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SYNTHESIS OF *myo*- AND *muco*-INOSITOL ESTERS, AND SOME NITROGEN DERIVATIVES THEREOF

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ABSTRACT

Starting from *myo*-inositol, 1,2-*O*-isopropylidene-3,4,5,6-tetra-*O*-(methylsulfonyl)-, 1,4,5,6-tetra-*O*-(methylsulfonyl)-, and 2,3-di-*O*-acetyl-1,4,5,6-tetra-*O*-(methylsulfonyl)-*myo*-inositol (**3**) were synthesized. Compound **3** was treated with sodium azide to give 3-azido-3-deoxy-1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol, reduction of whose diacetate led to a mixture of 3-amino-3-deoxy- and 3-acetamido-2-*O*-acetyl-3-deoxy-1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol. The configurations and conformations of these compounds were ascertained by n.m.r. spectroscopy. 3-Acetamido-3-deoxy-1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol and its 2,4-diacetate are also described.

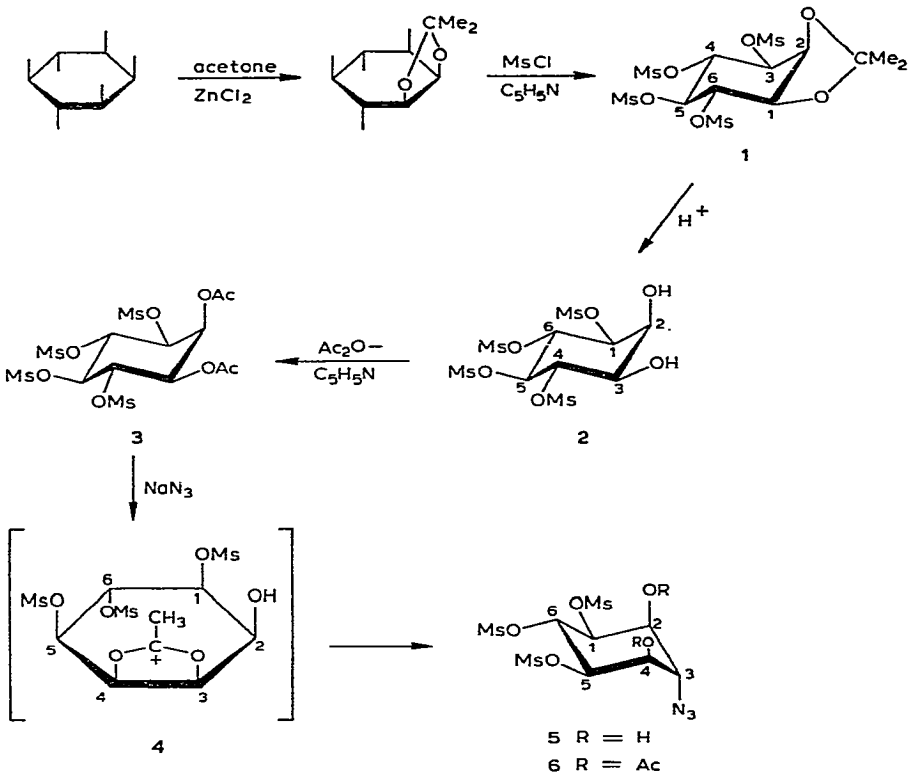
INTRODUCTION

In the present study, new mesyl derivatives of *myo*- and *muco*-inositol have been prepared from *myo*-inositol, and several acetyl and nitrogen derivatives obtained, as part of a project on the synthesis of potentially cytoactive compounds.

Scheme 1 shows* the first sequence of reactions, in which, by refluxing in acetone with anhydrous zinc chloride, *myo*-inositol gave the known 1,2-*O*-isopropylidene-*myo*-inositol[1]; subsequent treatment with methanesulfonyl chloride in pyridine led to 1,2-*O*-isopropylidene-3,4,5,6-tetra-*O*-(methylsulfonyl)-*myo*-inositol (**1**) in 69% yield.

