(0.029 g, 1.2 mmol), and the mixture was stirred for 0.5 h at 25 °C. Methyl iodide (0.075 mL, 1.2 mmol) was added and the mixture left at 25 °C for a further 0.5 h. The precipitate was filtered off and the solvent evaporated. To the residue was added aqueous KOH solution (40% w/w, 10 mL) and MeOH (10 mL), and the mixture was boiled under reflux for 12 h. The solution was acidified to pH 4 (concentrated HCl) and extracted with CH_2Cl_2 (7 × 20 mL). The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated. The crystalline residue was dissolved in Et_2O (50 mL) and the solution treated with ethereal diazomethane. Removal of excess of diazomethane and the solvent gave the methyl ester (0.078 g, 93%): ^1H NMR ($CDCl_3$) δ 7.78 (1 H, d, J = 3.4 Hz, thiophene 3-H), 7.54 (1 H, d, J = 4.5 Hz, thiophene 5-H), 7.09 (1 H, dd, J = 4.5, 3.4 Hz, thiophene 4-H), 3.83 (3 H, s, OCH_3); mass spectrum, m/z (relative intensity) 142 (M^+, 24), 111 (100).

Acknowledgment. A.J.C. is indebted to the SERC UK for a research studentship.

Registry No. **2**, 14313-93-0; **4**, 90642-98-1; **4** (dilithio intermediate), 98331-18-1; **5**, 98331-02-3; **6**, 76656-00-3; **7**, 98331-03-4; **8**, 98331-04-5; **9**, 98331-05-6; **10**, 98331-06-7; **11**, 98331-07-8; **12**, 98331-08-9; **13**, 98331-09-0; **14**, 98331-10-3; **14** (dilithio intermediate), 98331-19-2; **15**, 98331-11-4; **16**, 98331-12-5; **17**, 98331-13-6; **18**, 98331-14-7; **19**, 98331-15-8; **20**, 98331-16-9; **21**, 98331-17-0; **23**, 1451-95-2; **24**, 19991-68-5; **25**, 60166-84-9; LDA, 4111-54-0; *sec*-BuLi, 598-30-1; *n*-BuLi, 109-72-8; thiophene-2-carboxylic acid, 527-72-0; furan-2-carboxylic acid, 88-14-2; methyl thiophene-2-carboxylate, 5380-42-7; 5-(*N*,*N*-diethylcarboxamide)-2-thiophenecarboxylic acid, 98331-20-5; 5-deuterio-*N*,*N*-diethyl-2-thiophenecarboxamide, 98331-21-6; 2-(*N*,*N*-diethylcarboxamide)-3-thiophenecarboxylic acid, 98331-22-7; 5-(*N*-*tert*-butylcarbamoyl)thiophene-2-carboxylic acid, 98331-23-8; 5-(*N*-*tert*-butylcarbamoyl)furan-2-carboxylic acid, 98331-24-9; 2-(*N*-*tert*-butylcarbamoyl)-1-methylpyrrole-3-carboxylic acid, 98331-25-0; 5-(*N*-*tert*-butylcarbamoyl)-1-methylpyrrole-2-carboxylic acid, 98331-26-1; 1-methylpyrrole-2-carboxylic acid, 6973-60-0.

Efficient and Convenient Method for Synthesis of Solenopsin A and Its Analogues Using 1-Benzyl-2,6-dicyanopiperidine

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Received April 30, 1985

An efficient synthetic sequence proposed here provides a new method for preparation of not only solenopsin A, i.e., *trans*-2-methyl-6-undecylpiperidine, but also coniine, i.e., 2-propylpiperidine, and other 2,6-dialkylpiperidine alkaloids: A reaction of 1-benzyl-2,6-dicyanopiperidine (**1**) with alkyl halides selectively gives 2-alkyl- and 2,6-dialkyl-1-benzyl-2,6-dicyanopiperidines (**2** and **3**), decyanation of which affords respectively 2-alkyl- and 2,6-dialkyl-1-benzylpiperidines (**4** and **5**) in high yields.

