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Synthesis of several optically active *O*-methyl-inosamines and -inosadiamines from L-quebrachitol*

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ABSTRACT

A series of *p*-toluenesulfonic and methanesulfonic esters of L-quebrachitol have been prepared starting from the di-*O*-isopropylidene derivative of the cyclitol. Nucleophilic displacement of these sulfonates with azide ion in 2-methoxyethanol produced the azido compounds, hydrogenolysis of which with Raney nickel, followed by acetylation, gave thirteen optically active *O*-methyl-inosamine and two *O*-methyl-inosadiamine derivatives. The structures of the new aminocyclitols were established on the basis of ^{1}H-n.m.r. spectral data for the corresponding per-*O*-acetyl derivatives. The mechanisms of the substitution reactions, involving mainly neighboring-group participation, are discussed.

INTRODUCTION

The structure 5-*O*-methyl-*myo*-inosamine-2[‡] (**1**) was first assigned to the cyclitol moiety of antibiotic[2] KA-3093, related to hygromycin A (ref. 3), which contains a 1L-4,5-*O*-methylene-*neo*-inosamine-2 unit (**3**). Later, methoxyhygromycin was isolated[4] from the fermentation broth of *Streptomyces* sp. No. 207, and acid hydrolysis of the antibiotic gave 5-*O*-methyl-*neo*-inosamine-2[‡] (**2**), the structure of which was proposed[4] on the basis of ^{1}H- and ^{13}C-n.m.r. spectroscopic studies. Very recently, the gross structure of the antibiotic has been fully confirmed by a total synthesis[5]. Two *O*-methyl-inosamine derivatives were prepared[6] by azidolysis of pinitol sulfonates followed by hydrogenation. At least nine *O*-methyl nitrodeoxy inositols, potential precursors for *O*-methyl inosamines, have been synthesized by cyclization of 6-deoxy-3-*O*-methyl-6-nitro-D-glucose[7a], -L-idose[7a], -D-allose[7b], and -L-talose[7b].

Fortamine however, 1L-1-*N*-methyl-6-*O*-methyl-*chiro*-inosadiamine-1,4[‡] (**4**), was shown[8] to be a component of the antibiotic fortimicin A, and, later, several inosadiamines-1,4 and deoxy derivatives have been found in the clinically important fortimicin family[9]. In order both to elucidate structure-activity relationships and to improve antibacterial spectra, extensive attempts have been made to modify the diaminocyclitol moieties of these antibiotics[10].

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[*] Synthetic studies on quebrachitol, Part II. For Part I, see ref. 1.

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[‡] Earlier nomenclature, now superseded; "inosamine" is retained in the current IUPAC rules as a generic term only.

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Since L-quebrachitol, 1L-(−)-2-*O*-methyl-*chiro*-inositol (**5**), is readily isolable[1] from the aqueous phase of the latex of the rubber tree, its use as a starting material for chemical syntheses of naturally occurring compounds of biological interest, such as carba sugars[11], rare sugars[1], and other biologically active natural products[12], has been extensively studied. We describe here the preparation of five mono- and two di-sulfonic esters of **5**, from which the five theoretically possible aminodeoxy derivatives, along with eight *O*-methyl inosamines and two *O*-methyl inosadiamines were synthesized as the per-*O*-acetyl derivatives by nucleophilic substitution reactions[6,13] with azide ion, followed by hydrogenolysis. *O*-Methyl inosamines and inosadiamines are useful not only as modified cyclitol components of aminocyclitol antibiotics, but also as the starting compounds for further transformation into natural products of biological interest.

RESULTS AND DISCUSSION

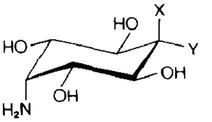
Preparation of the sulfonic esters. — Treatment of L-quebrachitol (**5**) with five molar equivalents of 2,2-dimethoxypropane and *p*-toluenesulfonic acid in *N,N*-dimethylformamide for 16 h at room temperature gave a mixture of products that were partitioned between water and ethyl acetate. Acetylation of the product from the aqueous layer furnished the syrupy acetate **11**, which was deacetalated to give the crystalline 1,3,4-triacetate[14] **17** (35% based on **5**). Crude di-*O*-isopropylidene derivative **6**, obtained from the organic layer, was converted into its crystalline acetate **7** (33% based on **5**).

Treatment of **7** with aqueous 80% acetic acid at room temperature produced the diol **10**, which was treated without purification with 1.5 molar equivalents of *p*-toluenesulfonyl (tosyl) chloride in pyridine. The mixture of tosylates formed was chromatographically separated after *O*-deisopropylidenation, to give syrupy 3-tosylate **18** (31%), crystalline 4-tosylate **20** (21%), and the 3,4-ditosylate **22** (12%), which were converted conventionally into the tetraacetates **19** and **21**, and the triacetate **23**. Compounds **18** and **20** were successively *O*-isopropylidenated in the usual way and acetylated to give the diacetates **13** (64%) and **15** (90%), respectively, and **22** was converted into **16** (90%). The structures of the tosylates were established on the basis of the ^{1}H-n.m.r. spectral data of their derivatives.

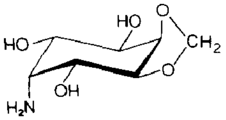
Treatment of **17** with 2 molar equivalents of tosyl chloride in pyridine gave selectively the 5-tosylate **24** (90%). However, when **17** was initially treated with one molar equivalent of benzoyl chloride in pyridine and then with mesyl chloride, it furnished the 6-mesylate **25** (82%). On treatment with excess mesyl chloride, **17** was readily converted into the 5,6-dimesylate **26** (94%).

Mesylation and tosylation of **6** (refs. 14, 15) gave the mesylate **8** and tosylate[15] **9** (99%), respectively. Compound **8** was *O*-deisopropylidenated and acetylated to give the tetraacetate **27** (90% overall yield).

Synthesis of O-*methyl inosamines.* — Treatment of **13** with 4 molar equivalents of sodium azide in aqueous 90% 2-methoxyethanol for 20 h at the reflux temperature gave



1 X = H, Y = OMe
2 X = OMe, Y = H



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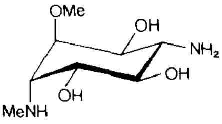

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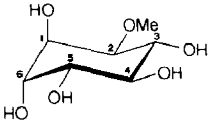

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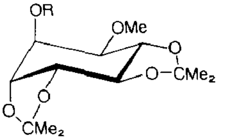
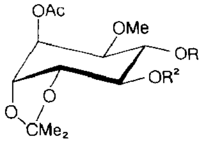
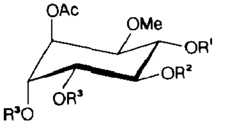


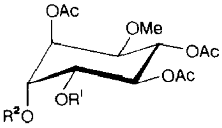
6 R = H
7 R = Ac
8 R = Ms
9 R = Ts



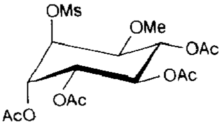
	R^1	R^2
10	H	H
11	Ac	Ac
12	Ts	H
13	Ts	Ac
14	H	Ts
15	Ac	Ts
16	Ts	Ts



	R^1	R^2	R^3
17	Ac	Ac	H
18	Ts	H	H
19	Ts	Ac	Ac
20	H	Ts	H
21	Ac	Ts	Ac
22	Ts	Ts	H
23	Ts	Ts	Ac