The n.m.r. spectrum of **1** in pyridine-d_5 shows a low-field displacement of the mesyl groups on O-3 and O-6; their methyl-group signals appear at τ 6.40 and 6.46 owing to the deshielding influence[2] of the dioxolane ring of the neighboring isopropylidene group and also of the mesyloxy groups on C-4 and C-5. The latter appeared as a six-proton singlet at higher field (τ 6.50). The isopropylidene methyl-groups appear, well separated, at τ 8.45 and 8.64; this difference has been attributed[3] to the different steric relationship of these groups to the rest of the molecule, the resonance to lower field being currently ascribed to the "endo" methyl group. On

*All of the compounds, except for the *meso* ones, are racemic, and the formulas depict one enantiomer of the corresponding racemate.



Scheme 1.

the other hand, in methyl sulfoxide-d_6, the mesyl-group resonances appeared as a broad singlet at higher field (τ 6.69), and the isopropylidene group showed its methyl resonances at practically the same field (τ 8.42 and 8.64) as in pyridine-d_5.

Hydrolysis of **1** with hydrochloric acid split off the isopropylidene group and afforded 1,4,5,6-tetra-*O*-(methylsulfonyl)-*myo*-inositol (**2**). Its n.m.r. spectrum in pyridine-d_5 showed one mesyl group at lower field (τ 6.38), two others as a six-proton singlet at τ 6.45 that can be ascribed to the 5- and 6-mesyloxy groups, as both are equatorially attached and in an analogous environment, and a fourth mesyl group at τ 6.58. It is difficult to assign the resonances of the mesyl groups on O-1 and O-4 without performing deuteration studies; however, the τ-6.38 resonance could be attributable to the equatorial substituent on O-1, on the basis of its close proximity to the axial 2-hydroxyl group; this proximity would allow the operation of deshielding, electrostatic dispersion-forces, electrostatic effects from the C–OH dipole, or long-range effects originating in the diamagnetic anisotropy of the oxygen atom[4]. As these forces depend on a close-neighboring relationship, their operation for the *trans*-equatorial C-3–C-4 pair of substituents would be comparatively negligible. As was observed with **1**, compound **2** showed, in dimethyl sulfoxide-d_6, the mesyl-group resonances at higher field, τ 6.64, 6.72, and 6.75, with intensities in the ratios of 1 : 2 : 1.

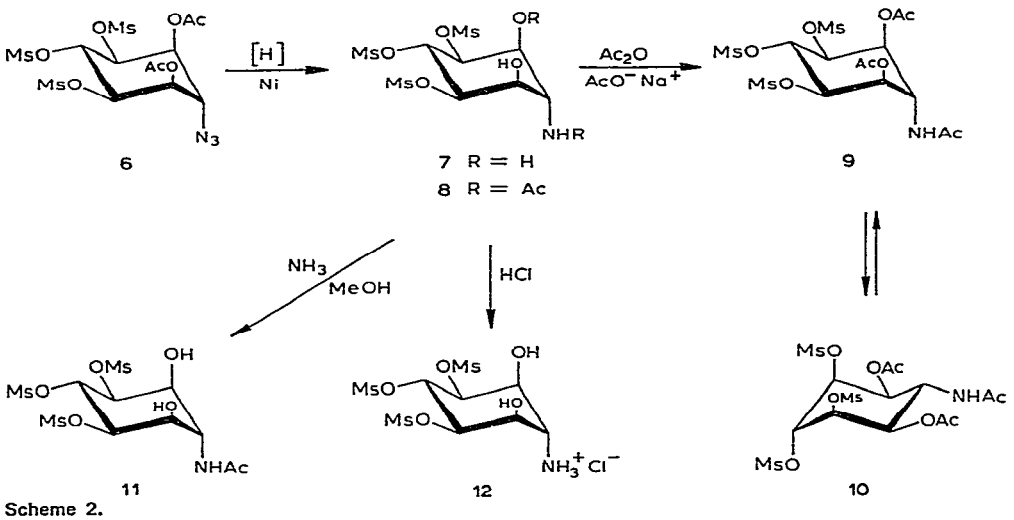
Acetylation of **2** gave 2,3-di-*O*-acetyl-1,4,5,6-tetra-*O*-(methylsulfonyl)-*myo*-

