Silene Stereochemistry. 7. The Stereochemistry of the Addition of Alkoxysilanes to Silenes. The Crystal and Molecular Structure of (*R*,*S*)- or (*S*,*R*)-5,5-Dimethyl-2-methoxy-2-phenyl-3-(triphenylsilyl)-2-silahexane

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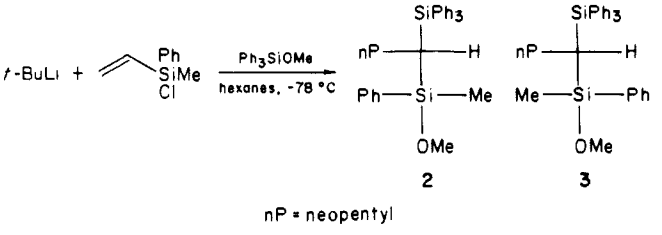
Received February 21, 1986

We recently demonstrated that the *E* and *Z* isomers of 1-methyl-1-phenyl-2-neopentylsilene (**1**) are configurationally stable up to 300 °C and that they react stereospecifically with methoxytrimethylsilane to give separable diastereomeric adducts.[1] We now report that the reaction between (*E*)- or (*Z*)-**1** and methoxytriphenylsilane is also stereospecific and the first unequivocal evidence that the reaction between alkoxysilanes and silenes is a syn addition.

The addition of methoxytriphenylsilane[2] to the silenes produced by the reaction of *tert*-butyllithium with vinylphenylmethylchlorosilane in hexanes at −78 °C gives a 42% yield of diastereomeric adducts **2** and **3** in the ratio of 31/69. The analogous



2 3

nP = neopentyl

reaction with methoxytrimethylsilane gives a 33/67 ratio of the corresponding diastereomers.[3]

When the pure anthracene adduct of (*E*)-**1** was subjected to sealed tube thermolysis,[1] at 300 °C for 10 h in the presence of a 5-fold excess of methoxytriphenylsilane, **3** was the only diastereomeric adduct obtained, showing that the reaction of **1** with $MeOSiPh_3$ like that with $MeOSiMe_3$ is also stereospecific. For characterization purposes a 45/55 mixture of **2** and **3** was prepared in 77% yield by trapping the *tert*-butyllithium adduct to vinylphenylmethylmethoxysilane with chlorotriphenylsilane.[4]

Crystals of pure **2** and **3** were separated and purified by recrystallization from absolute ethanol.[5] The molecular structure

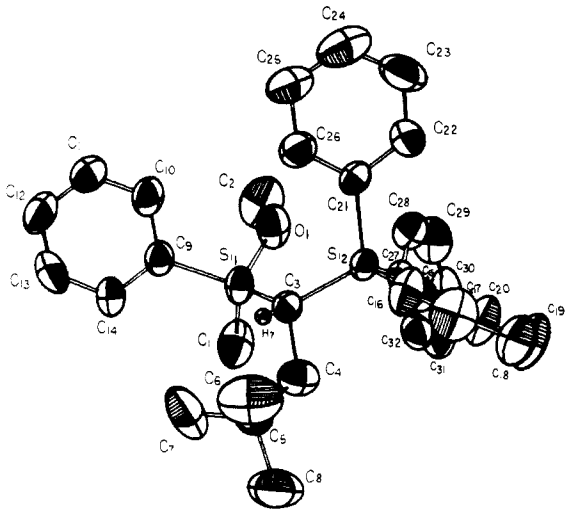


Figure 1. Structure of $Me_3CCH_2CH(SiPh_3)SiMe(OMe)Ph$ (**3**) showing the atom numbering scheme. For clarity, all hydrogens except H(7) on the chiral carbon are omitted. Important parameters: O(1)–Si(2) distance, 2.969 Å; Si(2)–C(3)–Si(1)–O(1) dihedral angle, 13.5°.

