Synthesis of a Sulfur-Containing Analogue of *myo*-Inositol, D,L-1-Deoxy-1-mercapto-*myo*-inositol, *via* an Intramolecular Sulfur-Delivery Reaction

Jean Pierre Guidot and Thierry Le Gall*

CEA, CE Saclay, Dêpartement de Biologie Cellulaire et Molêculaire, Service des Molêcules Marquées, Bt 547, 91191 Gif-sur-Yvette, France

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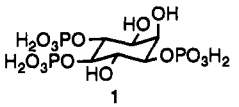
Introduction

The role of inositol lipids in cell signaling has been discovered recently and is now well documented.[1] D-*myo*-Inositol 1,4,5-trisphosphate (Ins(1,4,5)P_3, 1) is produced by the receptor-controlled hydrolysis of phosphatidylinositol 4,5-bisphosphate (PIP_2) by phospholipase C. Ins(1,4,5)P_3 binds specifically to receptors on the endoplasmic reticulum, thus stimulating the release of calcium ions from intracellular stores and initiating various physiological responses.

It would be of great value to find substances capable of altering this biological pathway; not surprisingly, much work has been devoted to the synthesis of structural analogues of *myo*-inositol.[2] Such compounds or their metabolites could act either as substrates or inhibitors of the enzymes involved in the cascade. Some of them have been reported to inhibit cell growth.[2c-e]



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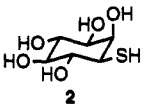

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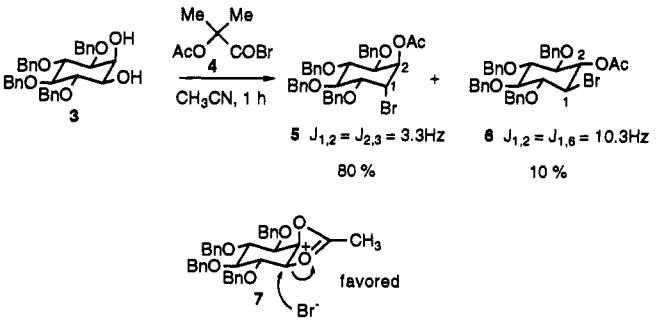
A particularly attractive isostere of *myo*-inositol is D-1-deoxy-1-mercapto-*myo*-inositol (**2**), an analogue which bears the same stereochemistry as *myo*-inositol, one hydroxyl group being replaced by a mercapto group. This compound could be incorporated in cellular inositol lipids and lead to analogues of PI, PIP, and PIP_2 bearing a thiophosphate moiety and hence would probably alter the action of phospholipase C. Its enantiomer, D-3-deoxy-3-mercapto-*myo*-inositol, was recently described and reported to display cell growth inhibitory activity.[2e] We present here the synthesis of D,L-1-deoxy-1-mercapto-*myo*-inositol.[3] Starting from a suitably protected *myo*-inositol derivative, the synthetic sequence involved two inversion steps at the 1-position in order to establish the desired *myo*-configuration of the target molecule.

Results and Discussion

Racemic 3,4,5,6-tetra-*O*-benzyl-*myo*-inositol (**3**) was prepared in three steps from *myo*-inositol, according to the procedure described by Gigg et al.[4] The reaction of this diol with α-acetoxyisobutyryl bromide (**4**)[5] (Scheme I) proceeded cleanly and with a remarkably good selectivity, giving rise to a 89/11 mixture of the *trans*-bromo acetates **5** and **6**, which were readily separated by silica gel chromatography. The coupling constants observed in the 300-MHz ^1H NMR of the two bromo acetates, especially the α-acetate protons, were used to identify the regioisomers. The proton H_2 of **5** exhibited small vicinal coupling constants (δ = 5.50 ppm; $J_{1,2} = J_{2,3}$ = 3.3 Hz) indicating its equatorial orientation. The proton H_1 of **6** exhibited large vicinal coupling constants (δ = 5.27 ppm; $J_{1,2} = J_{1,6}$ = 10.3 Hz) indicating its axial orientation.