In our previous paper, the stereoselective synthesis and the utility as synthetic reagents of 1-substituted 2,6-dicyanopiperidines have been reported.[1] We report here a new synthetic method for preparation of 2-alkyl- and 2,6-dialkylpiperidine alkaloids **6** and **7** using 1-benzyl-2,6-dicyanopiperidine (**1**). Reaction of **1** with various alkyl halides gave 2-alkyl- and 2,6-dialkyl-1-benzyl-2,6-dicyanopiperidines **2** and **3** in high yields. When the alkylated products **2** and **3** were heated at 70 °C with sodium borohydride in isopropyl alcohol, decyanation took place to give 2-alkyl- and 2,6-dialkyl-1-benzylpiperidines **4** and **5**.[3b] The subsequent debenzylation of **4** and **5** by catalytic hydrogenolysis[2] proceeded smoothly to give 2-monoalkyl- and 2,6-dialkylpiperidine alkaloids **6** and **7**, respectively (Scheme I). Solenopsin A, *trans*-2-methyl-6-*n*-undecylpiperidine (**7a**), which is a component in the venom of the fire ant (*Solenopsis saevissima*), is conveniently prepared by the present method. Several synthetic routes to solenopsin A have been reported: 2,6-Dimethylpyridine,[3a] 2-picoline,[3b] unsymmetrical alkane-2,5-diones,[3c] *N*-(methoxycarbonyl)-2-alkylpyridinium salts,[3d] α-alkylcyclopentanones,[3e] and 6-methyl-2-piperidone[3f] have been used as starting materials. Many of these methods, however, lack effective procedures or require starting materials which are difficult to synthesize. However, the present method is useful for preparation of not only solenopsin A but also other 2-alkylated and 2,6-dialkylated piperidines (**6** and **7**).

The alkylation of 1-phenyl-2,6-dicyanopiperidine gave predominantly symmetrical dialkylated products as reported in our previous paper.[2] Alkylation of the benzyl compound **1**, however, selectively gave monoalkylated products **2**. The selective formation of **2** is important for the subsequent preparation of unsymmetrical dialkylated products **3**. For example, the reaction of **1** with methyl iodide in tetrahydrofuran containing lithium isopropylamide gave 1-benzyl-2,6-dicyano-2-methylpiperidine (**2a**) in 82% yield. Likewise, the reaction of **1** with undecyl, tridecyl, *n*-propyl, and benzyl bromides gave the 2-alkyl-1-benzyl-2,6-dicyanopiperidines **2b**, **2c**, **2d**, and **2e** in 83–90% yields. The monoalkylated products **2** were isolated by means of column chromatography using Florisil. When silica gel was used, the products **2** decomposed on the column. The monoalkylated products such as **2b** and **2c** are easily isolated from a reaction mixture containing unreacted **1**, but isolation of **2a** and **2d** having shorter polymethylene chains is very difficult. Accordingly, the yields of **2a** and **2d** were estimated from the ^1H NMR spectra of the purified reaction mixture containing **1**.