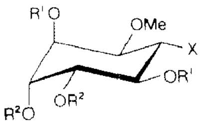


	R^1	R^2
24	Ts	H
25	Bz	Ms
26	Ms	Ms

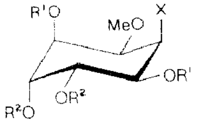


27

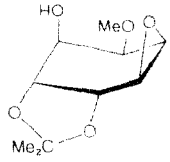
two azides, **28** (57%) and **33** (14%), which were converted into the acetates **29** and **34**, respectively. The ^{1}H-n.m.r. spectrum of **29** contained a triplet (δ 3.68, *J* 10 Hz) due to the proton attached to the carbon atom bearing the azido group, showing retention of the configurations at C-3 and C-4. In the ^{1}H-n.m.r. spectrum of **34**, the signals due to $H\mathrm{CN}_3$ and $H\mathrm{COCH}_3$ appeared at δ 3.77 and 4.15, being coupled (*J* 4 Hz) with each other, which indicated that the azido function existed *cis* to the methoxyl in the vicinal position. Mechanistically, the intermediate 3,4-acetoxonium ion, formed by anchimeric assistance at C-3 by the 4-acetoxyl group, was opened preferentially at C-3 by azide ion to give **28**, and, less favorably, direct SN2 displacement at C-3 gave **33**. When compound **13** was first converted into the epoxide (**39**) by treatment with methanolic sodium



28 − 32



33 − 38



39

	R'	R²	X
28, **33**	H	>CMe₂	N_3
29, **34**	Ac	>CMe₂	N_3
30, **35**	Ac	>CMe₂	NHAc
31, **36**	Ac	Ac	N_3
32, **37**	Ac	Ac	NHAc
38	Ac	Ac	OAc

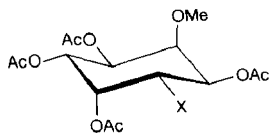
methoxide, subsequent azidolysis and acetylation afforded **28** exclusively in 83% yield. The flanking dioxolane ring seems to exert a remarkable stereoelectronic hindrance to nucleophilic attack at C-4. In fact, similar treatment of the tetraacetate **19** with azide ion afforded, as expected, mainly the two azides **31** (27%) and **40** (28%), along with the azide **36** (4%) and the *allo*-inositol derivative (**38**, 16%) formed by hydrolysis of the acetoxonium ion. The ^{1}H-n.m.r. spectrum of **38** showed two coupled triplets (J 2.5 Hz) at δ 5.65 and 3.69, due to H-2 and H-3. The ^{1}H-n.m.r. spectrum of **40** revealed a doublet of doublets (δ 4.03, J 2.5 and 11 Hz) due to HCN_3, being coupled with the C-2 equatorial proton, represented by a triplet at δ 5.62 (J 2.5).

The formation of **38** suggested that rear-side attack of the 3,4-cyclic acetoxonium ion with azide ion is rather hindered by the presence of the 5- and 6-acetoxy[§] functions, leading to competing, partial hydrolysis of the acetoxonium ion.

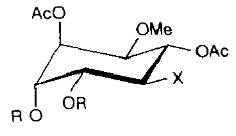
Hydrogenation of compounds **29** and **34**, in methanol containing acetic anhydride, in the presence of Raney nickel, gave, after conventional acetylation, the corresponding *O*-methyl-inosamine derivatives **30** (99%) and **35** (81%), *O*-deisopropylidenation of which followed by acetylation gave the penta-*N*,*O*-acetyl *O*-methyl inosamines **32** (89%) and **37** (97%), also obtained from **31** and **36**, respectively, by hydrogenation and acetylation.

Similar treatment of **15** with azide ion gave a single azide (**42**, 98%), which was hydrogenated and acetylated to give *N*-acetyl derivative **43** (82%), whereas the two azides **44** (15%) and **46** (68%) were obtained from the tetraacetate **21**, showing that the intermediate 4,5-acetoxonium ion[§] was preferentially opened at C-5. The ^{1}H-n.m.r. spectrum of **44** revealed a triplet (δ 3.80, J 10 Hz) and a doublet of doublets (δ 3.50, J 3 and 10 Hz), attributable to HCN_3 and HCOMe, respectively, and the corresponding signals of **46** appeared as two doublets of doublets (δ 3.34, J 9 and 10 Hz, and δ 3.17, J 3 and 4 Hz). Compounds **44** and **46** were hydrogenated and acetylated to give the penta-*N*,*O*-acetyl *O*-methyl inosamines **45** and **47**. Compound **45** was also obtained by hydrolysis of **43** followed by acetylation.

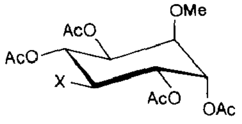
[§] The position numbering is that of the parent quebrachitol (**5**). This numbering is used to avoid confusion, in place of the actual numbering of the reactant or product.



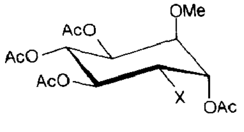
40 X = N_3
41 X = NHAc



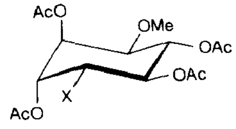
	R	X
42	$>$CMe$_2$	N_3
43	$>$CMe$_2$	NHAc
44	Ac	N_3
45	Ac	NHAc



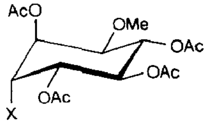
46 X = N_3
47 X = NHAc



48 X = N_3
49 X = NHAc



50 X = N_3
51 X = NHAc



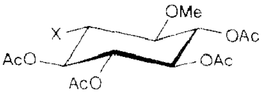
52 X = N_3
53 X= NHAc

Azidolysis of **24** followed by acetylation afforded the two azides **48** (43%) and **50** (14%), which were similarly converted into the inosamine derivatives **49** and **51**. The ^{1}H-n.m.r. spectrum of **49** revealed a doublet of doublets (δ 3.94, J 3.4 and 10 Hz) and a triplet (δ 3.83, J 3.3 Hz) due to *H*CN_3 and *H*COMe, respectively, supporting the assigned structure. Assuming that the reaction proceeds preferentially in the fashion of diaxial opening, the reaction intermediate would adopt the half-chair conformation having the methoxyl group in the equatorial position.

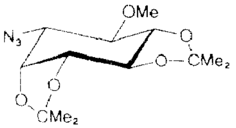
Azidolysis of **25** produced, after acetylation, two azides **52** (52%) and **54** (28%), which were similarly converted into the respective inosamine derivatives **53** (74%) and **55** (79%). The ^{1}H-n.m.r. spectra of **52** and **55** contained a doublet of doublets (δ 4.12, J 3 and 4 Hz) and a doublet of triplets (δ 4.15, J ~10 Hz) due to *H*CN_3 and *H*CNHAc, respectively, supporting the structures assigned. Compared with the product ratio observed in the analogous reaction[16] of DL-1,2,3,4,5-penta-*O*-acetyl-6-bromo-6-deoxy-*chiro*-inositol, the notable formation of the diequatorially opened product **54** suggests that some interaction between the intermediate 1,6-acetoxonium ion and the adjacent methoxyl group creates favorable stereoelectronic conditions for attack at C-1.

Azidolysis of **8** or **9** under standard conditions did not occur, but, when the solvent was replaced with dimethylsulfoxide, direct substitutions of **9** with azide ion proceeded smoothly at 120° to yield the azide **56** (71%) and the elimination product[15] **57** (17%). Compound **56** was converted into the azido acetate **58** (99%) and then into the inosamine derivative **59** (95%).

On the other hand, reaction of **27** with azide ion proceeded readily with formation of the 1,6-acetoxonium ion to give, after acetylation, two azides, **60** (94%) and **62** (5%), in a ratio consistent with the Fürst-Plattner rule, in contrast to the results observed in the case of **25**.



