(50 mL), and the ammonia was allowed to evaporate. To the residue were added ethyl ether (100 mL) and water (100 mL). The ether solution was extracted, dried, and evaporated, and phenyl methyl selenide was isolated (778 mg, 4.55 mmol, 90% yield) and then oxidized with Br_2 in CCl_4, giving a precipitate of phenyl methyl selenide dibromide: 1.115 g (3.3 mmol, 67% yield); after recrystallization from CCl_4, mp 141-143 °C (lit.[3] mp 143-144 °C).

Synthesis of *o*-Methylphenyl Methyl Selenide. *o*-Methylphenyl selenide ion was prepared as described above from 9.99 mmol of *o*-iodotoluene and 5.00 mmol of selenide ion with 4 h of irradiation, and then sodium metal was added in excess, followed by methyl iodide (5.2 mmol). Water (50 mL) was added and the ammonia was allowed to evaporated. To the residue were added ethyl ether (100 mL) and water (100 mL). The ether solution was separated, dried, and evaporated, and *o*-methylphenyl methyl selenide was isolated in 87% yield and purified by column chromatography.[12]

Acknowledgment. A.B.P. gratefully acknowledges receipt of a fellowship from the Consejo Universitario de Investigaciones, Universidad Nacional de Córdoba.

Registry No. Phenyl selenide ion, 14971-39-2; selenium, 7782-49-2; iodobenzene, 591-50-4; diphenyl diselenide, 1666-13-3; 1-iodonaphthalene, 90-14-2; 1-naphthyl phenyl selenide, 65490-21-3; phenyl methyl selenide, 4346-64-9; phenyl methyl selenide dibromide, 78763-69-6; *o*-methylphenyl selenide ion, 78763-70-9; *o*-iodotoluene, 615-37-2; (*o*-methylphenyl)methyl selenide, 1528-88-7; diphenyl selenide, 1132-39-4; diphenyl telluride, 1202-36-4; diphenyl ditelluride, 32294-60-3; phenyl methyl telluride, 872-89-9; bis(1-naphthyl) telluride, 4537-22-8; bis(1-naphthyl) ditelluride, 32294-58-9; $SeNa_2$, 1313-85-5; $TeNa_2$, 12034-41-2; Te, 13494-80-9.

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7-Amino-5-(Methylamino)heptanoic Acid: A Potential Putrescine Hapten

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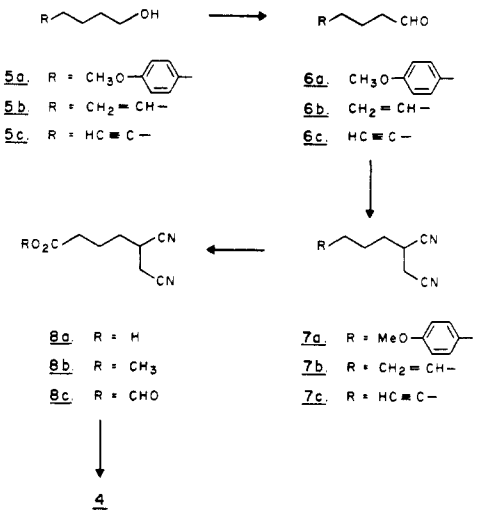
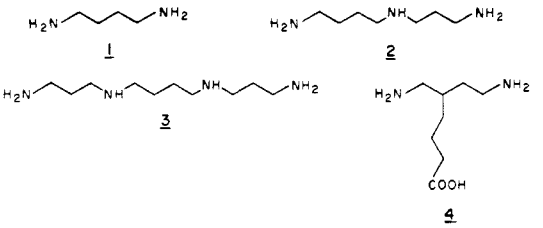
There is currently a significant interest in the development of specific and highly sensitive technqiues for analysis of the biologically ubiquitous di- and polyamines putrescine, spermidine, and spermine (1-3), respectively.[2-5] Radioimmunoassay techniques, currently available for spermidine[6] (2) and spermine[7,8] (3) but not putrescine (1), are of particular interest in view of their high sensitivity and specificity, low cost and convenience in clinical settings.[2,3] We have considered the structural requirements for a hapten suitable for developing a specific radioimmunoassay for the diamine putrescine (1). 7-Amino-5-(aminomethyl)heptanoic acid (4) was selected for initial study; this report describes an efficient synthesis of 4 which permits facile introduction of a ^{14}C label at the 5-aminomethyl carbon.