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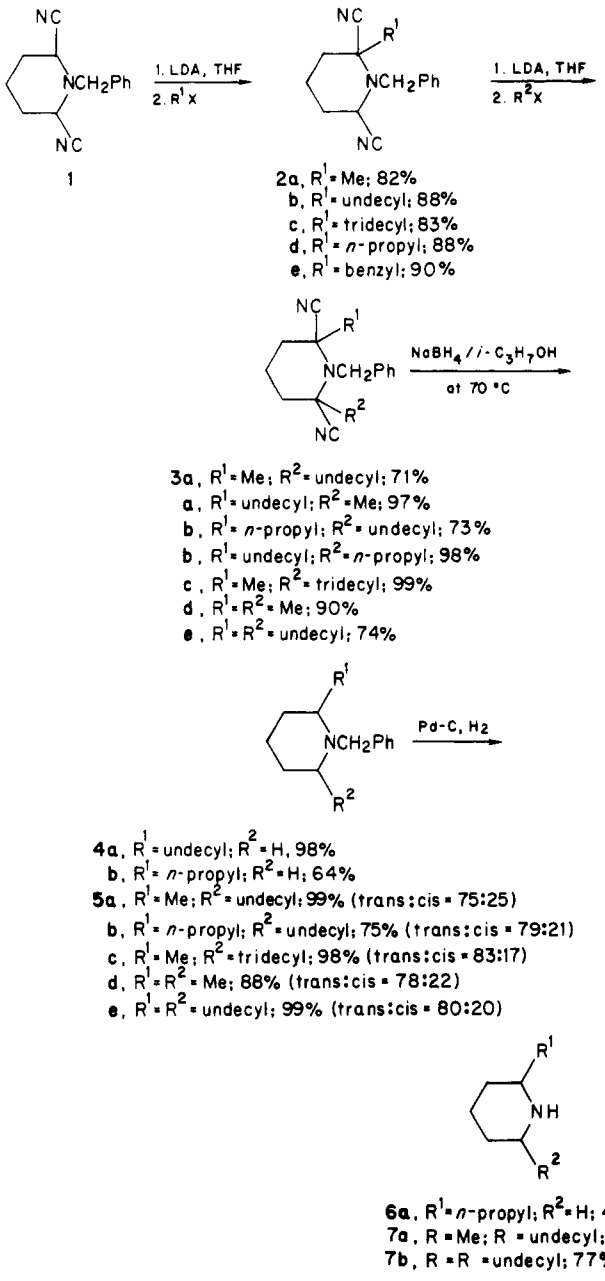
0022-3263/85/1950-4368$01.50/0

Scheme I



Dialkylated products **3** were prepared in 71–99% yields by reaction of **2** with alkyl halides under conditions similar to those for the alkylation of **1**. In general, the dialkylation proceeded favorably by the reaction of monoalkylated compound such as **2b** and **2c** having longer polymethylene chains with alkyl halides such as methyl iodide and *n*-propyl bromide having shorter polymethylene chains. The reversal reaction decreased the yield of **3**: The reaction of **2d** with undecyl bromide gave **3b** in lower yield than that by the reaction of **2b** with *n*-propyl bromide. Similar results are also obtained for preparation of **3a** (see Scheme I).

When the dialkylated products **3** were heated at 70 °C with sodium borohydride in isopropyl alcohol, decyanation[3b] took place to give 1-benzyl-2,6-dialkylpiperidines **5** in 75–99% yields. Likewise, the decyanation of the monoalkylated compounds **2b** and **2d** also proceeded to give 2-alkyl-1-benzylpiperidines **4a** and **4b** in good yield.

The configuration of **5** was examined by ^{1}H NMR: In the case of the trans isomer, the unequivalent benzyl methylene protons are expected to give two distinguishable doublets (J = 14 Hz, lit.[3b] J = 13 Hz). On the other hand, the corresponding protons of the cis isomer are expected to appear as a singlet. The major product was thus assigned as a trans isomer and the minor product as a cis isomer. The mole ratio of trans to cis isomers estimated by ^{1}H NMR is about 4:1 in all cases examined.

The debenzylation of **5** was carried out according to the procedure reported in the literature.[4] For example, **5a** was hydrogenated in a mixture of 15% hydrochloric acid and ethyl alcohol (1:10 v/v) containing 5% palladium–carbon; solenopsin A, 2-methyl-6-undecylpiperidine (**7a**), was obtained in 62% yield. Likewise, the hydrogenation of the *n*-propylpiperidine (**4b**) gave the well-known alkaloid coniine (**6a**) in 45% yield.