Table I. Relative Configurations of the Diastereomeric Adducts to (*E*)- and (*Z*)-1-Methyl-1-phenyl-2-neopentylsilane

addend	registry no.	rel config
$MeO–SiMe_3$	94597-05-4	(*R*,*R*),(*S*,*S*)
	94597-06-5	(*R*,*S*),(*S*,*R*)
$H–SiMe_3$	94597-08-7	(*R*,*S*),(*S*,*R*)
	94597-09-8	(*R*,*R*),(*S*,*S*)
$Cl–SiMe_3$	94597-10-1	(*R*,*R*),(*S*,*S*)
	94597-11-2	(*R*,*S*),(*S*,*R*)
$F–SiMe_3$	94597-12-3	(*R*,*R*),(*S*,*S*)
	94597-13-4	(*R*,*S*),(*S*,*R*)

of **3** Figure 1, shows it to be the (*R*,*S*), (*S*,*R*) diastereomer.[6] It follows that **2** must be the (*R*,*R*), (*S*,*S*) pair of diastereomers. On the basis of these results the relative configurations of the diastereomers which we have prepared previously may be assigned.[3] These are given in Table I. The O(1)–Si(2) distance in **3** is 0.65 Å shorter than the sum of the van der Waals radii of the elements, 3.62 Å.[8] This, coupled with the rather small Si(2)–C(3)–Si(1)–O(1) dihedral angle of 13.5°, is indicative of an interatomic interaction between oxygen and the γ-silicon which also appears to be significant in solution. In the ^{13}C NMR spectra of the diastereomers, for **3** and the (*R*,*S*), (*S*,*R*) methoxytrimethylsilyl or chlorotrimethylsilyl diastereomers,[3] the silicon methyl carbon is more shielded by the neopentyl group than in the (*R*,*R*), (*S*,*S*) diastereomers.

These results, coupled with our earlier work,[3] show conclusively that the reaction of alkoxysilanes with silenes is a stereospecific syn addition. It has been suggested on the basis of orbital symmetry considerations,[9] and the fact that a silene/THF adduct has been isolated,[10] that the addition of polar single bonds to silenes must be stepwise processes.

If this is the case in our system, the intermediate **4** must have substantial Si=C double bond character, which is not manifested in the structure of the silene/THF adduct.[10] Alternatively, **4** must have a lifetime shorter than that required for bond rotation. While

(1) Jones, P. R.; Lee, M. E. *J. Am. Chem. Soc.* **1983**, *105*, 6725-6726.
(2) Giao, D. H. *C. R. Acad. Sci.* **1965**, *260*, 5937.
(3) For experimental details, see: Cheng, A. H.-B.; Jones, P. R.; Lee, M. E.; Roussi, P. *Organometallics* **1985**, *3*, 581-584.
(4) To a solution of 3.56 g (20.0 mmol) of vinylphenylmethylmethoxysilane in 40 mL of dry THF cooled to −78 °C was added 11.1 mL of a 1.8 M solution of *tert*-butyllithium (20.0 mmol) in pentane. After stirring for 1 h, a solution of 8.85 g (30.0 mmol) of chlorotriphenylsilane in 25 mL of THF was added dropwise, and the mixture was allowed to warm to room temperature overnight with stirring. Following hydrolytic workup with saturated NH_4Cl solution and removal of solvent, GLC analysis indicated a 77% yield of a 45/55 mixture of **2** and **3**. MS, *m*/*z* (relative intensity) 479 (2) ((P — Me)$^+$), 417 (32), 259 (100), 181 (36), 147 (44) 121 (53), 105 (35). Anal. Calcd for $C_{32}H_{38}Si_2O$: C, 77.67% H, 7.74. Found for a mixture of **2** and **3**: C, 77.37; H, 7.58.
(5) Trituration of the oily mixture of **2** and **3** with absolute ethanol at 0 °C yielded crystals of ~90% pure **3**. Recrystallization from absolute ethanol gave pure **3**, mp 100.0–100.5 °C. ^1H NMR ($CDCl_3$) δ 0.20 s (3 H), 0.45 s (9 H), 1.73 m (2 H), 2.93 s (3 H), 0.1–0.5 m (1 H), 7.25–7.69 m (20 H). ^{13}C NMR ($CDCl_3$) δ −3.18 (q, SiMe), 7.42 (d, methine C), 29.33 (q, $C(CH_3)_3$), 31.87 (s, $C(CH_3)_3$), 37.79 (t, methylene C), 50.01 (q, OMe), 127–138 (aryl carbons). After a period of time pure **2** crystallized from the mother liquor, mp 102.8–103.2 °C. ^1H NMR ($CDCl_3$) δ 0.14 (s, 3 H), 0.40 (s, 9 H), 1.73 (m, 2 H), 3.12 (s, 3 H), 0.1–0.5 (m, 1 H), 7.25–7.69 (m, 20 H). ^{13}C NMR ($CDCl_3$) δ −1.49 (q) SiMe, 8.05 (d, methine C, 29.33 (q, $C(CH_3)_3$), 31.74 (s, $C(CH_3)_3$), 37.07 (t, methylene C), 50.27 (q, OMe), 127–138 (aryl carbons).
(6) Crystal data for **3**: $C_{32}H_{38}Si_2O$, M_r = 494.83, monoclinic, $P2_1/c$,o (No. 14), a = 12.202 (3) Å, b = 13.709 (3) Å, c = 17.500 (3) Å, β = 92.10 (2)°, V = 2925.3 Å^3, Z = 4, D(calcd) = 1.123 g cm^{-3}, μ(Mo Kα) = 1.37 cm^{-1}. Intensity data: 4563 unique reflections, Enraf-Nonium CAD-4, ω–2θ scan mode in range 3.0 < 2θ < 48.0°. The structure of **3** was solved (MULTAN)[7] and refined (full matrix, least squares) by using 2298 reflections with $I > 3\sigma(I)$. Final residuals: R = 0.0696, R_w = 0.0722.
(7) Main, P. MULTAN82, a direct method program for structure determination, University of York, York, England, 1982.
(8) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441-451.
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(10) Wiberg, N.; Wagner, G.; Meuller, G.; Riede, J. *J. Organomet. Chem.* **1984**, *271*, 381.