Scheme I





A number of criteria were employed in the design of 4 as a hapten for preparation of antiputrescine antibodies. The aliphatic chain containing the terminal carboxylic acid function to be used for attachment of the hapten to a protein carrier via amide linkage was placed β to the amine group of the putrescine moiety to minimize steric factors detrimental to antiputrescine antibody development. The length of the chain separating the carboxyl and amine functional groups was chosen to minimize intramolecular lactamization during coupling of the hapten to protein.[9]

The synthetic route used for construction of 4 is shown in Scheme I. In an initial synthesis, commercially available 4-(4-methoxyphenyl)butanol (**5a**) was oxidized to the corresponding aldehyde **6a** in 89% yield, using a procedure developed by Swern and co-workers.[10] Elaboration of a succinonitrile moiety with **6a** was accomplished by a one-step method reported by Whitely and Marianelli.[11] A dimethyl sulfoxide solution of aldehyde **6a**, potassium cyanide, and ethyl cyanoacetate was allowed to react at room temperature for 16 h and then acidified and heated to afford, after chromatographic purification, a 72% yield of dinitrile **7a**.

The selective oxidation of the aromatic ring of **7a** by ruthenium tetraoxide was used to construct the carboxyl group.[12] Treatment of **7a** with ruthenium tetraoxide resulted in an exothermic reaction with evolution of carbon dioxide and formation of carboxylic acid **8a**, which was methylated with diazomethane and purified by chroma-

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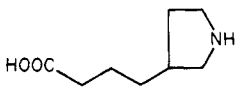
tography to yield dicyano ester **8b**, 37%. Catalytic hydrogenation of the cyano groups of **8b** generated the required amino functionalities and hydrolysis of the methyl ester completed the synthesis of the hapten 7-amino-5-(aminomethyl)heptanoic acid (**4**).

The low yield obtained upon ruthenium tetraoxide oxidation of **8b** led us to explore the use of olefinic (**5b**) and acetylenic (**5c**) moieties as latent carboxylic acid functions. Succinonitriles **7b** and **7c** were prepared from **5b** and **5c**, using the previously described procedure. Ozonolysis of **7b** in methanol followed by Jones oxidation of the ozonide gave an 80% yield of dicyano ester **8b**. Similarly, ozonolysis of acetylene **7c** afforded **8b** in 80% yield. This result is noteworthy since there are no literature reports of the preparative utility of ozonolysis of acetylenes to produce carboxylic acids. Mechanistic studies[13-15] of this reaction have shown that formyl anhydrides are formed;[14] our study confirms this result. ^{13}C and ^{1}H nuclear magnetic resonance (NMR) spectra of the intermediate ozonolysis product showed the presence of a formic anhydride. Ester **8b** was obtained following methanolysis of the anhydride and diazomethane methylation.

The catalytic reduction step (8 → 4) employed in the synthetic sequence requires comment. The crude product obtained upon hydrogenation of **7b** in acetic acid–hydrochloric acid over platinum oxide consisted of two compounds in the ratio of 7:3 as shown by ^{13}C NMR spectrometry. Esterification of the crude reduction product and recrystallization removed the minor component shown to be the pyrrolidine **9** by spectrometric examination. Hydrogenation of **8b** in ammoniacal methanol yielded **9** as the sole product.



9

Experimental Section

NMR spectra were obtained by using either a Varian Associates HA-100 or a JEOL FX90Q nuclear magnetic resonance spectrometer. Mass spectra were recorded with a CEC (Du Pont) 21-110 or a Du Pont 21-491 mass spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. Synthetic products were characterized by mass spectra and ^{1}H and ^{13}C nuclear magnetic resonance spectra.