The present method was thus found to be useful for preparation of 2-alkylpiperidine and unsymmetrical 2,6-dialkylpiperidine alkaloids. In addition, the hydrolysis of **2** and **3** in the presence of cuprous salts leads to unsymmetrical 1,5-diketones. Other utilities of **1** as synthetic reagents are in progress.

Experimental Section

All melting points were taken on a Yanagimoto micromelting point apparatus and are uncorrected. ^{1}H NMR spectra were determined with Hitachi R-24 (60 MHz) and JEOL FX-270 (270 MHz) nuclear magnetic resonance spectrometers using tetramethylsilane (Me_4Si) as an internal standard. IR and mass spectra were taken with diffraction grafting infrared (Japan Spectroscopic Co. Ltd., Type A-202) and high-resolution mass (Hitachi, Type RMU-7M) spectrometers, respectively. Microanalytical data were obtained by using a Perkin-Elmer 240 elemental analyzer. The synthetic method and the physical properties of 1-benzyl-2,6-dicyanopiperidine (**1**) have been reported in our previous paper.[1]

(I) Reaction of 1-Benzyl-2,6-dicyanopiperidine (1) with Alkyl Halides. Preparation of 1-Benzyl-2,6-dicyano-2-methylpiperidine (2a) as a Typical Example. Under dry nitrogen, diisopropylamine (1.33 g, 13 mmol) dissolved in dry THF (20 mL) was treated with *n*-butyllithium (7.74 mL of a 1.55 M solution in hexane, 12 mmol) at −78 °C, the mixture was slowly added dropwise over 30 min to a solution of 1-benzyl-2,6-dicyanopiperidine (**1**; 2.27 g, 10 mmol) dissolved in THF (36 mL) at −78 °C, and to the reaction mixture was added methyl iodide (1.56 g, 11 mmol). The reaction mixture was stirred for 2 h at −78 °C, poured into water (40 mL), and then extracted with diethyl ether (2 × 50 mL). The combined ether layers were dried (Na_2SO_4) and evaporated and the residue purified by means of column chromatography (Florisil, benzene–hexane). However, the isolation of pure **2a** was difficult, and a mixture of **2a** and unreacted **1** was obtained as a colorless oil. The yield of **2a** is 82% as estimated from the ^{1}H NMR spectrum of the mixture. Physical properties are summarized in Table I.

1-Benzyl-2,6-dicyano-2-undecylpiperidine (2b). By the same procedure, the reaction of **1** (2.28 g, 10 mmol) with undecyl bromide (2.59 g, 11 mmol) was carried out to give a yellow oil (4.29 g). The oil was chromatographed (Florisil benzene–hexane), and **2b** was obtained in 88% yield (3.34 g) (see Table I).

1-Benzyl-2,6-dicyano-2-tridecylpiperidine (2c). By the same procedure, the reaction of **1** (2.28 g, 10 mmol) with tridecyl bromide (2.73 g, 11 mmol) was carried out to give a yellow oil (4.44 g). Chromatography (Florisil, benzene–hexane and benzene–ethyl acetate) gave **2c** in 83% yield (3.37 g) (see Table I).

1-Benzyl-2,6-dicyano-2-propylpiperidine (2d). By the same procedure, the reaction of **1** (2.27 g, 10 mmol) with *n*-propyl bromide (1.42 g, 12 mmol) was carried out to give a yellow oil (2.99 g). Chromatography (Florisil, benzene–hexane) gave product **2d** (2.62 g) as a mixture with unreacted **1** as a colorless oil. The yield (88%) was determined by ^{1}H NMR. The product **2d** containing impurities was again chromatographed on a similar column, and the fractions containing pure **2d** were collected. The physical