Scheme I



The regiochemical outcome of this reaction is consistent with the mechanism proposed by Moffatt et al.[5] The opening of the presumed reaction intermediate, the dioxolenium cation **7**, by a bromide anion was expected to lead preferentially to the diaxial isomer **5**, on the basis of related studies by King and Allbutt.[6]

Several attempts to introduce sulfur by the reaction of **5** with sulfur nucleophiles failed, probably because of the strong interaction existing between the incoming nucleophile and the axial substituent on C_2, in the transition state.

We thus turned to an intramolecular displacement strategy similar to the one designed by Corey and colleagues to introduce an oxygen nucleophile[7] but applied here for the first time at the introduction of a sulfur nucleophile. Basically, we needed to functionalize the oxygen on C_2 as a thioester; the latter function should be easily converted to a thioenolate anion, which would then displace the bromide, establishing the desired configuration at C_1.

This was achieved as described in Scheme II. Cleavage of the acetoxy group of **5** had to be performed in a nonalkaline medium in order to avoid the formation of an epoxide, since even the use of a catalytic amount of KCN in MeOH[8] gave rise to some epoxide along with bromohydrin **8**. However, the deacetylation was readily performed, in 89% yield, using methanolic HCl.[9] Treatment of **8** with 1,1'-thiocarbonyldiimidazole afforded imidazolide **9**, which was then reacted at −78 °C with cyanomethyllithium. After 4 h at −78 °C followed by 20 h at room temperature, compound **10** was isolated in 65% yield.

(1) *Inositol Lipids in Cell Signalling*; Michell, R. H., Drummond, A. H., Downes, C. P. Eds.; Academic Press: London, 1989.

(2) For some examples of syntheses of such analogues, see: (a) Jiang, C.; Moyer, J. D.; Baker, D. C. *J. Carbohydr. Chem.* **1987**, *6*, 319–355. (b) Jiang, C.; Schedler, D. J. A.; Morris, P. E., Jr.; Zayed, A.-H. A.; Baker, D. C. *Carbohydr. Res.* **1990**, *207*, 277–285. (c) Kozikowski, A. P.; Fauq, A. H.; Rusnak, J. M. *Tetrahedron Lett.* **1989**, *30*, 3365–3368. (d) Kozikowski, A. P.; Fauq, A. H.; Powis, G.; Melder, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 4528–4531. (e) Powis, G.; Aksoy, I. A.; Melder, D.; Aksoy, S.; Eichinger, H.; Fauq, A. H.; Kozikowski, A. P. *Cancer Chemother. Pharmacol.* **1991**, *29*, 95–104. (f) Offer, J. L.; Voorheis, H. P.; Metcalfe, J. C.; Smith, G. A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 953–960. (g) Lowe, G.; McPhee, F. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1249–1253.

(3) The synthesis of 6-deoxy-6-mercapto-*epi*-inositol, which bears a stereochemistry different from that of *myo*-inositol, has been reported: McCastland, G. E.; Furuta, S.; Furst, A. *J. Org. Chem.* **1964**, *29*, 724–727.

(4) Gigg, R.; Warren, C. D. *J. Chem. Soc. C* **1969**, 2367–2371.

(5) Greenberg, S.; Moffatt, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 4016–4025.

(6) King, J. F.; Allbutt, A. D. *Can. J. Chem.* **1969**, *47*, 1445–1459.

(7) Corey, E. J.; Das, J. *Tetrahedron Lett.* **1982**, *23*, 4217–4220.

(8) Herzig, J.; Nudelman, A.; Gottlieb, H. E.; Fischer, B. *J. Org. Chem.* **1986**, *51*, 727–730.

(9) Byramova, N. E.; Ovchinnikov, M. V.; Backinowsky, L. V.; Kochetkov, N. K. *Carbohydr. Res.* **1983**, *124*, C8–C11.