inositol (**3**), whose n.m.r. spectrum in pyridine-d_5 showed the acetoxyl groups at τ 7.86 (axial) and 7.98 (equatorial). These values, although observed in pyridine-d_5, fall in the ranges described (with chloroform-*d*) for axial and equatorial OAc groups, respectively, suggesting that, in the former solvent, there are no appreciable solvent-effects on the OAc chemical shifts. In dimethyl sulfoxide-d_6, compound **3** showed the acetyl resonances at τ 7.78 and 8.00, which agree also with the tabulated values[2] for axial and equatorial acetyl groups, respectively. Again, a six-proton singlet at τ 6.40 in pyridine-d_5 can be attributed to 5- and 6-*O*-mesyl groups on the basis of their symmetrical environment. On the other hand, the other two mesyl groups, being differently affected by the vicinal acetoxyl substituents, resonate separately at higher field (τ 6.53 and 6.55). The relative displacements of the resonances of these mesyl groups, compared with the same groups in compound **2**, show that, whereas the resonance assigned in **2** to the 4-*O*-mesyl group changed slightly, that of the 1-*O*-mesyl group was displaced noticeably (0.15–0.17 p.p.m.) to higher field. Probably, the closer spatial relationship between the O-1*e*–O-2*a* substituents would allow the location of the 1-*O*-mesyl group in the shielding region of the induced magnetic field of the carbonyl group. In dimethyl sulfoxide-d_6, an upfield shift of the resonances of the mesyl groups to τ 6.66 (2) and τ 6.70 (2) takes place; this suggests that, whereas the acetyl groups are but little affected by the change of solvent, the mesyl groups interact in some way with pyridine.

Compound **3** reacted stereoselectively with sodium azide in 2-methoxyethanol (methylCellosolve) to give 3-azido-3-deoxy-1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol (**5**) in 81% yield. Structure **5** is postulated on the basis of known facts about the stereochemistry of the azidolysis reaction, as well as the characteristic resonances in the n.m.r. spectrum[5]. Formation of a cyclic acetoxonium ion (**4**) by displacement of the *trans*-mesyloxy group on C-4 would be an intermediate stage that leads, through a *trans*-diaxial opening by the azido ion, to compound **5**. Its n.m.r. spectrum in pyridine-d_5 showed the resonances of two mesyl groups as a six-proton singlet at τ 6.55, ascribable to the O-1 and O-5 substituents, both in equatorial orientation and in a symmetrical environment. The 6-*O*-mesyl group resonated at τ 6.64, and the two axial hydroxyl groups appeared as a singlet at τ 5.50. The *muco* configuration appears to be supported by the n.m.r. spectrum of 2,4-di-*O*-acetyl-3-azido-3-deoxy-1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol (**6**), which showed, in pyridine-d_5, a six-proton singlet at τ 7.85 corresponding to the two acetoxyl groups in a symmetrical structure, and indicated the axial orientation of both acetyl groups. This value is comparable to the range reported[2] (in chloroform-*d*) for axial acetoxyl groups, and is confirmed by the value of τ 7.86 obtained[2] in methyl sulfoxide-d_6. In this solvent, the resonances of the mesyl groups appeared at higher field, namely, τ 6.66 (2) and 6.59.