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Table I. Physical Properties of Mono- and Dialkylated Products 2 and 3

compd	mp, °C	IR (KBr) ν_{CN}, cm^{-1}	^1H NMR ($CDCl_3/Me_4Si$), δ [a]	microanalysis calcd (found) C	H	N
2a	oil	2220 (1f)	3.60 and 4.30 (d, J = 14 Hz, CH_2Ph), 3.75 (br s, 1 H)	[b]		
				for $C_{25}H_{37}N_3$ (M_r = 379.57)		
2b	42-43	2230	3.60 and 4.28 (d, J = 14 Hz, CH_2Ph), 3.70 (br s, 1 H)	79.11 (79.06)	9.82 (9.66)	11.07 (11.00)
				for $C_{27}H_{41}N_3$ (M_r = 407.62)		
2c	43-44	2220	3.58 and 4.22 (d, J = 14 Hz, CH_2Ph), 3.70 (br s, 1 H)	79.55 (79.85)	10.14 (10.18)	10.31 (10.23)
				for $C_{17}H_{21}N_3$ (M_r = 267.36)		
2d	oil	2230 (1f)	3.62 and 4.31 (d, J = 14 Hz, CH_2Ph), 3.80 (br m, 1 H)	76.37 (76.61)	7.92 (7.95)	15.72 (15.71)
				for $C_{21}H_{21}N_3$ (M_r = 315.40)		
2e	142-145	2230, 2210	2.83, 3.60, 3.72, and 4.50 (d, J = 14 Hz, CH_2Ph), 3.78 (br s, 1 H)	79.97 (79.76)	6.72 (6.73)	13.32 (13.27)
				for $C_{26}H_{39}N_3$ (M_r = 393.60)		
3a	70-71	2220	1.45 (s, 3 H, CH_3), 4.16 (s, 2 H, CH_2Ph)	79.34 (79.38)	9.99 (9.93)	10.68 (10.73)
				for $C_{28}H_{43}N_3$ (M_r = 421.65)		
3b	oil	2230 (1f)	4.15 (s, 2 H, CH_2Ph)	m/e 421.35 (M^+) [c]		
				for $C_{28}H_{43}N_3$ (M_r = 421.65)		
3c	73-74	2230	1.43 (s, 3 H, CH_3), 4.13 (s, 2 H, CH_2Ph)	79.76 (80.00)	10.28 (10.22)	9.97 (10.02)
				for $C_{16}H_{19}N_3$ (M_r = 253.34)		
3d	119-125	2240	1.41 (s, 6 H, CH_3 × 2), 4.14 (s, 2 H, CH_2Ph)	75.85 (75.75)	7.56 (7.49)	16.59 (16.51)
				for $C_{36}H_{59}N_3$ (M_r = 533.84)		
3e	35-36	2230	4.18 (s, 2 H, CH_2Ph)	80.99 (81.00)	11.14 (10.97)	7.87 (7.86)

[a] Only data of characteristic protons are listed. [b] Not isolated as a pure compound. [c] Data by a high-resolution mass spectroscopy are listed instead of microanalysis data (70 eV).