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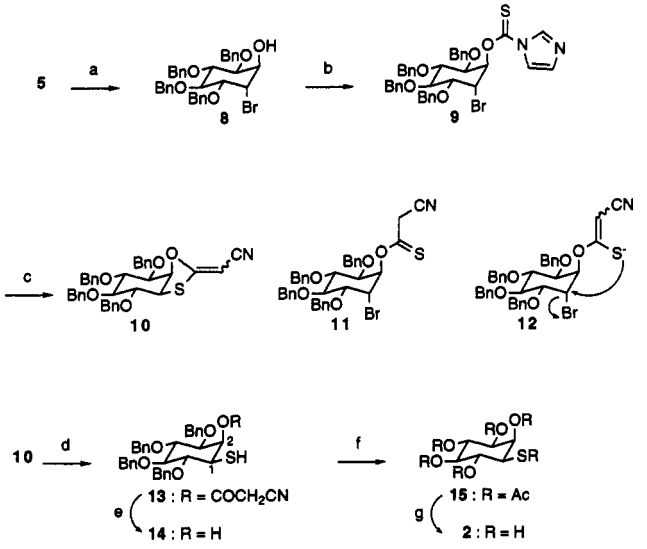
Scheme II[a]



[a] Reagents: (a) AcCl, MeOH–$CHCl_3$, reflux, 16 h, 89%; (b) 1,1'-thiocarbonyldiimidazole, THF, rt, 4 h, 90%; (C) $LiCH_2CN$, THF, −78 °C, 4 h, then rt, 20 h, 65%; (d) 3:1 THF–1 N HCl, reflux, 3 h, 90%; (e) K_2CO_3, THF–MeOH, rt, 20 h, 89%; (f) Na/NH_3–THF, −78 °C, then 1:1 Ac_2O–pyridine, rt, 20 h, 89%; (g) NH_3, MeOH, rt, 18 h, then DTT, H_2O, rt, 1 h, 89%.

Thioketene acetal **10** was obtained as a 2.4/1 mixture of geometric isomers at the newly created double bond. In ^1H NMR, the vinylic protons of the two isomers appear as singlets at 5.01 and 4.43 ppm. The ^{13}C NMR chemical shifts of the nitrile carbons (173.6 and 172.8 ppm) are also characteristic.

The likely series of events leading to the formation of **10** from **9** is the following: (a) $LiCH_2CN$ displaces the imidazolyl group to give activated thioester **11**; (b) the base imidazolyllithium abstracts an acidic proton; (c) the resulting sulfur anion **12** attacks intramolecularly at C_1, yielding thioketene acetal **10**.

Refluxing **10** in 3:1 THF–1 N HCl afforded ester **13**. The values observed in ^1H NMR for the vicinal coupling constants of H_1 and H_2 establish that the ester moiety is in axial position (H_1: δ = 5.66 ppm; $J_{1,2} = J_{2,3}$ = 2.6 Hz) and that the mercapto group is in equatorial position (H_2: δ = 3.06 ppm; $J_{1,6}$ = 10.6 Hz, $J_{1,2}$ = 2.2 Hz). Saponification of the mixed malonate gave rise to the expected mercapto alcohol **14** along with some of its corresponding disulfides (a mixture of two diastereomers, since **14** is racemic). The benzyl groups of **14** were then removed by reaction of this compound with sodium in liquid ammonia, and the hexaacetyl derivative of **2** was isolated after treatment of the crude product with pyridine–Ac_2O, followed by chromatographic purification. Hydrolysis of the ester functions (NH_3, MeOH) proceeded well, but a mixture of the racemic thiol and the corresponding diastereomeric disulfides was usually obtained. However, treatment of the mixture with an aqueous solution of dithiothreitol (DTT)[10] afforded D,L-1-deoxy-1-mercapto-*myo*-inositol (**2**) cleanly.

