elemental silicon. Steric considerations, the polymer's high solubility, and the propensity of related reactions to give cyclic and polycyclic compounds[5a,5b,10] suggest a sheetlike or open cage arrangement of fused rings.

While linear polysilanes exhibit strong σ-σ^* transitions (λ_{max} = 300-350 nm)[1] in the near UV, **1** exhibits a broad and more intense absorption band edge tailing into the visible (Figure 1), associated with extension of Si-Si σ-"conjugation" into three dimensions. Poly(*n*-hexylsilyne) is far more stable to photodegradation in an inert atmosphere than are linear polysilanes (Figure 1), possibly due to the more delocalized nature of excitations or to the greater propensity of a network structure to enforce recombination of photogenerated radicals. Both polydialkylsilanes and **1** photooxidize upon irradiation in air, but while polysilanes fragment to give cyclic oligomers, **1** crosslinks to form polymeric siloxane networks (Figure 2). Also in contrast to linear polysilanes,[1a] **1** converts directly (without pretreatment) upon pyrolysis to mixtures of Si/SiC without loss of volatile silicon fragments.[10] Further studies on the synthesis and properties of other members of this new class of silicon polymers are in progress.

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Registry No. Na/K, 12056-29-0; hexylSiCl$_3$ (homopolymer), 113219-09-3.

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New Tetrodotoxin Analogues from the Newt *Cynops ensicauda*

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Tetrodotoxin (TTX, **1**), a potent neurotoxin first isolated from puffers[1] and then from California newts,[2] has recently been reported from various biota.[3] Its use as a sodium channel blocker is also expanding. Yet we know little of its biosynthesis or natural analogues.[3a] Major obstacles are the lack of a detection method for TTX analogues and the poor resolution of ^{1}H and ^{13}C NMR spectra of TTX due to the hemilactal-lactone tautomerism (Figure 1). We previously isolated 4-*epi*TTX (**2**) and 4,9-anhydroTTX (**3**) from puffers.[4] Both compounds are derivable from TTX with acids and thus provide little information about metabolic pathways. Significantly, we have now isolated from the newt *Cynops ensicauda* 6-*epi*TTX, 11-deoxyTTX, and their conversion products.

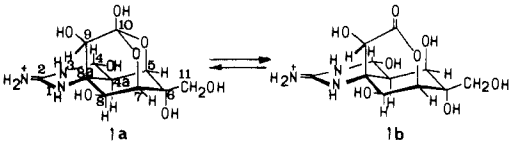
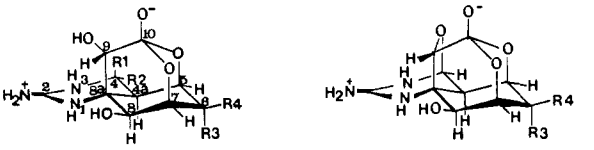


Figure 1. Hemilactal (**1a**) and lactone (**1b**) forms of TTX.

The newts (3.5 kg) collected in Okinawa, Japan, were extracted with hot 0.1% HOAc, and the extracts were chromatographed successively on columns of charcoal, BioGel P-2, BioRex 70, and Hitachi 3011C ion exchange gel.[4] Separation of TTX analogues was monitored by a TTX analyzer[5] and TLC. The following compounds were isolated: TTX (**1**, 120 mg), 4-*epi*TTX (**2**, 15 mg), 4,9-anhydroTTX (**3**, 20 mg), 6-*epi*TTX (**4**, 18 mg), 4,9-anhydro-6-*epi*TTX (**5**, 3 mg), 11-deoxyTTX (**6**, 30 mg), 11-deoxy-4-*epi*TTX (**7**, 2 mg), and 4,9-anhydro-11-deoxyTTX (**8**, 1 mg). The structural determination of the analogues was



		R1	R2	R3	R4
1	TTX	H	OH	OH	CH_2OH
2	4-epiTTX	OH	H	OH	CH_2OH
4	6-epiTTX	H	OH	CH_2OH	OH
6	11-deoxyTTX	H	OH	OH	CH_3
7	11-deoxy-4-epiTTX	OH	H	OH	CH_3

		R3	R4
3	4,9-anhydroTTX	OH	CH_2OH
5	4,9-anhydro-6-epiTTX	CH_2OH	OH
8	4,9-anhydro-11-deoxyTTX	OH	CH_3

achieved mainly through NMR measurements. Addition of CF_3COOD to the solvent markedly improved the resolution of signals in the NMR spectra of TTX and thus allowed us to assign for the first time all ^{1}H and ^{13}C signals by ^{1}H-^{1}H and ^{13}C-^{1}H COSY measurements (Table I).