Table II. Physical Properties of Decyanated Products 4 and 5

compd [a]	^1H NMR ($CDCl_3/Me_4Si$) δ [b]	microanalysis calcd (found) C	H	N
5b	2.52 (br s, 0.42 H, CH of cis), 2.73 (br s, 1.58 H, CH of trans), 3.64 and 3.74 (d, 1.58 H, J = 14 Hz, CH_2Ph of trans), 3.67 (s, 0.42 H, CH_2Ph of cis)	for $C_{26}H_{45}N$ (M_r = 371.63) 84.03 (83.97)	12.20 (12.15)	3.77 (3.77)
5c	2.40 and 2.60 (br m, 0.34 H, CH of cis), 2.70 and 2.90 (m, 1.66 H, CH of trans), 3.58 and 3.79 (d, 1.66 H, J = 14.5 Hz, CH_2Ph of trans), 3.72 (s, 0.34 H, CH_2Ph of cis)	for $C_{26}H_{45}N$ (M_r = 371.63) 84.03 (84.04)	12.20 (12.10)	3.77 (3.77)
5e	2.50 (br s, 0.4 H, CH of cis), 2.70 (br s, 1.6 H, CH of trans), 3.64 and 3.74 (d, 1.6 H, J = 14 Hz, CH_2Ph of trans), 3.66 (s, 0.4 H, CH_2Ph of cis)	for $C_{34}H_{61}N$ (M_r = 483.77) 84.40 (84.11)	12.71 (12.51)	2.89 (2.92)
4a	2.11 (br s, 2 H, CH), 2.64 (br s, 1 H, CH), 3.13 and 3.95 (d, 2 H, J = 13 Hz, CH_2Ph)	for $C_{23}H_{39}N$ (M_r = 329.55) 83.82 (83.93)	11.93 (12.01)	4.25 (4.46)
4b	1.95-2.45 (br m, 2 H, CH_2), 2.50-2.95 (br m, 1 H, CH), 3.15 and 3.98 (d, 2 H, J = 14.5 Hz, CH_2Ph)	for $C_{15}H_{23}N$ (M_r = 217.34) 82.89 (82.71)	10.67 (10.71)	6.44 (6.57)

[a] All products (4 and 5) are colorless oils. Products 5a and 5d are known compounds, and their physical properties agree with those reported in the literature.[3b,6] [b] Only data of characteristic protons are listed (270 MHz).

properties are shown in Table I.

1,2-Dibenzyl-2,6-dicyanopiperidine (2e). By the same procedure, the reaction of 1 (1.12 g, 5 mmol) with benzyl bromide (0.855 g, 5.5 mmol) was carried out to give a pale yellow solid (2.58 g). The solid dissolved with benzene (10 mL) was chromatographed (Florisil, benzene–ethyl acetate), and **2e** was obtained in 90% yield (1.356 g) (see Table I).

(II) Reaction of 2-Alkyl-1-benzyl-2,6-dicyanopiperidines 2 with Alkyl Halides. Preparation of 1-Benzyl-2,6-dicyano-2-methyl-6-undecylpiperidine (3a) as a Typical Example. Under dry argon or nitrogen, diisopropylamine (0.524 g, 5.2 mmol) dissolved in dry THF (5 mL) was treated at −78 °C with *n*-butyllithium (2.79 mL of a 1.55 M solution in hexane, 4.3 mmol), the mixture was added dropwise over 5 min at −78 °C to a solution of **2b** (1.358 g, 3.6 mmol) dissolved in THF (20 mL), and then methyl iodide (0.613 g, 4.3 mmol) was added to the reaction mixture. The reaction mixture was stirred for 1 h at −78 °C, poured into water (30 mL), and then extracted with diethyl ether (2 × 30 mL). The combined ether layers were dried ($NaSO_4$) and evaporated and the residue (1.639 g) purified by means of column chromatography (Florisil, benzene–ethyl acetate). Thus, **3a** was obtained in 97% yield (1.368 g). Physical properties of **3a** are summarized in Table I.

1-Benzyl-2,6-dicyano-2-propyl-6-undecylpiperidine (3b). By the same procedure, the reaction of **2b** (1.90 g, 5 mmol) with *n*-propyl bromide (0.738 g, 6 mmol) was carried out to give a yellow oil. Chromatography (Florisil benzene–ethyl acetate) gave **3b** in 98% yield (2.08 g) (see Table I).

1-Benzyl-2,6-dicyano-2-methyl-6-undecylpiperidine (3c). By the same procedure, the reaction of **2b** (1.358 g, 3.6 mmol) with methyl iodide (0.613 g, 4.3 mmol) was carried out to give a yellow oil (1.639 g). Chromatography (Florisil, benzene–ethyl acetate) gave **3c** in 97% yield (1.368 g) (see Table I).

1-Benzyl-2,6-dicyano-2,6-dimethylpiperidine (3d). By the same procedure, the reaction of 1 with methyl iodide (0.943 g, 6.6 mmol) in the presence of LDA (5.04 mmol) was carried out

to give a yellow oil (4.294 g). Chromatography (Florisil, benzene–hexane) gave **3d** in 88% yield (3.34 g) (see Table I).