Thus, we have developed the synthesis of a sulfur-containing analogue of *myo*-inositol which utilizes an unprecedented intramolecular sulfur-delivery reaction. Biological studies concerning the incorporation of this analogue into cellular phospholipids are in progress.

(10) Cleland, W. W. *Biochemistry* **1964**, *3*, 480–482.

Experimental Section

General Procedures. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl; CH_2Cl_2 and acetonitrile were distilled from CaH_2. All reactions were performed under a N_2 atmosphere. Reaction progress was monitored by TLC, performed on silica gel $60F_{254}$ plates (Merck), with detection by UV light or with aqueous $KMnO_4$. Column chromatography was performed on Merck silica gel. Melting points (uncorrected) were determined on a Kofler hot-stage apparatus. ^1H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively; chemical shifts, δ, are reported in ppm; coupling constants, J, are reported in Hz and refer to apparent multiplicities rather than true coupling constants.

(±)-2-*O*-Acetyl-3,4,5,6-tetra-*O*-benzyl-1-bromo-1-deoxy-*chiro*-inositol (5) and (±)-2-*O*-Acetyl-3,4,5,6-tetra-*O*-benzyl-1-bromo-1-deoxy-*scyllo*-inositol (6). To a solution of 989 mg (1.83 mmol) of (±)-3,4,5,6-tetra-*O*-benzyl-*myo*-inositol **3**[4] in 18 mL of CH_3CN cooled at 0 °C was added 300 μL (2.04 mmol) of α-acetoxyisobutyryl bromide. The mixture was stirred at room temperature for 1 h, diluted with ether (40 mL), washed with 5% aqueous $NaHCO_3$ (20 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Column chromatography (SiO_2, 100 g, hexane, then 90:10 hexane–AcOEt) afforded 119 mg (10%) of diequatorial bromo acetate **6** and 946 mg (80%) of diaxial bromo acetate **5**.

5 (white solid): mp 73 °C; IR (KBr pellet) 1745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.50 (t, J = 3.3 Hz, 1H), 4.24 (dd, J = 9.5, 3.2 Hz, 1H), 4.19 (t, J = 3.6 Hz, 1H), 3.90 (dd, J = 9.7, 9.6 Hz, 1H), 3.77 (dd, J = 9.7, 9.5 Hz, 1H), 3.73 (dd, J = 9.6, 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 169.0, 138.6, 138.5, 137.6, 137.5, 128.4, 128.1, 127.9, 127.6, 82.0, 81.6, 77.4, 76.0, 73.0, 72.5, 70.0, 48.0, 21.0; MS (CI, NH_3) 664 ($M^+ + NH_4$, 100), 662 ($M^+ + NH_4$, 44). Anal. Calcd for $C_{36}H_{37}BrO_6$: C, 66.98; H, 5.78. Found: C, 66.98; H, 5.76.

6 (oil): IR (film) 1745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.27 (t, J = 10.3 Hz, 1H), 3.89 (t, J = 10.8 Hz, 1H), 3.67 (t, J = 10.5 Hz, 1H), 3.66 (t, J = 9.7 Hz, 1H), 3.53 (t, J = 9.0 Hz, 1H), 3.46 (t, J = 9.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 169.5, 138.0, 137.7, 128.4, 128.2, 127.9, 127.7, 84.0, 82.5, 81.5, 77.5, 76.5, 75.5, 73.5, 52.5, 21.0; MS (CI, NH_3) 664 ($M^+ + NH_4$, 100), 662 ($M^+ + NH_4$, 83).