54 X = N_3
55 X = NHAc



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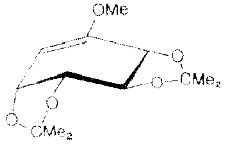

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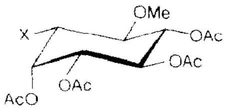
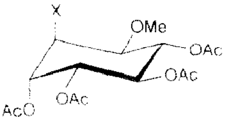
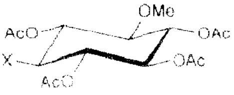


58 X = N_3
59 X = NHAc



60 X = N_3
61 X = NHAc

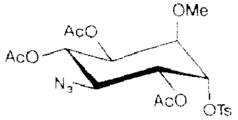


62 X = N_3
63 X = NHAc

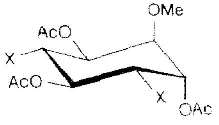
Azidolysis of **23** under standard conditions gave after acetylation the monoazide **64** in 45% yield, together with a complex mixture of side-products. In this case, further direct substitution at C-3[§] seems to be difficult owing to the presence of the adjacent *trans* OMe and *cis* OAc groups[16].

Synthesis of O-*methyl inosadiamines*. — Azidolysis of **26** under standard conditions occurred readily to give two diazides, **65** (42%) and **67** (14%), and one monoazide **69** (6%), the structures of which were confirmed by their ^{1}H-n.m.r. spectra (see Experimental).

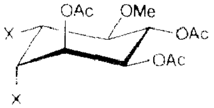
Mechanistically, the axial 1-acetoxy group initially attacked at C-6 to form the 1,6-cyclic acetoxonium ion, which was cleaved by azide ion to give the 1- and 6-azido[§] compounds. The former was subsequently substituted *via* preferential formation of the 5,6-acetoxonium ion[§] to afford the diaxially-opened product **67**, whereas the latter gave mainly the 4,5-acetoxonium ion, which produced **65** by a diaxial cleavage and **69** by hydrolysis. These results are in line with those observed in the cases of **24** and **25**.



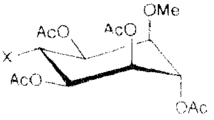
64



65 X = N_3
66 X = NHAc



67 X = N_3
68 X = NHAc



69 X = N_3
70 X = NHAc

Compounds **65**, **67**, and **69** were hydrogenated and acetylated to give the fully acetylated inosadiamines **66** (66%) and **68** (72%), and inosamine derivative **70** (91%).

Judging from the ^{1}H-n.m.r. spectra, *muco*-inositol derivatives **69** and **70** show a preference for conformations having the azido and acetamido functions in equatorial positions.

EXPERIMENTAL

General methods. — Melting points were determinated with a MEL-TEMP capillary melting-point apparatus and are uncorrected. Optical rotations were measured with a Jasco DIP-4 polarimeter. ^{1}H-N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with Jeol JNM EX-90 (90 MHz), GSX-270 (270 MHz), or GX-400 FT (400 MHz) instruments. T.l.c. was performed on Silica Gel 60 GF (Merck) with detection by charring with H_2SO_4. Column chromatography was conducted on Wakogel C-200 (200 mesh) or C-300 (300 mesh). Organic solutions were dried over anhydrous Na_2SO_4 and evaporated at < 50° under diminished pressure.

*1*L*-1-*O*-Acetyl-3,4:5,6-di-*O*-isopropylidene-2-*O*-methyl-*chiro*-inositol* (**7**) *and 1*L*-1,3,4-tri-*O*-acetyl-2-*O*-methyl-*chiro*-inositol* (**17**). — A mixture of L-quebrachitol (**5**, 10.0 g, 52 mmol), 2,2-dimethoxypropane (31 mL, 250 mmol), *p*-tolulenesulfonic acid monohydrate (0.5 g), and *N*,*N*-dimethylformamide (100 mL) was stirred for 16 h at room temperature. After neutralization with sodium hydrogencarbonate, the mixture was vigorously agitated with ethyl acetate (300 mL) and water (300 mL). The organic layer was dried and evaporated to give crude di-*O*-isopropylidene derivative (**6**, 6.9 g), which was treated with acetic anhydride (50 mL) in pyridine (50 mL) for 26 h at room temperature. The mixture was evaporated and the residue was crystallized from EtOH to give **7** (5.4 g, 33%), m.p. 109–109.5°; $[\alpha]_D^{25}$ +2° (c 1, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 5.55–5.43 (m, 1 H, H-1), 4.40–4.20 (m, 2 H), 3.80–3.50 (m, 3 H), 3.43 (s, 3 H, OCH_3), 2.14 (s, 3 H, CH_3CO), 1.50, 1.45, and 1.36 (3 s, 3, 6, and 3 H, 4 CCH_3).

Anal. Calc. for $C_{15}H_{24}O_7$: C, 56.95; H, 7.65. Found: C, 57.00; H, 7.48.

The aqueous layer was concentrated to give crude monoisopropylidene derivative, which was acetylated conventionally to give the triacetate (**11**, 11 g). This was treated with aqueous 80% acetic acid (20 mL) for 24 h at 55°, and then evaporated. The residue was eluted from a column of silica gel with 3:2 ethyl acetate–toluene to give **17** (5.6 g, 35%), m.p. 122–124° (from EtOH); $[\alpha]_D^{25}$ −75° (c 1, $CHCl_3$); lit.[14] m.p. 129–130°, $[\alpha]_D$ −76° ($CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$); δ 5.50 (t, 1 H, $J_{1,2} = J_{1,6}$ = 3.5 Hz, H-1), 5.30–5.05 (m, 2 H, H-3,4), 4.15–3.50 (m, 4 H), 3.47 (s, 3 H, OCH_3), 3.30–3.10 (m, 1 H), 2.13, 2.08, and 2.05 (3 s, 9 H, 3 CH_3CO).

Anal. Calc. for $C_{13}H_{20}O_9$: C, 48.75; H, 6.29. Found: C, 48.44; H, 6.12.

*1*L*-1-*O*-Acetyl-2-*O*-methyl-3-* (**18**) *and -4-*O*-*p*-tolylsulfonyl-* (**20**), *and -3,4-di-*O*-*p*-tolylsulfonyl-*chiro*-inositol* (**22**). — A mixture of **7** (12.7 g, 40.2 mmol) and aqueous 80% acetic acid (150 mL) was stirred for 4 h at room temperature, and evaporated to give the syrupy, crude mono-*O*-isopropylidene derivative **10**, which was then treated with *p*-toluenesulfonyl chloride (11.5 g, 60.3 mmol) in pyridine (80 mL) for 20 h at room temperature. The mixture was diluted with ethyl acetate (300 mL), washed with water thoroughly, dried, and evaporated to give a mixture of the monotosylates **12** and **14**, and the ditosylate **16**. The mixture was treated with aqueous 80% acetic acid (80 mL) for 16 h at 50° and evaporated. Column chromatography of the residue (18.8 g) with 3:2→1:0 ethyl acetate–toluene afforded **18** (4.79 g, 31%), $[\alpha]_D^{23}$ −39° (*c* 2.9, MeOH); **20** (3.36 g, 21%), m.p. 162–163° (from EtOH); $[\alpha]_D^{23}$ −23° (*c* 1.2, MeOH); and **22** (1.09 g, 5%), $[\alpha]_D^{23}$ −14° (*c* 0.8, $CHCl_3$). ^{1}H-N.m.r. data (90 MHz, $CDCl_3$) for **22**: δ 7.99, 7.75, 7.35, and 7.26 (4 d, 8 H, J 9 Hz, 2 $CH_3C_6H_4$), 5.43 (t, 1 H, $J_{1,2} = J_{1,6} = 3$ Hz, H-1), 4.96, 4.76 (2 t, 2 H, $J_{2,3} = J_{3,4} = J_{4,5} = 9$ Hz, H-3,4), 4.1–3.9 (m, 3 H, H-5,6, and O*H*), 3.53 (dd, 1 H, H-2), 3.1–2.9 (m, 1 H, O*H*), 2.76 (s, 3 H, OCH_3), 2.46, 2.43 (2 s, 6 H, 2 $CH_3C_6H_4$), and 2.05 (s, 3 H, CH_3CO).