1-Benzyl-2,6-dicyano-2,6-diundecylpiperidine (3e). By the same procedure, the reaction of **1** (2.25 g, 10 mmol) with undecyl bromide (5.17 g, 22 mmol) in the presence of LDA (22 mmol) was carried out to give a yellow oil (6.33 g). Chromatography (Florisil, benzene) gave **3e** in 74% yield (3.92 g) (see Table I).

(III) Decyanation of Mono- and Dialkylated Products 2 and 3. Preparation of 1-Benzyl-2-methyl-6-undecylpiperidine (5a) as a Typical Example. Under dry argon or nitrogen, sodium borohydride (50.7 mg, 1.2 mmol) was added to a solution of **3a** (0.137 g, 0.35 mmol) dissolved in isopropyl alcohol (14 mL). The reaction mixture was heated at 70 °C for 9 h until disappearance of **3a** was confirmed by thin-layer chromatography (TLC). The mixture was cooled, diluted with water, and extracted with ether. The ether layer was dried ($NaSO_4$) and evaporated and the residue chromatographed (silica gel benzene–hexane). Thus, **5a** was obtained as a mixture of two stereoisomers in 99% yield (0.119 g). The ratio of trans–cis was 75:25 (^1H NMR). The spectrum agreed with that in the literature.[3b]

1-Benzyl-2-*n*-propyl-6-*n*-undecylpiperidine (5b). By the same procedure, the mixture of **3b** (1.09 g, 2.6 mmol) with $NaBH_4$ (0.328 g, 7.8 mmol) was heated at 70 °C for 21 h to give a colorless oil (0.9035 g). Chromatography (silica gel, benzene–hexane) gave **5b** as a mixture of trans and cis isomers (79:21) in 75% yield (0.658 g) (see Table II).

1-Benzyl-2-methyl-6-tridecylpiperidine (5c). By the same procedure, the mixture of **3c** (0.416 g, 0.99 mmol) and $NaBH_4$ (0.139 g, 3.3 mmol) was heated at 70 °C for 8 h to give a colorless oil (0.394 g). Chromatography (silica gel, benzene–hexane) gave **5c** as a mixture of trans and cis isomers (83:17) in 98% yield (0.358 g) (see Table II).

1-Benzyl-2,6-dimethylpiperidine (5d). By the same procedure, the mixture of **3d** (1.026 g, 4.1 mmol) and $NaBH_4$ (0.529 g, 13 mmol) was heated at 70 °C for 21 h to give a colorless oil (0.869 g). Chromatography (silica gel, benzene–ethyl acetate) gave **5d** as a mixture of trans and cis isomers (78:22) in 88% yield (0.722 g). ^1H NMR spectrum of the two isomers agreed with that reported in the literature.[6]

1-Benzyl-2,6-diundecylpiperidine (5e). By the same procedure, the mixture of **3e** (0.906 g, 1.7 mmol) and $NaBH_4$ (0.128 g, 5.1 mmol) was heated at 70 °C for 9 h to give a colorless oil. Chromatography (silica gel, benzene–hexane) gave **5e** as a mixture of trans and cis isomers (80:20) in 99% yield (0.739 g) (see Table II).

1-Benzyl-2-undecylpiperidine (4a). By the same procedure, the mixture of **2b** (0.374 g, 0.99 mmol) and $NaBH_4$ (0.166 g, 3.9 mmol) was heated at 70 °C for 18 h to give a colorless oil (0.337 g). Chromatography (silica gel, benzene–ethyl acetate) gave **4a** in 98% yield (0.318 g) (see Table II).