(±)-3,4,5,6-Tetra-*O*-benzyl-1-bromo-1-deoxy-*chiro*-inositol (8). To a solution of 3.14 g (4.85 mmol) of bromo acetate **5** in 10 mL of $CHCl_3$ were added 25 mL of methanol and 1 mL of acetyl chloride. The mixture was refluxed for 16 h and then cooled to room temperature, and 50 mL of saturated aqueous $NaHCO_3$ was added. After extraction with ether (3 × 50 mL), the combined organic layers were washed with saturated aqueous NaCl (25 mL), dried over $MgSO_4$, and concentration *in vacuo*. Column chromatography (SiO_2, 500 g, hexane, then 90:10 hexane–AcOEt) afforded 2.62 g (89%) of bromo alcohol **8** (oil): IR (film) 3440 cm^{-1} (broad); ^1H NMR (C_6D_6) δ 4.40 (m, 1H), 4.17 (dd, J = 9.5, 2.5 Hz, 1H), 4.11 (t, J = 10.3 Hz, 1H), 4.07 (m, 1H), 3.99 (dd, J = 9.3, 3.6 Hz, 1H), 3.89 (t, J = 9.4 Hz, 1H); ^{13}C NMR (acetone-d_6) δ 139.8, 139.2, 128.6, 128.3, 128.1, 128.0, 127.6, 82.9, 82.0, 79.6, 77.6, 75.8, 72.6, 71.9, 70.3, 52.8; MS (CI, NH_3) 622 ($M^+ + NH_4$, 61), 620 ($M^+ + NH_4$, 100). Anal. Calcd for $C_{34}H_{35}BrO_5$: C, 67.66; H, 5.85. Found: C, 67.81, H, 5.94.

(±)-2-*O*-(1-Imidazolylthiocarbonyl)-3,4,5,6-tetra-*O*-benzyl-1-bromo-1-deoxy-*chiro*-inositol (9). To a solution of 1.29 g (2.14 mmol) of bromo alcohol **8** in 20 mL of THF was added a solution of 525 mg (2.94 mmol) of dry 1,1'-thiocarbonyldiimidazole 5 mL of THF. The mixture was refluxed, for 4 h and then cooled to room temperature, poured into 1 N HCl (10 mL), and extracted with ether (3 × 20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (20 mL) and with H_2O (20 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The crude product was then filtered through a short pad of Florisil (60-100 μm, 5 cm × 1 cm, eluent 70:30 hexane–AcOEt); 1.37 g (90%) of imidazolide **9** was obtained. **9** (white solid): mp 88 °C; ^1H NMR ($CDCl_3$) δ 8.24 (s, 1H), 7.47 (s, 1H), 7.07 (s, 1H), 5.91 (t, J = 3.2 Hz, 1H), 4.38 (dd, J = 9.7, 2.6 Hz, 1H), 4.36 (t, J = 3.6 Hz, 1H), 3.95 (t, J = 9.1 Hz, 1H), 3.95 (t, J = 9.3 Hz, 1H), 3.58 (dd, J = 9.0, 3.8 Hz, 1H); MS (CI, NH_3) 715 ($M^+ + H$, 12), 713 ($M^+ + H$, 9). Anal. Calcd for $C_{38}H_{37}BrN_2O_5S$: C, 63.95; H, 5.23; N, 3.93. Found: C, 63.84; H, 5.36; N, 3.71.

(±)-1-*S*-2-*O*-(Cyanovinylidene)-3,4,5,6-tetra-*O*-benzyl-1-deoxy-1-mercapto-*myo*-inositol (10). Butyllithium (1.4 mL,