Anal. Calc. for $C_{16}H_{22}O_9S\cdot0.5\ H_2O$: C, 48.11; H, 5.80. Found for **18**: C, 48.12; H, 5.66. Calc. for $C_{16}H_{22}O_9S$: C, 49.22; H, 5.68. Found for **20**: C, 49.00; H: 5.66. Calc. for $C_{23}H_{28}O_{11}S_2$: C, 50.73; H, 5.18. Found for **22**: C, 50.82; H, 5.29.

*1*L*-1,4-Di-*O*-acetyl-5,6-*O*-isopropylidene-2-*O*-methyl-3-*O*-*p*-tolylsulfonyl-*chiro*-inositol* (**13**). — A mixture of **18** (4.71 g, 12.1 mmol), 2,2-dimethoxypropane (7.4 mL, 60 mmol), $TsOH\cdot H_2O$ (0.2 g), and *N,N*-dimethylformamide (50 mL) was stirred for 23 h at 55°. After neutralization with sodium hydrogencarbonate, the mixture was diluted with ethyl acetate (300 mL), washed thoroughly with water, dried, and evaporated. The crude diol obtained was acetylated conventionally. Column chromatography of the product with 1:6 butanone–toluene gave **13** (3.66 g, 64%), $[\alpha]_D^{18}$ −66° (*c* 0.94, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.80, 7.30 (2 d, 4 H, J 9 Hz, $CH_3C_6H_4$), 5.59 (t, 1 H, $J_{1,2} = J_{1,6} = 3$ Hz, H-1), 5.37–5.11 (m, 1 H, H-4), 4.81 (dd, 1 H, $J_{2,3}$ 7.8, $J_{3,4}$ 9.5 Hz, H-3), 4.36–4.14 (m, 2 H, H-5,6), 3.61 (dd, 1 H, H-2), 3.19 (s, 3 H, OCH_3), 2.44 (s, 3 H, $CH_3C_6H_4$), 2.14, 2.04 (2 s, 6 H, 2 CH_3CO), 1.53, and 1.34 (2 s, 6 H, 2 CCH_3).

Anal. Calc. for $C_{21}H_{28}O_{10}S$: C, 53.38; H, 5.97. Found: C, 53.01; H, 6.04.

*1*L*-1,3-Di-*O*-acetyl-5,6-di-*O*-isopropylidene-2-*O*-methyl-4-*O*-*p*-tolylsulfonyl-*chiro*-inositol* (**15**). — Compound **20** (0.40 g, 1.03 mmol) was *O*-isopropylidenated as in the preparation of **13**, and the product was acetylated. Column chromatography of the crude compound with 1:6 butanone–toluene gave **15** (0.44 g, 90%), $[\alpha]_D^{18}$ −70° (*c* 1.7, $CHCl_3$); ^{1}H-n.m.r. (90MHz, $CDCl_3$): δ 7.80, 7.30 (2 d, 4 H, J 9 Hz, $CH_3C_6H_4$), 5.45 (dd, 1 H, $J_{1,2}$ 3, $J_{1,6}$ 4 Hz, H-1), 5.21 (dd, 1 H, $J_{2,3}$ 6.5, $J_{3,4}$ 9 Hz, H-3), 4.93–4.65 (m, 1 H, H-4), 4.38–4.15 (m, 2 H, H-5,6), 3.61 (dd, 1 H, H-2), 3.42 (s, 3 H, OCH_3), 2.44 (s, 3 H, $CH_3C_6H_4$), 2.12, 2.05 (2 s, 6 H, 2 CH_3CO), 1.50, and 1.32 (2 s, 6 H, 2 CCH_3).

Anal. Calc. for $C_{21}H_{28}O_{10}S$: C, 53.38; H, 5.97. Found: C, 53.24; H, 6.13.

*1*L*-1,2,3,6-Tetra-*O*-acetyl-5-*O*-methyl-4-*O*-*p*-tolylsulfonyl-*chiro*-inositol* (**19**). — Compound **18** (3.94 g, 10.1 mmol) was acetylated conventionally and the product was purified by column chromatography with 1:10 ethyl acetate–toluene to give **19** (4.03 g, 77%), $[\alpha]_D^{19}$ −10° (*c* 1.2, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.78, 7.32 (2 d, 4 H, J 9 Hz, MeC_6H_4), 5.61–5.11 (m, 4 H, H-1,2,3,6), 4.92 (t, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 3.51 (dd, 1 H, $J_{5,6}$ 3.4 Hz, H-5), 3.06 (s, 3 H, OCH_3), 2.16, 2.11, 2.07, and 1.98 (4 s, 12 H, 4 CH_3CO).

Anal. Calc. for $C_{22}H_{28}O_{12}S$: C, 51.16; H, 5.46. Found: C, 51.15; H, 5.65.

*1*L*-1,2,4,6-Tetra-*O*-acetyl-5-*O*-methyl-3-*O-p*-tolylsulfonyl-*chiro*-inositol* (**21**). — Compound **20** (2.90 g, 7.43 mmol) was conventionally acetylated and the product was purified by column chromatography with 1:8 ethyl acetate–toluene as eluent to give **21** (3.68 g, 96%), m.p. 129–131° (from EtOH); $[\alpha]_D^{23}$ $-17°$ (*c* 1.2, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.70, 7.28 (2 d, 4 H, *J* 9 Hz, $CH_3C_6H_4$), 5.51–5.13 (m, 4 H, H-1,2,4,6), 5.02 (t, 1 H, $J_{2,3} = J_{3,4} = 9.4$ Hz, H-3), 3.58 (dd, 1 H, $J_{4,5}$ 9.4, $J_{5,6}$ 2.5 Hz, H-5), 3.38 (s, 3 H, OCH_3), 2.44 (s, 3H, $CH_3C_6H_4$), 2.21, 2.16, 2.04, and 1.89 (4 s, 12 H, 4 CH_3CO).

Anal. Calc. for $C_{22}H_{28}O_{12}S$: C, 51.16; H, 5.46. Found: C, 51.23; H, 5.08.

*1*L*-1,2,6-Tri-*O*-acetyl-5-*O*-methyl-3,4-di-*O-p*-tolylsulfonyl-*chiro*-inositol* (**23**). — Compound **22** (960 mg, 1.76 mmol) was acetylated and the product was purified by column chromatography with 1:4 ethyl acetate–toluene to give **23** (925 mg, 84%), m.p. 145–146° (from EtOH); $[\alpha]_D^{23}$ $-10°$ (*c* 1.6, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.88, 7.75, 7.31, 7.29 (4 d, 8 H, *J* 9 Hz, 2 $CH_3C_6H_4$), 5.42–5.17 (m, 3 H, H-1,2,6), 5.12, 4.79 (2 t, 2 H, $J_{2,3} = J_{3,4} = J_{4,5} = 9$ Hz, H-3,4), 3.42 (dd, 1 H, $J_{5,6}$ 2 Hz, H-5), 2.73 (s, 3 H, OCH_3), 2.43 (s, 6 H, 2 $CH_3C_6H_4$), 2.14, 2.11, and 1.96 (3 s, 9 H, 3 CH_3CO).

Anal. Calc. for $C_{27}H_{32}O_{13}S_2$: C, 51.59; H, 5.13. Found: C, 51.29; H, 5.24.