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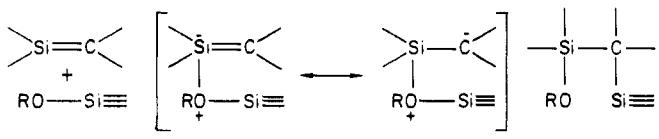

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species such as **4** may exist on the potential surface for the addition of alkoxysilanes to silenes, they are apparently not chemically significant.

Acknowledgment. This work was supported by the National Science Foundation, Grant CHE 8100668, The Robert A. Welch Foundation, and the North Texas State Faculty Research Fund.

Supplementary Material Available: Details of the X-ray structure determination of **3**, including tables of bond lengths, bond angles, fractional coordinates, and thermal parameters (10 pages). Ordering information is given on any current masthead page.

Jaspamide, a Modified Peptide from a *Jaspis* Sponge, with Insecticidal and Antifungal Activity

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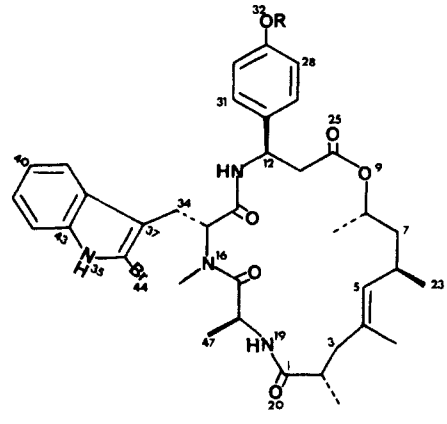
Received February 14, 1986

Sponges of the genus *Jaspis* have received limited attention from marine natural products chemists with only one group of metabolites, the isomalabaricane triterpenes, being previously reported.[2] We now wish to report the isolation of a novel metabolite, jaspamide (*1*), of mixed peptide/polyketide biosynthesis from a



1 R = H

3 R = Ac

Jaspis sp. collected both at Suva Harbor, Fiji, and a marine lake in Palau.[3] Jaspamide exhibited potent insecticidal activity against

Table I. ^{1}H and ^{13}C NMR Data ($CDCl_3$) for Jaspamide (**1**)