2.3 mmol) 1.6 M in hexane was cooled to −78 °C under Ar. Three mL of THF was added, followed by a solution of 127 μL (2.4 mmol) of CH_3CN in 1 mL of THF. After 1 h of stirring at −78 °C, a solution of 1.37 g (1.9 mmol) of imidazolide **9** in 6 mL of THF was slowly added to the white suspension. The mixture was stirred for 4 h at −78 °C and at room temperature overnight. The reaction mixture was poured into saturated aqueous NH_4Cl (25 mL) and extracted with ether (3 × 25 mL). The combined organic layers were washed with H_2O (25 mL), dried ($MgSO_4$), and concentrated *in vacuo*. Column chromatography (SiO_2, 200 g; 80:20 hexane–AcOEt) afforded 760 mg (65%) of thioketene acetal **10** as a 2.4/1 mixture of isomers (ratio determined using the integrations of the vinylic protons in ^1H NMR). **10** (viscous oil): IR (film) 2210 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.01 (s, 1H, major isomer), 4.43 (s, 1H, minor isomer), 4.0–3.4 (m, 6H); ^{13}C NMR ($CDCl_3$) major isomer δ 173.6, 117.3, 85.3, 83.5, 82.2, 80.5, 77.7, 76.2, 75.7, 75.4, 73.5, 69.8, 50.9; minor isomer δ 172.8, 115.4, 84.8, 83.6, 81.8, 80.2, 77.5, 75.9, 75.0, 75.0, 72.8, 66.5, 51.0; resonances observed for the phenyl groups 137.8, 137.8, 137.5, 137.3, 137.0, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5; MS (CI, NH_3) 623 ($M^+ + NH_4$, 100), 200 (30); HRMS (EI) calcd for $C_{37}H_{35}NO_5S$ 605.2236, found 605.2253.

(±)-2-*O*-(Cyanoacetyl)-3,4,5,6-tetra-*O*-benzyl-1-deoxy-1-mercapto-*myo*-inositol (13). To a solution of 760 mg (1.26 mmol) of thioketene acetal **10** in 15 mL of THF was added 3 mL of 1 N HCl. The mixture was refluxed for 20 h and then cooled to room temperature. Saturated aqueous $NaHCO_3$ was added until pH = 7. After extraction with ether (3 × 20 mL), the combined organic layers were washed with saturated aqueous NaCl (20 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Column chromatography (SiO_2, 200 g, 80:20 C_6H_{12}–AcOEt) afforded 760 mg (83%) of thiol ester **13** (viscous oil): IR (film) 1755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.66 (t, *J* = 2.6 Hz, 1H), 3.82 (t, *J* = 9.7 Hz, 1H), 3.65 (t, *J* = 9.8 Hz, 1H), 3.58 (s, 2H), 3.56 (broad d, *J* = 9.8 Hz, 1H), 3.51 (t, *J* = 9.5 Hz, 1H), 3.06 (ddd, *J* = 10.6, 6.2, 2.2 Hz, 1H), 1.96 (d, *J* = 6.1 Hz, 1H); MS (CI, NH_3) 655 ($M^+ + NH_4$, 100); HRMS (EI) calcd for $C_{37}H_{37}NO_6S$ 623.2341, found 623.2359.

(±)-3,4,5,6-Tetra-*O*-benzyl-1-deoxy-1-mercapto-*myo*-inositol (14). To a solution of 722 mg (1.16 mmol) of thiol ester **13** in 22 mL of THF and 31 mL of methanol were added 800 mg of K_2CO_3. The mixture was stirred at room temperature for 20 min and then directly concentrated *in vacuo*. The crude compound was filtered through a short pad of SiO_2 (eluent 60:40 hexane–AcOEt); column chromatography (SiO_2, 200 g, 70:30 hexane–AcOEt) afforded 488 mg (76%) of thio alcohol **14** and 41 mg of a mixture of the corresponding disulfides. **14** (white solid): mp 108–110 °C; IR (film) 3440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.12 (t, *J* = 2.0 Hz, 1H), 3.93 (t, *J* = 9.3 Hz, 1H), 3.72 (t, *J* = 10.1 Hz, 1H), 3.48 (dd, *J* = 7.9, 2.5 Hz, 1H), 3.47 (t, *J* = 9.3 Hz, 1H), 2.84 (ddd, *J* = 10.6, 8.1, 1.8 Hz, 1H), 2.65 (s, 1H), 2.21 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 138.4, 138.2, 137.4, 128.4, 128.2, 128.0, 127.9, 127.7, 127.5, 85.3, 81.9, 81.3, 75.8, 72.9, 70.7, 43.7. Anal. Calcd for $C_{34}H_{36}O_5S$: C, 73.35; H, 6.52. Found: C, 73.12; H, 6.45.