*1*L*-1,3,4-Tri-*O*-acetyl-2-*O*-methyl-5-*O-p*-tolylsulfonyl-*chiro*-inositol* (**24**). — A mixture of **17** (105 mg, 0.33 mmol), *p*-toluenesulfonyl chloride (125 mg, 0.65 mmol), and pyridine (1 mL) was stirred for 8 h at room temperature, then poured into ice-water. The mixture was extracted with ethyl acetate (30 mL), and the extract was washed with water throughly, dried, and evaporated. The residue was eluted from a column of silica gel with 1:6 butanone—toluene to give **24** (140 mg, 90%), $[\alpha]_D^{23}$ $-66°$ (*c* 2.9, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.80–7.20 (m, 4 H, $CH_3C_6H_4$), 5.54 (t, 1 H, $J_{1,2} = J_{1,6} =$ 3.5 Hz, H-1), 5.42 (t, 1 H, $J_{3,4} = J_{4,5} = 9$ Hz, H-4), 5.19 (t, 1 H, $J_{2,3}$ 9 Hz, H-3), 4.74 (dd, 1 H, $J_{5,6}$ 3 Hz, H-5), 4.24 (dd, 1 H, H-6), 3.70 (dd, 1 H, H-2), 3.35 (s, 3 H, OCH_3), 2.92 (d, 1 H, *J* 3.2 Hz, OH), 2.46 (s, 3 H, $CH_3C_6H_4$), 2.15, 2.01, and 1.73 (3 s, 9 H, 3 CH_3CO).

Anal. Calc. for $C_{20}H_{26}O_{11}S$: C, 50.63; H, 5.52. Found: C, 50.37; H, 5.83.

*1*L*-1,3,4-Tri-*O*-acetyl-5-*O*-benzoyl-6-*O*-methylsulfonyl-2-*O*-methyl-*chiro*-inositol* (**25**). — Compound **17** (125 mg, 0.48 mmol) was treated with benzoyl chloride (55 μL, 0.48 mmol) in pyridine (1.5 mL) for 2 h at room temperature, and then with methanesulfonyl chloride (184 μL, 2.4 mmol) for 15 h. The mixture was diluted with ethyl acetate and filtered. The filtrate was evaporated and the residue was chromatographed on silica gel with 1:15 ethyl acetate–toluene to give **25** (196 mg, 80%) as a syrup, $[\alpha]_D^{26}$ $-49°$ (*c* 0.92, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 8.2–7.2 (m, 5 H, Ph-H), 5.68 (dd, 1 H, $J_{1,2}$ 3.5, $J_{1,6}$ 4.5 Hz, H-1), 5.60–5.19 (m, 4 H, H-3,4,5,6), 3.73 (dd, 1 H, $J_{2,3}$ 9 Hz, H-2), 3.41 (s, 3 H, OCH_3), 3.00 (s, 3 H, CH_3SO_2), 2.23, 2.10, and 1.96 (3 s, 9 H, 3 CH_3CO).

Anal. Calc. for $C_{22}H_{26}O_{12}S$: C, 51.36; H, 5.59. Found: C, 51.08; H, 4.96.

*1*L*-1,3,4-Tri-*O*-acetyl-2-*O*-methyl-5,6-di-*O*-methylsulfonyl-*chiro*-inositol* (**26**). — To a solution of **17** (1.0 g, 3.1 mmol) in pyridine (10 mL) was added methanesulfonyl chloride (0.97 mL, 13 mmol) at 0°, and the mixture was stirred for 13 h at room temperature, then diluted with ethyl acetate (100 mL), and poured into ice–water. The organic layer was washed with water, dried, and evaporated. The residue was eluted from a column of silica gel with 1:3 butanone–toluene to give **26** (1.35 g, 94%), $[\alpha]_D^{27}$

$-51°$ (c 1, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 5.65 (t, 1 H, $J_{1,6} = J_{1,2} = 3.2$ Hz, H-1), 5.55–4.90 (m, 4 H, H-3,4,5,6), 3.77–3.60 (m, 1 H, H-2), 3.47 (s, 3 H, OCH_3), 3.18, 3.08 (2 s, 6 H, 2 CH_3SO_2), 2.18, 2.08, and 2.07 (3 s, 9 H, CH_3CO).

Anal. Calc. for $C_{15}H_{24}O_{13}S_2$: C, 37.81; H, 5.08. Found: C, 37.51; H, 4.91.

*1*L*-1,2,3,4-Tetra-*O*-acetyl-5-*O*-methyl-6-*O*-methylsulfonyl-*chiro*-inositol* (**27**). — A mixture of **6** (325 mg, 1.2 mmol), methanesulfonyl chloride (183 μL, 2.36 mmol), and pyridine (2 mL) was stirred for 15 h at room temperature, and then diluted with ethyl acetate (10 mL). The solution was washed thoroughly with water, dried, and evaporated. The mesylate **8** thereby obtained was treated with a mixture of ethanol (1 mL) and M hydrochloric acid (4 mL) for 3 h at room temperature. The mixture was concentrated and the residue was acetylated conventionally. Column chromatography of the product with 1:4 butanone–toluene as eluent gave **27** (467 mg, 90%), $[\alpha]_D^{26}$ $-27°$ (c 1.4, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 5.63–5.50 (m, 1 H, H-1), 5.45–5.20 (m, 3 H, H-2,3,4), 5.08 (dd, 1 H, J 3.5 and 5 Hz, H-6), 3.76–3.54 (m, 1 H, H-5), 3.48 (s, 3 H, OCH_3), 3.20 (s, 3 H, CH_3SO_2), 2.17, 2.08, 2.02, and 1.98 (4 s, 12 H, 4 CH_3CO).

Anal. Calc. for $C_{16}H_{24}O_{12}S$: C, 43.63; H, 5.49. Found: C, 43.33; H, 5.15.

*1*L*-4-Azido-4-deoxy-1,2-*O*-isopropylidene-5-*O*-methyl-*chiro*-inositol* (**28**) *and 1*D*-2-azido-2-deoxy-5,6-*O*-isopropylidene-3-*O*-methyl-*allo*-inositol* (**33**). — A mixture of **13** (876 mg, 1.83 mmol), sodium azide (476 mg, 7.32 mmol), and aqueous 90% 2-methoxyethanol (10 mL) was refluxed for 20 h, and evaporated to dryness. The residue was extracted with ethyl acetate (100 mL) and the extract was evaporated. Column chromatography of the residue with 1:17 EtOH–toluene as eluent gave **28** (272 mg, 57%), m.p. 80–81° (from EtOH); $[\alpha]_D^{21}$ $-35°$ (c 0.2, $CHCl_3$), and **33** (66 mg, 14%), $[\alpha]_D^{24}$ $-28°$ (c 1, $CHCl_3$).

Anal. Calc. for $C_{10}H_{17}N_3O_5$: C, 46.33; H, 6.61; N, 16.21. Found for **28**: C, 46.47; H, 6.38; N, 15.92; for **33**: C, 46.11; H, 6.39; N, 16.41.

*1*L*-1,4-Di-*O*-acetyl-3-azido-3-deoxy-5,6-*O*-isopropylidene-2-*O*-methyl-*chiro*-inositol* (**29**). — Compound **28** (15 mg) was acetylated conventionally and purified by elution from a column of silica gel with 1:6 ethyl acetate–hexane to give **29** (19 mg, 97%), m.p. 123.5–124.5° (from EtOH); $[\alpha]_D^{24}$ $-95°$ (c 0.65, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 5.70 (t, 1 H, $J_{1,2} = J_{1,6} = 2.7$ Hz, H-1), 5.16–4.85 (m, 1 H, H-4), 4.28–4.05 (m, 2 H, H-5,6), 3.68 (t, 1 H, $J_{2,3} = J_{3,4} = 10$ Hz, H-3), 3.48 (dd, 1 H, H-2), 3.46 (s, 3 H, OCH_3), 2.15, 2.14 (2 s, 6 H, 2 CH_3CO), 1.54, and 1.34 (2 s, 6 H, 2 CCH_3).