Preparation of Aldehydes 6a–c. The procedure of Swern et al.[10] was used. To a solution of 2.77 mL of oxalyl chloride in 60 mL of methylene chloride at −60 °C was added dropwise with stirring 4.72 mL of dimethyl sulfoxide in 15 mL of methylene chloride. When addition was complete 5 g of alcohol **5a** (obtained from Aldrich Chemical Co.) in 25 mL of methylene chloride was added over a 5-min interval. The solution was stirred in the cold for 15–20 min before adding 19 mL of triethylamine, which caused a heavy white precipitate to form. After 20–25 min, the reaction mixture was removed from the cooling bath and allowed to warm to room temperature. Distilled water (125 mL) was added and the organic layer was removed. The aqueous layer was extracted with methylene chloride and discarded; the organic layers were combined and washed with 5% hydrochloric acid solution followed by a saturated sodium chloride solution. After drying over magnesium sulfate and filtering, the solvent was evaporated under reduced pressure to yield 4.4 g of aldehyde **6a**, which was used without further purification: ^{1}H NMR ($CDCl_3$) δ 1.8 (m, 2 H), 2.24 (t, 2 H), 2.47 (t, 2 H), 3.63 (s, 3 H), 6.81 (AB, 4 H).

Similarly, from 18 g (0.18 mol) of 5-hexenol (**5b**) there was obtained 16 g of crude 5-hexenal (**6b**), which was used without further purification: ^{1}H NMR ($CDCl_3$) δ 1.5–1.85 (m, 2 H), 1.9–2.2 (m, 2 H), 2.25–2.45 (m, 2 H), 4.85–5.1 (m, 2 H), 5.6–5.95 (m, 1 H), 9.68 (t, 1 H); ^{13}C NMR δ 21.29, 32.99, 43.12, 115.50, 137.50, 202.18.

From 29.4 g (0.3 mol) of 5-hexynol (**5c**) there was obtained 19.6 g (66%) of 5-hexynal (**6c**) after distillation: bp 62–64 °C (33 mm), lit.[16] bp 61–62 °C (30 mm); ^{1}H NMR ($CDCl_3$) δ 1.01 (m, 2 H), 2.01 (t, 1 H), 2.23 (m, 2 H), 9.68 (t, 1 H); ^{13}C NMR δ 20.37, 23.3, 43.99, 69.66, 82.88, 195.70.

Preparation of Substituted Succinonitriles 7a–c. To 7.5 mL of dry dimethyl sulfoxide and 0.83 g (7 mmol) of ethyl cyanoacetate was added 0.5 g (7 mmol) of finely powdered potassium cyanide. The mixture was heated gently under nitrogen to dissolve the potassium cyanide and then cooled in an ice bath to 15 °C. To this solution was added 1.3 g (7 mmol) of 4-(4-methoxyphenyl)butanal (**6a**). After the mixture was stirred for 15 min, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature and stand overnight. The mixture was again cooled to 15 °C and 0.65 mL of concentrated hydrochloric acid was added. After 15 min the reaction mixture was heated to 100 °C over a period of 1 h; 1.5 mL of water was added and the temperature of the reaction mixture was raised to 135–145 °C and maintained for 7 h. The reaction mixture was then cooled and poured into 100 mL of ice water. The resulting aqueous solution was extracted 5 times with ether. The combined ether extract was washed with water and saturated sodium chloride solution and dried, and the solvent was removed. The resulting dark oily residue was chromatographed over silica gel with 2% ethyl acetate in dichloromethane for elution to give 1.2 g (72%) of 5-(4-methoxyphenyl)-1,2-dicyanopentane (**7a**) as an oil: ^{1}H NMR ($CDCl_3$) δ 1.68 (m, 4 H), 2.55 (m, 4 H), 2.77 (m, 1 H), 3.69 (s, 3 H), 6.90 (AB, 4 H).

Anal. Calcd for $C_{14}H_{16}N_2O$: C, 73.66; H, 7.07; 12.27. Found: C, 73.73; H, 7.05; N, 12.35.

In similar reactions, **7b** was obtained in 59% overall yield from 5-hexenol (**5b**): ^{1}H NMR ($CDCl_3$) δ 1.5–1.8 (m, 2 H), 2.6–2.8 (m, 2 H), 2.8–3.0 (m, 1 H), 4.9–5.2 (m, 2 H), 5.6–6.0 (br, 1 H); ^{13}C NMR δ 21.02, 25.79, 28.39, 30.83, 32.67, 115.55, 115.88, 119.02, 137.06; mass spectrum, *m/e* 148 ($M^{+\cdot}$), 147.

Anal. Calcd for $C_9H_{12}N_2$: C, 72.94; H, 8.16; N, 18.90. Found: C, 72.98; H, 8.12; N, 18.95.