(±)-2,3,4,5,6-Penta-*O*-acetyl-1-deoxy-1-(acetylthio)-1-deoxy-*myo*-inositol (15). To a solution of 90 mg (0.16 mmol) of compound **14** in 5 mL of THF and 15 mL of liquid NH_3 cooled at −78 °C were added small pieces of sodium metal until the blue color persisted for 20 min. Powdered NH_4Cl was then added until the blue color disappeared. NH_3 was evaporated under a stream of N_2, and a mixture was concentrated *in vacuo*. Six mL of pyridine was added, and after the mixture was cooled at 0 °C, 5 mL of Ac_2O was added. The mixture was stirred at room temperature for 15 h and then directly concentrated *in vacuo*. Column chromatography (SiO_2, 10 g, 50:50 hexane–AcOEt) afforded 65 mg (90%) of thioacetate **15** (white solid): mp 210 °C; IR (film) 1755, 1690 cm^{-1}; ^1H NMR (C_6D_6) δ 5.86 (t, *J* = 10.3 Hz, 1H), 5.85 (t, *J* = 2.3 Hz, 1H), 5.75 (dd, *J* = 12.1, 9.6 Hz, 1H), 5.46 (t, *J* = 9.6 Hz, 1H), 5.19 (dd, *J* = 9.7, 2.2 Hz, 1H), 4.13 (dd, *J* = 12.1, 2.3 Hz, 1H); ^{13}C NMR (C_6D_6) δ 191.8, 169.3, 73.7, 71.2, 70.4, 69.9, 69.6, 45.0, 29.7, 20.1, 19.7; MS (CI, NH_3) 466 ($M^+ + NH_4$, 100), 389 (11), 184 (10), 119 (19); HRMS (EI) calcd for $C_{18}H_{24}O_{11}S$ 448.1039, found 448.1034. Anal. Calcd for $C_{18}H_{24}O_{11}S$: C, 48.21; H, 5.39. Found: C, 47.70; H, 5.17.

(±)-1-Deoxy-1-mercapto-*myo*-inositol (2). Fifteen mL of NH_3 was condensed into a solution of 116 mg (0.26 mmol) of thioacetate **15** in 10 mL of methanol cooled at −78 °C. The solution was stirred for 18 h at room temperature. NH_3 was evaporated under a stream of N_2, and the mixture was concentrated to dryness *in vacuo*. The residue was dissolved in 5 mL of H_2O, and 79 mg of DTT (0.5 mmol) was added. After 1 h at room temperature, the solution was extracted with CH_2Cl_2 (10 × 5 mL). The aqueous solution was concentrated to dryness *in vacuo* to afford 45 mg (89%) of (±)-1-deoxy-1-mercapto-*myo*-inositol (**2**) as a gray solid: mp 250 °C dec; IR (film) 3380 cm^{-1}; ^1H NMR (D_2O) δ 4.21 (t, *J* = 2.2 Hz, 1H), 3.83 (t, *J* = 9.3 Hz, 1H), 3.76 (dd, *J* = 9.8, 2.4 Hz, 1H), 3.64 (t, *J* = 10.2 Hz, 1H), 3.49 (t, *J* = 9.0 Hz, 2H), 3.10 (dd, *J* = 10.9, 2.1 Hz, 1H); ^{13}C NMR (D_2O) δ 76.5, 74.0, 73.8, 73.2, 72.6, 44.5; MS (CI, NH_3) 214 ($M^+ + NH_4$, 100); HRMS (EI) calcd for $C_6H_8O_3S$ ($M - 2H_2O$) 160.0194, found 160.0206.