Scheme 2 shows the sequence of reactions conducted in the *muco*-inositol series. Reduction of the azido derivative **6** with a modified, Raney nickel catalyst[6] gave 3-amino-3-deoxy-1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol (**7**) and 3-acetamido-2-*O*-acetyl-3-deoxy-1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol (**8**). The latter compound would be the result of an O→N migration of an acetyl group during reduction,

probably induced by the slightly alkaline catalyst. The mixture was quantitatively separated by means of a sulfonic resin. The n.m.r. spectrum of **7** in deuterium oxide showed two mesyl groups, probably those on O-1 and O-5, as a six-proton singlet at τ 6.65, and the 6-*O*-mesyl group at τ 6.63. That a change in conformation did not take place in **7** (with reference to **5** or **6**) is suggested by the resonances of the OAc (τ 7.85) and NAc groups (τ 7.98) for compound **8**; these values fall in the range ascribed[2] to axial orientations for these groups, as those equatorially oriented resonate typically at τ values of 7.93 and 8.05, respectively. The resonances of the mesyl groups in **8** appeared as for **7**, *viz.*, at τ 6.65 (two mesyl groups) and τ 6.63.



Scheme 2.

The axial position of the amino group in this series, having the *muco* configuration, was also confirmed by the n.m.r. spectrum (in D_2O) of 3-acetamido-3-deoxy-1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol (**11**), obtained by treatment of **8** with methanolic ammonia; the resonance of the NAc group was at τ 7.95, and those of the mesyl groups were the same as for **8**.

The acetylation of **8** was difficult, as the usual, mild procedure employing acetic anhydride–pyridine proved to be ineffective. 3-Acetamido-2,4-di-*O*-acetyl-3-deoxy-1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol (**9**) was obtained by heating **8** with acetic anhydride and sodium acetate. The resonances of the *O*-acetyl groups in **9** appeared, in methyl sulfoxide-d_6, as a six-proton singlet at τ 7.94, and that of the *N*-acetyl group at τ 8.15. These values, compared with those recorded[2] for a series of inositol derivatives in dimethyl sulfoxide-d_6 are limiting values for an axial orientation of these groups, suggesting an equilibrium between conformers **9** and **10**, a reasonable hypothesis on the basis of three axial and three equatorial substituents present in the molecule. However, the presence of two mesyl groups as a six-proton singlet at τ 6.68 (presumably O-1 and O-5 substituents), and the third mesyl group at τ 6.60, indicates a single conformation: in an equilibrium of conformers, a nine-proton singlet would

be foreseeable. In acetone-d_6, the acetyl resonances did not change appreciably, whereas those of the mesyl groups shifted to higher field by ~0.07 p.p.m.

As was observed for compounds **1**, **2**, and **3**, compounds **5** and **6** also showed noticeable shifts to lower field for the resonances of the mesyl groups, when the spectra were measured in pyridine-d_5, whereas acetyl groups seemed to be affected to a lesser extent. This behavior could be related to an analogous effect observed with amides[7], which was attributed to a particular geometry of the solvent–solute complex determined by the non-symmetrical, electronic structure of pyridine. The formal, strong, positive character of the sulfur atom would orientate the pyridine molecule in a way opposed to the shielding by the ring electrons.

The mixture of **7** and **8**, without separation, was also submitted to hydrolysis of the acetyl groups with M hydrochloric acid, and the hydrochloride of 3-amino-3-deoxy-1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol (**12**) was obtained as the only product. This compound showed, in its n.m.r. spectrum in deuterium oxide, a nine-proton singlet at τ 6.65.

For all of the compounds studied, the resonances of the ring protons (at 60 MHz) were not amenable to a full, first-order analysis.

EXPERIMENTAL

General procedures. — Melting points are not corrected. T.l.c. was conducted on plates (250 μm) of Silica Gel G (Merck) with the following eluants: (*A*) 1:1 (v/v) chloroform–ethanol, (*B*) 7:13 ethyl acetate–benzene, (*C*) 1:4 absolute ethanol–benzene, and (*D*) 1:19 methanol–benzene. The spots were detected with the following spray reagents: (*E*) alkaline hydroxylamine–ferric nitrate for esters[8], (*F*) ninhydrin in 1-butanol for amino compounds[9], (*G*) iodine vapor, and (*H*) 30% sulfuric acid in ethanol, and subsequent heating for 2 h at 140°. N.m.r. spectra were recorded at 20–25° with a Varian A-60 spectrometer, with tetramethylsilane as the standard.