6-*epi*TTX (**4**); $[\alpha]^{25}_D$ -4.8° (*c* 0.33, 0.05 N HOAc). The molecular formula by high resolution FABMS[6] was identical with that of TTX, $C_{11}H_{17}N_3O_8$ (MH^+, *m/z* 320.1094, found 320.1106). The LD_{50} of **4** to mice was 60 μg/kg (ip). ^{13}C and ^{1}H NMR spectra revealed double sets of signals, thereby indicating that **4** exists as hemilactal-lactone tautomers, as does TTX. The tautomerism was evidenced by negative crosspeaks due to saturation transfer between corresponding protons in a phase sensitive NOESY spectrum. The ratio of hemilactal-lactone tautomers was 6:4. Comparison of ^{13}C and ^{1}H NMR signals of TTX and 6-*epi*TTX is shown in Table I. Assignments of the signals were derived from ^{1}H-^{1}H and ^{13}C-^{1}H COSY measurements. Signals in **4** due to H-4a, H-8, H-11, C-4a, C-5, C-6, and C-7 were significantly shifted from the corresponding signals of TTX, supporting the 6-epi assignment. Proton COSY of **4**, showed couplings between H-4/H-4a, H-4a/H-5, H-5/H-7 (W-type), and H-7/H-8, analogous with TTX. The coupling patterns also agreed with those of TTX. Thus structure changes at C-4a, C-5, C-7, and C-8 were ruled out. Because 4,9-anhydro-6-*epi*TTX (**5**)[7] isolated from the same newts was convertible in acid in **4**, as is 4,9-anhydroTTX to TTX, C-8a and C-9 of **4** must have the same stereochemistry as in TTX. NOE measurements and difference spectra confirmed the axial substitution of C-11; irradiation at

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(6) The HRFABMS was measured on a JEOL JMS-DX303HF mass spectrometer by K. Nojima of JEOL Co.
(7) 4,9-anhydro-6-*epi*TTX (**5**); $[\alpha]^{25}_D$ +10.0° (*c* 0.08, 0.05 N HOAc); HRFABMS, MH^+ *m/z* 302.0999 (calcd for $C_{11}H_{16}N_3O_7$ 302.0988); ^{1}H NMR of a hemilactal form δ 5.54 (H-4, s), 2.87 (H-4a, d, J_{4a-5} = 2.3 Hz), 4.33 (H-5, dd, J_{5-4a} = 2.3, J_{5-7} = 2.0 Hz), 4.20 (H-7, t, J_{7-5}, J_{7-8} = 2.0 Hz), 4.41 (H-8, d, J_{8-7} = 2.0 Hz), 4.61 (H-9, s), 3.65, 3.67 (CH_2-11, d, J_{gem} = 12.7 Hz). When irradiated at δ 3.65 (CH_2-11), 12.4% and 13.4% of NOE were observed on H-4a and H-8, respectively.

Table I. NMR Spectral Data of TTX, 6-*epiTTX*, and 11-deoxyTTX[a]

	TTX[b]				6-*epi*-TTX[c]				11-deoxyTTX[c]			
	hemilactal		lactone		hemilactal		lactone		hemilactal		lactone	
	C	H	C	H	C	H	C	H	C	H	C	H
2	156.6		155.9		156.5		155.8		156.4		-	
4	75.1	5.50 (d 9.4)	74.8	5.50 (d 9.4)	75.1	5.55 (d 9.4)	75.1	5.55 (d 8.9)	75.0	5.49 (d 9.4)	74.8	5.51 (d 9.6)
4a	40.7	2.35 (d 9.5)	46.5	2.35 (d 9.5)	41.8	2.01 (d 9.0)	46.9	2.13 (d 9.0)	40.5	2.37 (d 9.4)	46.2	2.37 (d 9.4)
5	73.8	4.25 (br s)	69.2	4.03	75.4	4.30 (d 1.6)	68.4	4.03 (br s)	77.5	4.08 (br s)	72.0	3.87 (br s)
6	71.5		-[d]		72.8		77.0		69.1		-	
7	79.7	4.08 (t 1.8)	82.5	4.55 (br s)	82.0	4.08 (br s)	85.5	4.62 (br s)	83.6	3.91 (t 1.6)	86.8	4.35 (t 2.0)
8	72.8	4.30 (d 1.5)	71.5	4.44 (br s)	72.9	4.17 (br s)	71.7	4.26 (br s)	72.6	4.30 (d 1.6)	71.3	4.46 (d 2.3)
8a	59.7		60.4		59.6		60.1		59.1		59.8	
9	70.9	3.96 (s)	74.0	4.57 (s)	70.8	4.00 (s)	73.7	4.59 (s)	70.8	3.94 (s)	73.9	4.55 (s)
10	110.8		176.1		110.7		175.8		110.6		175.4	
11	65.5	4.02 (d 12.6) 4.04 (d 12.6)	65.2	3.77 (d 12.6) 4.01 (d 12.6)	65.1	3.74 (s)	66.2	3.68 (d 14.0) 3.69 (d 14.0)	25.1	1.64 (s)	24.5	1.51 (s)

[a] ^{13}C NMR 75.5 MHz, $^{13}CD_3COOD$ = 22.4 ppm (GN-300); ^1H NMR, CHD_2COOD = 2.06 ppm. Information in parentheses denotes multiplet and J in Hz. [b] ^1H NMR 360 MHz (NT360) and solvent 1% CF_3COOD, 4% CD_3COOD/D_2O. [c] ^1H NMR 300 MHz (GN-300), and solvent 4% CD_3COOD/D_2O. [d] Unassignable carbons.