Anal. Calc. for $C_{14}H_{21}N_3O_7$: C, 48.98; H, 6.17; N, 12.24. Found: C, 48.82; H, 6.03; N, 11.87.

*1*D*-1,4-Di-*O*-acetyl-2-azido-2-deoxy-5,6-*O*-isopropylidene-3-*O*-methyl-*allo*-inositol* (**34**). — Compound **33** (15 mg) was acetylated conventionally and purified as in the preparation of **18** to give **34** (19 mg, 97%), m.p. 85–88° (from EtOH); $[\alpha]_D^{24}$ $-89°$ (c 0.65, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$); δ 5.61 (ddd, 1 H, $J_{1,2}$ 3, $J_{1,3}$ 1, $J_{1,6}$ 4 Hz, H-1), 4.95 (dd, 1 H, $J_{3,4}$ 3, $J_{4,5}$ 7 Hz, H-4), 4.42–4.19 (m, 2 H, H-5,6), 4.15 (ddd, 1 H, $J_{2,3}$ 4 Hz, H-3), 3.77 (dd, 1 H, H-2), 3.46 (s, 3 H, OCH_3), 2.19, 2.17 (2 s, 6 H, 2 CH_3CO), 1.56, and 1.44 (2 s, 6 H, 2 CCH_3).

Anal. Calc. for $C_{14}H_{21}N_3O_7$: C, 48.98; H, 6.17; N, 12.24. Found: C, 49.14; H, 6.06; N, 12.09.

Selective preparation of **29** *via the epoxide* **39** *derived from* **13**. — Compound **13** (3.53 g, 5.36 mmol) was treated with M methanolic sodium methoxide (10 mL) for 2 h at room temperature, and the mixture was neutralized with sodium hydrogencarbonate and evaporated. The residue was extracted with ethyl acetate and the extract was evaporated to give crude epoxide **39** (1.1 g). Treatment of this product with sodium azide (1.39 g, 21.4 mmol) and ammonium chloride (1.14 g, 21.4 mmol) in aqueous 90% 2-methoxyethanol (10 mL) for 1 h at reflux, followed by processing as in the preparation of **28** and **33**, gave, after conventional acetylation, **29** (1.52 g, 83%) as crystals, identical in all respects with the compound obtained before.

*1*L*-3-Acetamido-1,4-di-O-acetyl-3-deoxy-5,6-O-isopropylidene-2-O-methyl-*chiro-*inositol* (**30**). — A mixture of **29** (1.52 g, 4.4 mmol) in ethanol (15 mL) containing acetic anhydride (2.1 mL, 22 mmol) was vigorously stirred in the presence of Raney nickel T-4 (ref. 17; 0.5 mL) under hydrogen at atmospheric pressure for 22 h at room temperature. The mixture was filtered and the filtrate was evaporated. Column chromatography of the residue with 1:12 EtOH–toluene as eluent afforded **30** (1.58 g, 99%), m.p. 128–129° (from EtOH); $[\alpha]_D^{23}$ $-37°$ (c 1.2, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 9.43 (d, 1 H, $J_{3,NH}$ 8 Hz, N*H*), 5.37 (dd, 1 H, $J_{1,2}$ 3, $J_{1,6}$ 5 Hz, H-1), 4.99 (dd, 1 H, $J_{3,4}$ 10, $J_{4,5}$ 9 Hz, H-4), 4.50–4.30 (m, 2 H, H-5,6), 4.16 (ddd, 1 H, $J_{2,3}$ 5 Hz, H-3), 3.52 (dd, 1 H, H-2), 3.46 (s, 3 H, OCH_3), 2.15, 2.11, 1.96 (3 s, 9 H, 3 CH_3CO), 1.48, and 1.35 (2 s, 6 H, 2 CCH_3).

Anal. Calc. for $C_{16}H_{25}NO_8$: C, 53.47; H, 7.01; N, 3.90. Found: C, 53.12; H, 6.85; N, 3.61.

*1*L*-3-Acetamido-1,4,5,6-tetra-O-acetyl-3-deoxy-2-O-methyl-*chiro-*inositol* (**32**). — A mixture of **30** (40 mg, 0.11 mmol) and aqueous 75% acetic acid (1 mL) was stirred for 15 h at 55° and evaporated. The residue was acetylated and the product was eluted from a column of silica gel with 1:8 EtOH–toluene to give **32** (39 mg, 89%) m.p. 187–188° (from EtOH); $[\alpha]_D^{21}$ $-14°$ (c 0.8, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 5.60–5.20 (m, 5 H, H-1,4,5,6,N*H*), 4.50–4.15 (m, 1 H, H-3), 3.55 (dd, 1 H, $J_{1,2}$ 3, $J_{2,3}$ 11Hz, H-2), 3.35 (s, 3 H, OCH_3), 2.19, 2.14, 2.03, 1.99, and 1.98 (5 s, 15 H, 5 CH_3CO).

Anal. Calc. for $C_{17}H_{25}NO_{10}$: C, 50.62; H, 6.25; N, 3.47. Found: C, 50.53; H, 6.03; N, 3.34.

*1*D*-2-Acetamido-1,4-di-O-acetyl-2-deoxy-5,6-O-isopropylidene-3-O-methyl-*allo-*inositol* (**35**). — Compound **34** (44 mg, 0.13 mmol) was hydrogenated and acetylated as described for the preparation of **30** to give, after column chromatography with 1:12 EtOH–toluene as eluent, **35** (37 mg, 81%), $[\alpha]_D^{23}$ $-7°$ (c 0.3, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 6.07 (d, 1 H, $J_{2,NH}$ 9 Hz, N*H*), 5.47 (dd, 1 H, $J_{3,4}$ 3, $J_{4,5}$ 4.5 Hz, H-4), 5.07 (dd, 1 H, $J_{1,2}$ 4, $J_{1,6}$ 5 Hz, H-1), 4.75 (ddd, 1 H, $J_{2,3}$ 3 Hz, H-2), 4.47–4.12 (m, 2 H, H-5,6), 3.70 (t, 1 H, H-3), 3.42 (s, 3 H, OCH_3), 2.17, 2.10, 2.02 (3 s, 9 H, 3 CH_3CO), 1.51, and 1.36 (2 s, 6 H, 2 CCH_3).

Anal. Calc. for $C_{16}H_{25}NO_8$: C, 53.47; H, 7.01; N, 3.90. Found: C, 53.21; H, 6.98; N, 3.76.

*1*D*-2-Acetamido-1,4,5,6-tetra-O-acetyl-2-deoxy-3-O-methyl-*allo-*inositol* (**37**). — Compound **35** (30 mg, 0.083 mmol) was hydrolyzed and acetylated as described for the preparation of **32** to give **37** (33 mg, 97%), $[\alpha]_D^{20}$ +8.5° (*c* 1.2, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 6.10 (d, 1 H, $J_{2,NH}$ 9 Hz, N*H*), 5.52–5.00 (m, 4 H, H-1,4,5,6), 5.00–4.70 (m, 1 H, H-2), 3.78 (t, 1 H, *J* 3 and 3.5 Hz, H-3), 3.40 (s, 3 H, OC*H*$_3$), 2.16, 2.07, and 2.03 (3 s, 3, 9, and 3 H, 5 C*H*$_3$CO).

Anal. Calc. for $C_{17}H_{25}NO_{10}$: C, 50.62; H, 6.25; N, 3.47. Found: C, 50.34; H, 6.31; N, 3.34.