Dinitrile **7c** was obtained in 60% overall yield from 5-hexynol (**5c**): ^{1}H NMR ($CDCl_3$) δ 1.5–2.0 (m, 4 H), 2.05 (t, 1 H), 2.31 (m, 2 H), 2.7–2.8 (m, 2 H), 2.8–3.2 (m, 1 H); ^{13}C NMR δ 17.52, 20.80, 25.13, 27.89, 30.16, 69.72, 82.60, 115.88, 118.87; mass spectrum, *m/e* 146 ($M^{+\cdot}$), 145.

Anal. Calcd for $C_9H_{10}N_2$ C, 73.93; H, 6.90; N, 19.17. Found: C, 73.85; H, 7.01; N, 19.28.

Methyl 5,6-Dicyanohexanoate (8b). Method A. To a solution of 1 g of 5-(5-methoxyphenyl)-1,2-dicyanopentane (**7a**) in 80 mL of acetone was added 20 mL of water containing 4 g of sodium peroidate followed by 50 mg of ruthenium chloride. After a few seconds the resulting orange solution began to warm, carbon dioxide was evolved, and a precipitate of sodium iodate formed. When the exothermic reaction had subsided, the reaction mixture was diluted with 150 mL of acetone and the excess oxidizing agent was destroyed by addition of 30 mL of 2-propanol. The precipitate was separated and washed with 100 mL of acetone. Acetone was removed from the combined filtrates under reduced pressure and the resulting aqueous concentrate was made basic with saturated sodium bicarbonate solution and extracted with ether (discarded). The aqueous phase was then acidified (hydrochloric acid) and extracted with ether. The dried ether solution was concentrated to 50 mL and an ethereal solution of diazomethane was added protionwise until the color perisisted. Excess diazomethane was consumed by dropwise addition of acetic acid, the solvent was removed, and the residue was chromatographed over silica gel with dichloromethane and ethyl acetate for elution to yield 0.29 g (37%) of methyl 5,6-dicyanohexanoate (**8b**): ^{1}H NMR ($CDCl_3$) δ 1.7–1.9 (m, 4 H), 2.3–2.5 (m, 2 H), 2.7–2.8 (m, 2 H), 2.8–3.0 (m, 1 H), 3.68 (s, 3 H); mass spectrum, *m/e* 149 (M − OCH_3).

Anal. Calcd for $C_9H_{12}N_2O_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.12; H, 6.85; N, 15.43.

Method B. A solution of 19.1 g of 6,7-dicyanohept-1-ene (**7b**) in 300 mL of dichloromethane–methanol (3:1) at −78 °C was

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treated with ozone until the blue color persisted. The solvent was then removed and the oily residue was dissolved in acetone and added over 1 h to 485 mL of Jones reagent maintained at -5 °C. After addition was complete, the reaction mixture was maintained at -5 °C for an additional hour and allowed to warm to room temperature (~3 h). The reaction mixture was then recooled to -5 °C and 30 mL of 2-propanol was added. After 1 h the cooling bath was removed and following an additional hour of stirring the organic phase of the reaction mixture was separated. Water (400 mL) was added to the aqueous phase, which was then extracted 4 times with 200-mL portions of ethyl acetate. The combined organic extract was dried and the solvent removed. Esterification with CH_2N_2 (Et_2O) furnished after removal of the solvent a colorless syrupy residue which was chromatographed over silica gel with 5% ethyl acetate in dichloromethane to yield 16.4 (80%) of methyl 5,6-dicyanohexanoate (**8b**).

Method C. A solution of 19.6 g of 6,7-dicyanohept-1-yne (**7c**) in 650 mL of dichloromethane was ozonized in three portions at -78 °C until the blue color persisted. Methanol (100 mL) cooled to -78 °C was then added and the reaction mixture was allowed to warm slowly to -10 °C during 24 h. (More rapid warming results in a vigorous exothermic reaction with no adverse effect on product yield.) The solvent was then removed and the resulting oil was dissolved in methanol and heated on a steam bath for 20 min. Carbon tetrachloride was then added to the reaction mixture, and solvents were distilled under reduced pressure to ensure that residual formic acid was removed. The residual oil dissolved in ethyl acetate was treated with ethereal diazomethane and chromatographed as described to yield 18.9 g (78%) of methyl 5,6-dicyanohexanoate (**8b**).