1-Benzyl-2-*n*-propylpiperidine (4b). By the same procedure, the mixture of **2d** (0.347 g, 1.30 mmol) and $NaBH_4$ (0.173 g, 3.2 mmol) was heated at 70 °C for 6 h to give a colorless oil. Chromatography (silica gel, benzene–hexane) gave **4b** in 64% yield (0.182 g) (see Table II).

(IV) Debenzylation of the Products 4 and 5. Preparation of Solenopsin A, 2-Methyl-6-Undecylpiperidine (7a), as a Typical Example. The debenzylation of **5a** was carried out according to the procedure reported in the literature:[4] To a solution of **5a** (1.38 g, 2.9 mmol) dissolved with ethyl alcohol (50 mL) was added 15% hydrochloric acid (5 mL) and 5% Pd–C (0.951 g). The mixture was hydrogenated on Parr apparatus for 1 h at room temperature under 1 atm. After the catalyst was filtered off and washed with water (ca. 10 mL), the filtrate was made just alkali with a 10% aqueous solution of sodium carbonate and extracted with diethyl ether (2 × 30 mL). The combined ether layers were dried with $MgSO_4$ and distilled off. Thus, **7a** was obtained as a mixture of the trans and cis isomers in 62% yield (0.100 g). The mole ratio of the trans to the cis isomers of **7a** was same with that (75:25) of **5a**. ^1H NMR spectrum of **7a** was identical with that of trans[3a] and cis[3c] 2-methyl-6-undecylpiperidine reported in the literature.

2,6-Diundecylpiperidine (7b). By the same procedure, the hydrogenation of **5e** (1.38 g, 2.9 mmol) was carried out for 3 h in a mixture of 15% hydrochloric acid (5 mL) and Pd–C (0.951 g). Thus, **7b** was obtained in 77% yield (0.879 g): colorless oil; ^1H NMR ($CDCl_3/Me_4Si$, 60 MHz) δ 0.69–1.05 (m, 6 H), 1.05–1.80 (m, 46 H), 2.70 (br s, 2 H). The hydrochloric salt of **7b** was prepared and recrystallized from a mixture of methyl alcohol and water. Anal. Calcd for $C_{27}H_{55}N\cdot HCl$: C, 75.38; H, 13.12; N, 3.26. Found: C, 75.23; H, 13.00; N, 3.26.

2-*n*-Propylpiperidine (6a), Coniine. By the same procedure, the hydrogenation of **4b** (0.182 g, 0.84 mmol) was carried out for 10 h in a mixture of ethyl alcohol (30 mL), 15% hydrochloric acid (3 mL), and 5% Pd–C (1.16 g). Thus, **6a** was obtained as a colorless oil in 45% yield (0.0474 g). The ^1H NMR spectrum of **6a** was identical with that in the literature.[7]

Registry No. 1, 98195-08-5; **2a**, 98195-09-6; **2b**, 98195-10-9; **2c**, 98195-11-0; **2d**, 98195-12-1; **2e**, 98195-13-2; **3a**, 98195-14-3; **3b**, 98195-15-4; **3c**, 98217-01-7; **3d**, 98195-16-5; **3e**, 98195-17-6; **4a**, 98195-26-7; **4b**, 98195-27-8; *trans*-**5a**, 98195-18-7; *cis*-**5a**, 98195-19-8; *trans*-**5b**, 98195-20-1; *cis*-**5b**, 98195-21-2; *trans*-**5c**, 98195-22-3; *cis*-**5c**, 98195-23-4; *trans*-**5d**, 4209-64-7; *cis*-**5d**, 4209-63-6; *trans*-**5e**, 98195-24-5; *cis*-**5e**, 98195-25-6; **6a**, 3238-60-6; *trans*-**7a**, 76094-26-3; *cis*-**7a**, 92619-72-2; **7b**, 98195-28-9; **7b**·HCl, 98195-29-0; undecyl bromide, 693-67-4; tridecyl bromide, 765-09-3; *n*-propyl bromide, 106-94-5; benzyl bromide, 100-39-0.

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