*1*L*-1,2,3,6-Tetra-*O*-acetyl-4-azido-4-deoxy-5-*O*-methyl-*chiro- (**31**), *1*D*-1,4,5,6-tetra-*O*-acetyl-2-azido-2-deoxy-*allo- (**36**), *1*D*-1,2,4,5,6-penta-*O*-acetyl-3-O-methyl-*allo- (**38**), *and 1*L*-1,2,4,6-tetra-*O*-acetyl-3-azido-3-deoxy-5-*O*-methyl-*neo-*inositol* (**40**). — A mixture of **19** (412 mg, 0.87 mmol), sodium azide (284 mg, 4.4 mmol), and aqueous 90% 2-methoxyethanol was refluxed for 10 h, and then evaporated and the residue was acetylated. T.l.c. in 1:2 ethyl acetate–hexane indicated the presence of four major components (R_F 0.50, 0.47, 0.30, and 0.15). Column chromatography of the products with 1:3 ethyl acetate–hexane afforded in turn **31** (92 mg, 27%), $[\alpha]_D^{19}$ −4° (*c* 1, $CHCl_3$); **40** (94 mg, 28%), $[\alpha]_D^{19}$ +19.5° (*c* 0.8, $CHCl_3$); **36** (16 mg, 4%), $[\alpha]_D^{19}$ +24.7° (*c* 0.8, $CHCl_3$); and **38** (58 mg, 16%), m.p. 123.5–125° (from EtOH); $[\alpha]_D^{24}$ −2.3° (*c* 1.7, $CHCl_3$). ^{1}H-N.m.r. data (90 MHz, $CDCl_3$): **31**, δ 5.55–5.00 (m, 4 H, H-1,2,3,6), 3.90–3.48 (m, 2 H, H-4,5), 3.45 (s, 3 H, OC*H*$_3$), 2.17, 2.15, 2.11, and 1.98 (4 s, 12 H, 4 C*H*$_3$CO); **36**, δ 5.55–5.05 (m, 4 H, H-1,4,5,6), 4.30–4.12 (m, 1 H, H-2), 3.80 (t, 1 H, $J_{2,3} = J_{3,4}$ = 3.5 Hz, H-3), 3.47 (s, 3 H, OC*H*$_3$), 2.19, 2.14, 2.09, and 2.01 (4 s, 12 H, 4 C*H*$_3$CO); **38**, δ 5.65 (t, 1 H, $J_{1,2} = J_{2,3}$ = 2.5 Hz, H-2), 5.55–5.12 (m, 4 H, H-1,4,5,6), 3.69 (t, 1 H, $J_{3,4}$ 2.5 Hz, H-3), 3.49 (s, 3 H, OC*H*$_3$), 2.13, 2.12, 2.10, 2.04, and 2.02 (5 s, 15 H, 5 C*H*$_3$CO); **40**, δ 5.62 (t, 1 H, $J_{1,2} = J_{2,3}$ = 2.5 Hz, H-2), 5.40–5.05 (m, 3 H, H-1,4,6), 4.03 (dd, 1 H, $J_{3,4}$ 11 Hz, H-3), 3.96 (t, 1 H, $J_{4,5} = J_{5,6}$ = 2.5 Hz, H-5), 3.51 (s, 3H, OC*H*$_3$), 2.18, 2.14, 2.07, and 1.98 (4 s, 12 H, 4 C*H*$_3$CO).

Anal. Calc. for $C_{15}H_{21}N_3O_9$: C, 46.51; H, 5.46; N, 10.84. Found for **31**: C, 46.39; H, 5.28; N, 10.85; for **36**: C, 46.15; H, 5.33; N, 10.70; for **40**: C, 46.70; H, 5.31; N, 10.73. Calc. for $C_{17}H_{24}O_{11}$: C, 50.50; H, 5.98. Found for **38**: C, 50.34; H, 5.87.

Compound **31** (37 mg, 0.10 mmol) was hydrogenated and acetylated as described above to give **32** (34 mg, 88%), identical to the compound obtained from **30**.

Compound **36** (10 mg, 0.03 mmol) was converted into **37** (8.5 mg, 83%), identical to the product derived from **35**.

*1*D*-1-Acetamido-2,3,4,6-tetra-*O*-acetyl-1-deoxy-5-*O*-methyl-*neo-*inositol* (**41**). — Compound **40** (35 mg, 0.090 mmol) was hydrogenated in ethanol (1 mL) containing acetic anhydride (0.1 mL) in the presence of Raney nickel T-4 (0.1 mL) for 1.5 h under hydrogen at atmospheric pressure. Column chromatography of the product with 1:8 EtOH–toluene as eluent gave **41** (32 mg, 88%), m.p. 270–280° (from EtOH); $[\alpha]_D^{20}$ + 3° (*c* 0.5, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 5.60 (d, 1 H, $J_{1,NH}$ 9 Hz, N*H*), 5.50 (t, 1 H, $J_{1,2} = J_{2,3}$ = 3 Hz, H-2), 5.40 (dd, 1 H, $J_{3,4}$ 10 Hz, H-3), 5.15 (dd, 1 H, $J_{1,6}$ 12, $J_{5,6}$ 3 Hz, H-6), 5.08 (dd, 1 H, $J_{4,5}$ 3 Hz, H-4), 4.76 (ddd, 1 H, H-1), 3.86 (t, 1 H, H-5), 3.54 (s, 3 H, OC*H*$_3$), 2.16, 2.10, 1.95, and 1.90 (4 s, 3, 6, 3, and 3 H, 5 C*H*$_3$CO).

Anal. Calc. for $C_{17}H_{25}NO_{10}$: C, 50.62; H, 6.25; N, 3.47. Found: C, 50.53; H, 6.15; N, 3.47.

*1*L*-1,3-Di-*O*-acetyl-4-azido-4-deoxy-5,6-*O*-isopropylidene-2-*O*-methyl-*chiro-*inositol* (**42**). — A mixture of **15** (480 mg, 0.81 mmol), sodium azide (260 mg, 4.0 mmol), and aqueous 90% 2-methoxyethanol (4 mL) was refluxed for 14 h, and then evaporated, and the residue was acetylated. Column chromatography of the crude product with 1:6 ethyl acetate–hexane as eluent gave **42** (270 mg, 98%), $[\alpha]_D^{20}$ −55° (c 1.8, CHCl$_3$); ^{1}H-n.m.r. (90 MHz, CDCl$_3$): δ 5.37 (dd, 1 H, $J_{1,2}$ 3, $J_{1,6}$ 5 Hz, H-1), 4.91 (dd, 1 H, $J_{2,3}$ 6, $J_{3,4}$ 10 Hz, H-3), 4.43–4.06 (m, 2 H, H-5,6), 3.69 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 3.50 (dd, 1 H, H-2), 3.43 (s, 3 H, OCH_3), 2.14 (s, 6 H, 2 CH_3CO), 1.55, and 1.37 (2 s, 6 H, 2 CCH_3).

Anal. Calc. for C$_{14}$H$_{21}$N$_3$O$_7$: C, 48.98; H, 6.17; N, 12.24. Found: C, 48.96; H, 5.91; N, 12.25.

*1*L*-3-Acetamido-4,6-di-*O*-acetyl-3-deoxy-1,2-*O*-isopropylidene-5-*O*-methyl-*chiro-*inositol* (**43**). — Compound **42** (118 mg, 0.34 mmol) was hydrogenated and acetylated as for the preparation of **28** to give **43** (102 mg, 82%), m.p. 133–135° (from EtOH); $[\alpha]_D^{22}$ −55° (c 1.2, CHCl$_3$); ^{1}H-n.m.r. (90 MHz; CDCl$_3$): δ 5.74 (d, 1 H, $J_{3,NH}$ 9 Hz, NH), 5.55 (dd, 1 H, $J_{1,6}$ 4.2, $J_{5,6}$ 3 Hz, H-6), 5.02 (dd, 1 H, $J_{3,4}$ 8, $J_{4,5}$ 7.5 Hz, H-4), 4.52–4.02 (m, 3 H, H-1,2,3), 3.67 (dd, 1 H, H-5), 3.44 (3 s, 3 H, OCH_3), 2.15, 2.10, 1.97 (3 s, 9 H, 3 CH_3CO), 1.56, and 1.45 (2 s, 6 H, CCH_3).

