.0)	57.7, d	4.76, br	58.1, d
	19a	1.86, m	33.5, d	1.76, m	33.7, d
	19b	0.96, m, 1.38, m	27.0, t	0.96, m, 1.38, m	27.0, t
	19c	0.835, t (7.0)	10.8, q	0.831, t (7.0)	10.9, q
	19d	0.95, d (6.4)	15.9, q	0.99, d (6.4)	16.2, q
	20a	3.24, s	33.0, q	3.13, s	33.1, q
Val	21		175.2, s		175.4, s
	22	4.74, t (8.4)	56.1, d	4.61, t (8.6)	56.3, d
	22a	2.12, m	31.7, d	2.01, m	31.8, d
	22b	1.021, d (6.5)	19.4, q	1.01, d (6.5)	19.7, q
	22c	1.10, d (6.5)	20.0, q	1.016, d (6.5)	19.3, q
	23	8.06, d (8.4)		8.10, d (8.6)	
Dov	24		172.5, s		172.7, s
	25	2.70, d (8.7)	75.62, d	2.68, d (9.0)	75.56, d
	25bc	2.314, s	42.4, q × 2	2.307, s	42.4, q × 2
	26	2.03, m	28.8, d	2.03, m	28.8, d
	27	0.85, d (6.4)	19.2, q	0.84, d (6.7)	19.3, q
	28	0.96, d (6.4)	20.2, q	0.96, d (6.4)	20.2, q

[a] Numbering system for dolastatin 10 (**2**)[6] adopted. [b] Multiplicity deduced from the HMQC spectrum.

Scheme 1. Comparison of the Mass Spectral Fragmentation of Symplostatin 3 (1) and Dolastatin 10 (2) by ESI-MS/MS[a]



[a] See also Pettit et al.[6] for fragmentation of dolastatin 10 (2) by SP-SIMS coupled with CAD