C	^{13}C,[b] ppm	^{1}H (mult, *J*, Hz),[c] δ	^{1}H-^{1}H connections
1	175.1[a]		
2	40.1	2.50 (m)	H-3 (A & B), Me-21
3	40.7	2.38 (A) (dd, 15.7, 10.8), 1.89 (B) (d, 15.7)	H-3B, H-2, H-5[d] (A); H-3A, H-5[d] (B)
4	131.1		
5	127.8	4.75 (d, 7.1)	H-6, H-3 (A & B)[d]
6	29.2	2.23 (m)	H-5, H-7, Me-23
7	43.3	1.32 (m)	H-6, H-8
8	70.8	4.62 (m)	H-7, Me-24
10	174.4[a]		
11	39.7	2.65 (A) (dd, 4.7, 15.0), (B) 2.65 (dd, 5.5, 15.0)	H-11B, H-12 (A); H-11A, H-12 (B)
12	49.0	5.26 (dd, 4.7, 8.4)	H-11 (A & B), H-13 H-27,[d] H-31[d]
13		7.65 (d, 8.4)	H-12
14	170.5[a]		
15	55.5	5.85 (dd, 6.4, 10.2)	H-34 (A & B)
17	168.9[a]		
18	45.8	4.75 (m)	Me-47, H-19
19		6.63 (bs)	H-18[d]
21	20.3	1.12 (d, 6.8)	H-2
22	18.5	1.56 (s)	
23	21.9	0.81 (d, 6.5)	H-6
24	19.0	1.05 (d, 6.3)	H-8
26	133.6		
27	127.1	6.94 (d, 8.3)	H-28, H-12[d]
28	115.6	6.66 (d, 8.3)	H-27
29	155.7		
30	115.6	6.66 (d, 8.3)	H-31
31	127.1	6.94 (d, 8.3)	H-30, H-12[d]
34	23.2	3.38 (A) (dd, 6.3, 15.2), 3.24 (B) (dd, 10.5, 15.2)	H-34B, H-15 (A); H-34A, H-15 (B)
35		8.70 (br s)	
36	109.0		
37	111.1		
38	131.3		
39	118.1	7.24 (d, 7.3)	H-40
40	122.3	7.13 (dd, 7.3, 7.7)	H-39, H-41
41	120.9	7.10 (dd, 7.3, 7.7)	H-40, H-42
42	110.6	7.56 (br d, 7.3)	H-41, H-35[d]
43	136.1		
45	30.8	2.98 (s)	
47	17.8	0.70 (d, 6.9)	H-18, H-19*d*

[a] Interchangeable. [b] Measured at 100 MHz. [c] Measured at 300 MHz. [d] Proton connectivities observed in the COSY spectrum.

Heliothis virescens (LC_{50} 4 ppm, azadirachtin exhibited an LC_{50} of 1 ppm in this assay)[4] and antimicrobial activity against *Candida albicans* (11-mm zone of inhibition around a 7.6-mm disk impregnated with 1 μg of jaspamide). Jaspamide is one of the most potent metabolites against *Candida albicans* encountered in this program; however, it was completely inactive against a variety of Gram positive and Gram negative bacteria.

A MeOH extract of *Jaspis* obtained by soaking 73 g of pulverized freeze-dried tissue was subjected to a solvent partition to give 500 mg of combined CCl_4- and $CHCl_3$-soluble material. Filtration of this material through a silica gel 60 column (2.4 cm × 10 cm, EtOAc) followed by HPLC (Partisil 10, 4.6 mm × 25 cm; EtOAc/Hexane, 8:2) gave jaspamide (**1**) as a colorless oil (80 mg, 0.10% yield): $[\alpha]_D$ + 65.8° (*c* 1.535, CH_2Cl_2), $C_{36}H_{45}N_4O_6Br$ (HRFABMS, MH^+ 709.2596; requries 709.2602).

The depsipeptide nature of jaspamide was evident from IR bands at 1715, 1684, 1674, and 1638 cm^{-1} and ^{13}C NMR signals at 175.1, 174.4, 170.5, and 168.9 ppm indicating the presence of four units. An alanine unit was readily assigned from NMR spectral data including ^{1}H-^{1}H and ^{1}H-^{13}C 2D COSY experiments (see Table I). A 2-bromoabrine (*N*-methyltryptophan) unit was

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(1) Alfred P. Sloan Foundation Fellow, 1985-1987.
(2) (a) Ravi, B. N.; Wells, R. J.; Croft, K. D. *J. Org. Chem.* **1981**, *46*, 1998. (b) Ravi, B. N.; Wells, R. J. *Aust. J. Chem.* **1982**, *35*, 39.
(3) The specimen collected at Suva, Fiji, was identified as a *Jaspis* sp. by Dr. Avril Ayling, Sea Research, Daintree, Queensland 4873, Australia.
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