δ 3.74 (CH_2-11) enhanced signal intensities of H-4a (10.6%) and H-8 (10.3%) of **4**, while irradiation of CH_2-11 of TTX gave no NOE on both protons. All these data support the structural assignment of **4**.

The other analogue, 11-deoxyTTX (**6**), crystallized as colorless needles from 4% HOAc [202 °C dec, $[\alpha]^{25}_D$ +5.37° (*c* 0.34, 0.05 N HOAc)]; the LD_{50} to mice was 71 μg/kg (ip); the molecular formula by high resolution FABMS $C_{11}H_{17}N_3O_7$ (MH^+, *m/z* 304.1145, found 304.1155) corresponded to a monodeoxy derivative of TTX. Proton COSY of **6** showed that the coupling patterns, including a W-type coupling between H-4a and H-9, are essentially the same as those of TTX (Table I), thus suggesting their structural resemblance. Homo and heteronuclear COSY spectra of **6** indicated that the CH_2-11 signals in TTX were replaced by a methyl signal (Table I). Comparison of ^{13}C NMR spectra of **6** and TTX further supported reduction at C-11. A signal assignable to C-6 was shifted upfield, and those of C-5 and C-7 were shifted downfield, while other signals of **6** agreed with those of TTX within 0.6 ppm (Table I). Me-11 was assigned equatorial conformation because no NOE was observed between H-4a and Me-11. These data establish the structure of the new analogue as 11-deoxyTTX, **6**. The spectral data indicated that **6** also exists as hemilactal–lactone tautomers (7:3). Two analogues derivable from **6** with acid were also isolated from the newts and identified as 4-*epi*-11-deoxyTTX (**7**)[8] and 4,9-anhydro-11-deoxyTTX (**8**).[9]

Biosynthesis of TTX supposedly involves arginine and a C5 unit derived from either amino acids, isoprenoids, shikimates, or branched sugars.[10] The occurrence of 6-epi and 11-deoxy analogues renders branched sugars unlikely precursors, and the shikimate pathway does not seem plausible because it rarely yields 1,2,4-trialkylcyclohexanes. An isoprenoid unit is favored because it possesses both an sp^2 carbon oxidizable to either TTX or 6-*epi*TTX and a methyl that remains in 11-deoxyTTX. The analogues will also be important for structure-activity relationships because chemical transformations of TTX are difficult.

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(8) 11-deoxy-4-*epi*TTX (**7**); SIMS (Hitachi M-80) MH^+ *m/z* 304; ^1H NMR of a hemilactal form δ 5.13 (H-4, d, J_{4-4a} = 4.9 Hz), 2.87 (H-4a d, J_{4a-4} = 5.0 Hz), 4.13 (H-5, d, J_{5-7} = 1.5 Hz). 3.91 (H-7, t, J_{7-5}, J_{7-8} = 1.5 Hz), 4.29 (H-8, d, J_{8-7} = 1.5 Hz), 3.96 (H-**9**, s), 1.64 (Me-11, s).

(**9**) 4,9-anhydro-11-deoxyTTX (**8**): SIMS (Hitachi M-80) NH^+ *m/z* 286; ^1H NMR of a hemilactal form δ 5.51 (H-4, s), 2.95 (H-4a, d, J_{4a-5} = 3.0 Hz), 4.15 (H-5, dd, J_{5-4a} = 3.0 Hz, J_{5-7} = 2.0 Hz), 4.01 (H-7, t, J_{7-5}, J_{7-8} = 2.0 Hz), 4.63 (H-8, d, J_{8-7} = 2.0 Hz), 4.56 (H-9, s), 1.61 (Me-11, s). The signals of **5**, **7**, and **8** were assigned by ^1H-^1H COSY measured with a GN-300 spectrometer by using 4% CD_3COOD in D_2O as the solvent.

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Models for the $Fe^{II}Fe^{III}$ and $Fe^{II}Fe^{II}$ Forms of Iron-Oxo Proteins

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The importance of redox active, binuclear iron centers in proteins is well established.[1] In an attempt to probe these centers, several crystallographically characterized synthetic analogues of the binuclear iron center in methemerythrin and ribonucleotide reductase have been reported, demonstrating the thermodynamic stability of the (μ-oxo)bis(μ-carboxylato)diiron(III) unit.[2-4] Analogues of mixed valence sites in semimethemerythrin and reduced purple acid phosphatases have also been reported, but none are structurally characterized.[5-7] In addition, only one model

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