1,2-O-Isopropylidene-3,4,5,6-tetra-O-(methylsulfonyl)-myo-inositol (**1**). — *myo*-Inositol (10 g) was refluxed, with constant stirring, with acetone (200 mL) and anhydrous zinc chloride for 50 h. Then pyridine (100 mL) was added, and the solution was kept overnight at 0°. The complex of zinc chloride–pyridine was filtered off, and washed with a little acetone. The solution was evaporated to dryness, the residue was dissolved in dry pyridine (37 mL), and methanesulfonyl chloride (6.5 mL) was added, with stirring and external cooling. The solution was kept overnight at room temperature, and then evaporated to dryness. The residue was treated with water, yielding a dark, amorphous solid, which, after recrystallization from acetone–water, gave **1** (19.2 g, 69%), m.p. 218°. T.l.c. (solvent *D*, reagent *G*) gave one spot, R_F 0.61; n.m.r. data (pyridine-d_5): τ 4.58 (6 H, ring protons), 6.40, 6.46, and 6.50 (1:1:2 intensity, mesyl groups), 8.45 and 8.64 (1:1 intensity, isopropylidene groups).

Anal. Calc. for $C_{13}H_{24}O_{14}S_4$: C, 29.32; H, 4.70; S, 24.59. Found: C, 30.06; H, 4.79; S, 24.38.

1,4,5,6-Tetra-O-(methylsulfonyl)-myo-inositol (**2**). — Compound **1** (500 mg)

was refluxed with a mixture of M hydrochloric acid (25 mL) and ethanol (10 mL) during 1 h. The solution was evaporated to dryness, and the residue was recrystallized from water. Product **2** (280 mg, 89% yield), m.p. 227–228°, was obtained. T.l.c. (solvent *D*, reagent *G*) gave one spot, R_F 0.10; n.m.r. data (pyridine-d_5): τ 4.20–4.60 (6 H, ring protons), 4.90 (2 H, hydroxyl groups), 6.38, 6.45 and 6.58 (1:2:1 intensity, mesyl groups).

Anal. Calc. for $C_{10}H_{20}O_{14}S_4$: C, 24.39; H, 4.06; S, 26.01. Found: C, 24.49; H, 4.10; S, 25.70.

2,3-Di-O-acetyl-1,4,5,6-tetra-O-(methylsulfonyl-myo-*inositol* (**3**). — Compound **2** (1 g) was dissolved in 1:1 acetic anhydride–pyridine (4 mL), and the solution was kept overnight at room temperature, warmed for 15 min in a boiling-water bath, and evaporated to dryness. Recrystallization of the residue from water gave **3** (1.2 g, 78% yield), m.p. 226–227°. T.l.c. (solvent *B*, reagent *E*) showed one spot, R_F 0.35; n.m.r. data (pyridine-d_5): τ 4.10–4.30 (6 H, ring protons), 6.40, 6.53, and 6.55 (2:1:1 intensity, mesyl groups), 7.86 (OAc-axial) and 7.98 (OAc-eq.); in Me_2SO-d_6: τ 7.78 (OAc-axial), 8.00 (OAc eq.), and 6.66 and 6.70 (1:1 intensity, mesyl groups).

Anal. Calc. for $C_{14}H_{24}O_{16}S_4$: C, 29.16; H, 4.16; S, 22.22. Found: C, 29.10; H, 4.22; S, 22.18.