7-Amino-5-(aminomethyl)heptanoic Acid (4). A mixture of 9.2 g of methyl 5,6-dicyanohexanoate (**8b**) in 300 mL of ethanol-concentrated hydrochloric acid (1:1) and 1 g of platinum oxide was shaken under 2 atm of hydrogen until uptake of hydrogen ceased. The catalyst was removed, and the solvents were distilled to afford a semicrystalline solid, which was triturated first with acetone and then with cold ether–ethanol (1:4) to yield 7 g (55%) of 7-amino-5-(aminomethyl)heptanoic acid dihydrochloride: mp 196–198 °C; ^{1}H NMR (D_2O) δ 1.4–2.2 (m, 7 H), 2.62 (t, 2 H), 3.22 (m, 4 H); ^{13}C NMR δ 20.97, 28.55, 29.42, 33.80, 34.08, 37.60, 42.64, 178.50; mass spectrum, *m/e* 175 (MH^+), 156.

Evaporation from the ether–ethanol solvent yielded 2.2 g (21%) of 4-(pyrrolidin-3-yl)butyric acid (**9**): ^{13}C NMR (D_2O) δ 23.30, 30.18, 31.64, 34.13, 37.60, 45.78, 50.49, 178.34; mass spectrum, *m/e* 157 ($M^{+\cdot}$).

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Registry No. 4, 78790-58-6; 4·2HCl, 78790-59-7; **5a**, 52244-70-9; **5b**, 821-41-0; **5c**, 928-90-5; **6a**, 56047-51-9; **6b**, 764-59-0; **6c**, 29329-03-1; **7a**, 78790-60-0; **7b**, 78790-61-1; **7c**, 78790-62-2; **8b**, 78790-63-3; **9**, 78790-64-4; ethyl cyanoacetate, 105-56-6.

Reduction of Esters to Alcohols by means of Sodium Borohydride in Polyethylene Glycols

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It is well-known that esters are essentially inert toward reduction by sodium borohydride,[2] although in some instances a few exceptions are reported. In fact, esters containing participating neighboring groups[3] as well as some heterocyclic aromatic esters[4] can be converted into the corresponding alcohols. The above reaction can be also performed by use of reagents which are added to $NaBH_4$, thus enhancing its reducing power by deeply changing the reacting species.[5,6] In addition, the nature of the solvent plays a very important role in the rate and kind of reduction, as it has been pointed out also very recently.[7]

We have previously suggested that polyethylene glycols (PEG) could be used as complexing solvents of inorganic salts, in order to enhance the reactivity of the anion with the organic substrate.[8,9] In the first report,[8] we had observed that $NaBH_4$ in PEG 400 was able to reduce carbonyl compounds, the reaction being in contrast with the behavior of $NaBH_4$ in crown ethers[10] and polyethylene glycol ethers.[11] In these systems, where the anion could be brought into solution, a lowered reactivity was observed. As extension of our observation, we have studied the reduction of esters in PEG 400 by $NaBH_4$ (see Scheme I), which is unable to accomplish such a reaction itself. The reaction was successfully carried out with several substrates, the yields generally good (Table I).

Table I. Reduction of Esters to Alcohols by $NaBH_4$ in PEG 400[a]

substrate	product	yield, %[b]
1a	2a	80
1b	2b	82
1c	2c	73[c]
1d	2d	75
1e	2e	65
1g	2g	90
1h	2h	80
1i	*d*	86
1l	2l	80
1m	$C_{14}H_{43}OH$	90

[a] Molar ratio of $NaBH_4$/ester of 3:1, unless otherwise stated, temperature 65 °C, time 10 h. [b] Yields refer to isolated products. Purity and identity of compounds were established by usual spectroscopic methods as well as by TLC and GC. [c] 10% of 4-aminobenzyl alcohol was present. [d] 3-Phenylpropanol was the only detectable product of the reaction. [e] 24 h at 65 °C, $NaBH_4$/ester molar ratio of 9:1.

As a comment to our results, no substantial difference has been noticed between ethyl and methyl esters, and, unless otherwise stated, an average 10-h reaction time has been established as optimum. Only a small amount of reduction of the nitro group of **1c** was noticed (10% of the products), and **1i** was not reduced to **2i** but to 3-phenylpropanol, as in the sodium borohydride reduction of α,β-unsaturated ketones to saturated alcohols.[12] In agreement with results of Maki and co-workers,[13] *p*-amino- and *p*-

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