Supporting Information

Viscosamine: The First Naturally Occurring Trimeric 3-Alkyl Pyridinium Alkaloid

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Table 1. NMR-spectroscopical data of viscosamine (1) in DMSO-*d*₆. Chemical shifts δ are given in [ppm]^a, coupling constants *J* in [Hz]. For comparison chemical shifts of cyclostelletamine C (2)^{2k} are given in the last two columns of the table.

no. ^b	$\delta(^{13}\text{C})^c$	$\delta(^1\text{H})$	int. ^d	mult. (<i>J</i> _{HH}) ^e	¹ <i>J</i> _{CH} ^f	COSY ^g	HMBC ^h	$\delta(^{13}\text{C})^i$	$\delta(^1\text{H})^i$
1	(214)	---	---	---	---	---	---	---	---
2	143.7	9.03	1	s	188	---	3, 4, 6, 7, 8, 19	144.5	8.87
3	143.0	---	---	---	---	---	---	146.2	---
4	144.9	8.48	1	<i>d</i> (8.0)	170	5	2, 6, 19	146.2	8.45
5	127.4	8.08	1	<i>dd</i> (6.1, 8.0)	182	4, 6	3, 6	128.3	8.02
6	142.1	8.94	1	<i>d</i> (6.1)	191	5	2, 4, 5, 7	142.5	8.81
7	60.4	4.56	2	<i>t</i> (7.2)	n. d.	8	2, 6, 8	62.7	4.61
8	30.2	1.90	2	<i>m</i>	n. d.	7, 9	7	31.9	2.00
9	---	1.20	2	<i>br</i>	n. d.	8	---	26.4	1.23
10-16	---	1.20	14	<i>br</i>	n. d.	---	---	range	range
17	---	1.25	2	<i>br</i>	n. d.	18	---	range	1.26
18	29.3	1.63	2	<i>m</i>	n. d.	17, 19	3, 19	30.8	1.73
19	31.2	2.78	2	<i>t</i> (7.5)	n. d.	18	2, 3, 4, 18	33.0	2.89

^a ¹H and ¹³C chemical shifts are referenced to the DMSO-*d*₆ signal (2.50 and 39.5 ppm).

^b Since 1 is C₃ symmetric, 1 stands for 1, 1' and 1''; 2 for 2, 2' and 2'' etc.

^c For position no. 1 $\delta(^{15}\text{N})$ is given. ¹⁵N-NMR spectra were not calibrated with an external standard. The δ value has an accuracy of about 1 ppm in reference to NH₃ (0 ppm).

^d Relative integrals obtained from the 1D proton spectrum.

^e Multiplicity of the proton signals, the corresponding coupling constants in Hz are given in parenthesis.

^f The ¹*J*_{CH} coupling constants (in Hz) were only determined for the ring atoms (n. d. stands for not determined).

^g COSY correlations are given for both sides of the diagonal.

^h HMBC correlations are given from protons to carbons. The following ¹H, ¹⁵N-HMBC correlations were observed: H-2 to /N-1 (weak), H-5 to N-1 (strong) and H-6 to N-1 (weak).

ⁱ Chemical shifts of cyclostelletamine C (2), data taken from ref. 2k.

^j It was not possible to assign a single chemical shift value.

Table 2. HR-ESIMS data obtained for viscosamine (M = 780).

observed mass	charge ^a	calc. Mass	Δm [mDa]	Δm [ppm]	molecule ion
446.8403	2	893.6985	-17.9	-20.0	C ₅₆ H ₉₀ N ₃ O ₂ F ₃ (1 + TFA)
419.8607	2	839.7268	-5.4	-6.4	C ₅₆ H ₉₃ N ₃ O ₂ (1 + CH ₃ CO ₂ H)
389.8506	2	779.7010	-4.7	-6.0	C ₅₄ H ₈₉ N ₃ (1 - H)
260.2313	3	780.7135	-19.6	-25.1	C ₅₄ H ₉₀ N ₃ (1)

^a Due to the splitting of the isotope peaks.

Proton NMR spectrum of Viscosamine
(*Haliclona viscosa*)

HRMS of Viscosamine (*Haliclona viscosa*)

1: TOF MS ES+
5.83e3

MS/MS of Viscosamine (*Haliclona viscosa*)