*3-Azido-3-deoxy-1,5,6-tri-*O-(*methylsulfonyl*)-muco-*inositol* (**5**). — A mixture of **3** (2.5 g) and sodium azide (2.5 g) was refluxed for 40 h in 1:9 water–2-methoxyethanol (110 mL). The solution was evaporated to dryness, and the dark residue was extracted with hot ethanol (2 × 30 mL). On cooling, the ethanol extracts gave **5** (1.4 g; 81% yield), m.p. 227°. T.l.c. (solvent *B*, reagent *G*) showed one spot, R_F 0.12; ν_{max}^{Nujol} 2100 cm^{-1} (azido group); n.m.r. data (pyridine-d_5): τ 3.6–4.6 (6 H, ring protons), 5.50 (2 H, hydroxyl groups), and 6.55 (6 H) and 6.64 (3 H), mesyl groups; in Me_2SO-d_6: τ 5.12 (2 H, hydroxyl groups), and 6.62 and 6.74 (2:1 intensity, mesyl groups).

Anal. Calc. for $C_9H_{17}N_3O_{11}S_3$: C, 24.60; H, 3.87; N, 9.56; S, 21.86. Found: C, 24.77; H, 4.16; N, 9.59; S, 21.83.

*2,4-Di-O-acetyl-3-azido-3-deoxy-1,5,6-tri-*O-(*methylsulfonyl*)-muco-*inositol* (**6**). — Compound **5** (1 g) was dissolved in 1:1 acetic anhydride–pyridine (12 mL), and the solution was kept overnight at room temperature, heated for 1 h in a boiling-water bath, and evaporated to dryness. The residue, recrystallized from ethanol, gave **6** (1 g, 83% yield), m.p. 146–147°. T.l.c. (solvent *B*, reagent *E*) showed one spot, R_F 0.38; ν_{max}^{Nujol} 2100 cm^{-1} (azido group); n.m.r. data (pyridine-d_5): τ 4.15–4.25 (6 H, ring protons), 6.48 and 6.55 (2:1 intensity, mesyl groups), 7.85 (6 H, acetyl groups); in Me_2SO-d_6: τ 7.86 (s, 6 H, OAc), and 6.59 (3 H) and 6.66 (6 H), mesyl groups.

Anal. Calc. for $C_{13}H_{21}N_3O_{13}S_3$: C, 29.82; H, 4.01; N, 8.22; S, 18.33. Found: C, 30.24; H, 4.28; N, 8.39; S, 18.07.

*3-Amino-3-deoxy-1,5,6-tri-*O-(*methylsulfonyl*)-muco-*inositol* (**7**). — Raney nickel T_4 catalyst[6] (2 g) was suspended in ethanol (15 mL), and hydrogenated for 30 min; then, compound **6** (300 mg) dissolved in hot ethanol (80 mL) was added. The hydro-

genation was conducted in a Parr apparatus for 6 h at 55 lb.in.$^{-2}$; after filtration of the suspension, the filtrate was evaporated to dryness. The residue was dissolved in ethanol, and, on standing, a white, amorphous powder (150 mg) precipitated. In t.l.c. (solvent *A*, reagent *G*), it showed two spots, R_F 0.35 and 0.76. The former gave a positive reaction with reagent *F*, and the latter, with reagent *E*. As repeated recrystallization did not afford pure products, the mixture was passed through a column (16 × 400 mm) of Dowex 50 (H^+) resin (74 mL). Elution with water (12 × 50 mL) gave compound **8** (see the following paragraph), and subsequent elution with 2M aqueous ammonia (12 × 50 mL) afforded compound **7** (110 mg; 46.6% yield) that, recrystallized from ethanol, had m.p. 185°; n.m.r. data (D_2O): τ 4.60–4.50 (6 H, ring protons), and 6.63 and 6.65 (1:2 intensity, mesyl groups).

Anal. Calc. for $C_9H_{19}NO_{11}S_3$: C, 26.15; H, 4.60; N, 3.38; S, 23.24. Found: C, 26.42; H, 4.84; N, 3.12; S, 23.07.

*3-Acetamido-2-*O*-acetyl-1,5,6-tri-*O*-(methylsulfonyl)-muco-inositol* (**8**). — Evaporation of the aqueous fractions from the resin column gave **8** (33 mg; 28.5% yield) which, recrystallized from water, had m.p. 205–206° and gave one spot in t.l.c. (solvent *C*, reagents *G* and *H*) of R_F 0.35; n.m.r. data (D_2O): τ 4.55–4.80 (6 H, ring protons), 6.63 and 6.65 (1:2 intensity, mesyl groups), 7.85 (OAc), and 7.98 (NAc).

Anal. Calc. for $C_{13}H_{23}NO_{13}S_3$: C, 31.38; H, 4.62; N, 2.81; S, 19.31. Found: C, 31.57; H, 4.72; N, 2.83; S, 19.07.

*3-Acetamido-2,4-di-*O*-acetyl-1,5,6-tri-*O*-(methylsulfonyl)-muco-inositol* (**9**). — Compound **8** (50 mg) was acetylated with acetic anhydride (2 mL) and sodium acetate (35 mg) by boiling the mixture for 2 min. The solution was kept overnight at room temperature, heated for 2 h in a boiling-water bath, and evaporated to dryness in a vacuum desiccator. The residue, recrystallized from ethanol, gave **9** (47 mg, 86% yield), m.p. 242° (sinters at 238°); t.l.c. (solvent *C*, reagents *G* and *H*) showed one spot, R_F 0.44; n.m.r. data (acetone-d_6): τ 4.50–4.70 (6 H, ring protons), 6.68 and 6.75 (1:2 intensity, mesyl groups), 7.94 (6 H, OAc), 8.17 (NAc); in Me_2SO-d_6: τ 6.60 and 6.68 (1:2 intensity, mesyl groups), 7.94 (6 H, OAc), and 8.15 (NAc).

Anal. Calc. for $C_{15}H_{25}NO_{14}S_3$: C, 33.39; H, 4.63; N, 2.59; S, 17.81. Found: C, 33.57; H, 4.86; N, 2.85; S, 17.78.

*3-Acetamido-1,5,6-tri-*O*-(methylsulfonyl)-muco-inositol* (**11**). — Compound **8** (250 mg) was dissolved in 13% methanolic ammonia (25 mL), and the solution kept for 24 h at room temperature, and concentrated to a small volume; compound **11** (150 mg, 69% yield) crystallized. On recrystallization from water, it had m.p. 183–184°; t.l.c. (solvent *C*, reagents *G* and *H*) showed one spot, R_F 0.20; n.m.r. data (D_2O); τ 4.50–5.85 (6 H, ring protons), 6.62 and 6.65 (1:2 intensity, mesyl groups), and 7.95 (NAc).

Anal. Calc. for $C_{11}H_{21}NO_{12}S_3$: C, 29.01; H, 4.61; N, 3.07; S, 21.09. Found: C, 29.44; H, 4.83; N, 3.18; S, 20.89.

*3-Amino-3-deoxy-1,5,6-tri-*O*-(methylsulfonyl)-muco-inositol hydrochloride* (**12**). — The mixture (128 mg) obtained by reduction of compound **6**, without the previous separation already described, was submitted to hydrolysis by refluxing with M hydro-

chloric acid (8.5 mL) for 4 h. Then, the solution was evaporated to dryness, and the residue was crystallized from ethanol, giving 120 mg (85.9% yield) of **12**, m.p. 186–187°; t.l.c. (solvent *A*, reagent *G*) showed one spot, R_F 0.45; n.m.r. data (D_2O): τ 6.65 (9 H, mesyl groups).

Anal. Calc. for $C_9H_{20}ClNO_{11}S_3$: C, 24.02; H, 4.44; N, 3.11; S, 21.35. Found: C, 23.88; H, 4.62; N, 3.13; S, 21.78.

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