Anal. Calc. for C$_{16}$H$_{25}$NO$_8$: C, 53.47; H, 7.01; N, 3.90. Found: C, 53.24; H, 6.88; N, 3.68.

*1*L*-3-Acetamido-1,2,4,6-tetra-*O*-acetyl-3-deoxy-5-*O*-methyl-*chiro-*inositol* (**45**). — Compound **43** (89 mg, 0.25 mmol) was *O*-deisopropylidenated as in the preparation of **18**, **20**, and **22**, and acetylated, to give **45** (76 mg, 76%), $[\alpha]_D^{21}$ −12° (c 1.1, CHCl$_3$); ^{1}H-n.m.r. (90 MHz, CDCl$_3$): δ 5.66 (d, 1 H, $J_{3,NH}$ 10 Hz, NH), 5.44, 5.30 (2 dd, 2 H, $J_{1,2} = J_{5,6} = 3.5$, $J_{1,6}$ 4.5 Hz, H-1,6), 5.13 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 5.08 (t, 1 H, $J_{3,4} = J_{4,5} = 10$ Hz, H-4), 4.53 (overlapping dt, 1 H, H-3), 3.64 (dd, 1 H, H-5), 3.37 (s, 3 H, OCH_3), 2.16, 2.13, 2.08, 2.00, and 1.90 (5 s, 15 H, 5 CH_3CO).

Anal. Calc. for C$_{17}$H$_{25}$NO$_{10}$; C, 50.62; H, 6.25; N, 3.47. Found: C, 50.88; H, 6.09; N, 3.44.

*1*L*-1,2,4,6-Tetra-*O*-acetyl-3-azido-3-deoxy-5-*O*-methyl-* (**44**) *and 1*D*-1,2,4,5-tetra-*O*-acetyl-3-azido-3-deoxy-6-*O*-methyl-*chiro-*inositol* (**46**). — A mixture of **21** (700 mg, 1.48 mmol), sodium azide (480 mg, 7.4 mmol), and aqueous 90% 2-methoxyethanol (7 mL) was refluxed for 20 h, and then evaporated. The residue was acetylated and the products were chromatographed with 1:6 ethyl acetate–toluene to give **44** (84 mg, 15%), m.p. 102–103° (from EtOH); $[\alpha]_D^{19}$ + 11° (c 0.3, CHCl$_3$), and **46** (392 mg, 68%), m.p. 91–93° (from EtOH); $[\alpha]_D^{19}$ + 14° (c 1.1, CHCl$_3$). ^{1}H-N.m.r. data (90 MHz, CDCl$_3$): **44**, δ 5.48 (t, 2 H, $J_{1,2} = J_{1,6} = 3$ Hz, H-1,6), 5.18 (t, $J_{3,4} = J_{4,5} = 10$ Hz, H-4), 5.07 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 3.80 (t, 1 H, H-3), 3.50 (dd, 1 H, H-5), 3.33 (s, 3 H, OCH_3), 2.18, 2.17, 2.07 (3 s, 3, 6, and 3 H, 4 CH_3CO); **46**, δ 5.52 (dd, 1 H, $J_{1,2}$ 4, $J_{1,6}$ 3 Hz, H-1), 5.36 (dd, 1 H, $J_{3,4}$ 9, $J_{4,5}$ 10 Hz, H-4), 5.14 (dd, 2 H, $J_{2,3}$ 10, $J_{5,6}$ 4 Hz, H-2,5), 3.34 (dd, 1 H, H-6), 3.50 (s, 3 H, OCH_3), 2.16, 2.10, and 2.08 (3 s, 3, 3, and 6 H, 4 CH_3CO).

Anal. Calc. for C$_{15}$H$_{21}$N$_3$O$_9$: C, 46.51; H, 5.46; N, 10.84. Found for **44**: C, 46.49; H, 5.31; N, 10.88; for **46**: C, 46.41; H, 5.27; N, 10.79.

Compound **44** (36 mg, 0.99 mmol) was hydrogenated and acetylated to give **45** (32 mg, 85%), identical to the product derived from **43**.

*1D-3-Acetamido-1,2,4,5-tetra-*O*-acetyl-3-deoxy-6-*O*-methyl-*chiro*-inositol* (**47**). — Compound **46** (105 mg, 0.27 mmol) was hydrogenated and acetylated to give, after column chromatography with 1:10 ethanol–toluene, **47** (100 mg, 91%), m.p. 144–145 (from EtOH); $[\alpha]_D^{19}$ +15° (*c* 1.3, $CHCl_3$); ^1H-n.m.r. (90 MHz, $CDCl_3$): δ 5.04 (d, 1 H, $J_{3,NH}$ 10 Hz, N*H*), 5.01 (dd, 1 H, $J_{1,2}$ 3, $J_{1,6}$ 4 Hz, H-1), 5.30–5.10 (m, 3 H, H-2,4,5), 4.75–4.35 (m, 1 H, H-3), 3.72 (dd, 1 H, $J_{5,6}$ 2 Hz, H-6), 3.49 (s, 3 H, OCH_3), 2.36, 2.15, 2.07, 2.04, and 1.90 (5 s, 15 H, 5 CH_3CO).

Anal. Calc. for $C_{17}H_{25}NO_{10}$: C, 50.62; H, 6.25; N, 3.47. Found: C, 50.67; H, 6.12; N, 3.44.

*1D-1,3,4,5-Tetra-*O*-acetyl-2-azido-2-deoxy-6-*O*-methyl-* (**48**) *and 1L-1,3,4,6-tetra-*O*-acetyl-2-azido-2-deoxy-5-*O*-methyl-*chiro*-inositol* (**50**). A mixture of **23** (419 mg, 0.88), sodium azide (230 mg, 3.5 mmol), and aqueous 90% 2-methoxyethanol (4 mL) was refluxed for 20 h, and then evaporated to dryness. The residue was acetylated and the products were fractionated by column chromatography with 1:10 butanone–toluene to give **48** (143 mg, 43%), m.p. 83–83.5° (from EtOH); $[\alpha]_D^{27}$ +29° (*c* 1.1, $CHCl_3$); and **50** (48 mg, 14%), $[\alpha]_D^{23}$ −41° (*c* 1.4, $CHCl_3$). ^1H-N.m.r. data (90 MHz, $CDCl_3$): **48**, δ 5.50–5.05 (m, 4 H, H-1,3,4,5), 3.94 (dd, 1 H, $J_{1,2}$ 3.4, $J_{2,3}$ 10.2 Hz, H-2), 3.83 (t, 1 H, $J_{1,6}$ = $J_{5,6}$ = 3.3 Hz, H-6), 3.50 (s, 3 H, OCH_3), 2.12, 2.10, 2.06, and 2.00 (4 s, 12 H, 4 CH_3CO); **50**, δ 5.53–5.20 (m, 4 H, H-1,3,4,6), 3.94 (dd, 1 H, $J_{1,2}$ 3, $J_{2,3}$ 10 Hz, H-2), 3.62–3.45 (m, 1 H, H-5), 3.35 (s, 3 H, OCH_3), 2.16, 2.15, 2.10, and 2.07 (4 s, 12 H, 4 CH_3CO).

Anal. Calc. for $C_{15}H_{21}N_3O_9$: C, 46.51; H, 5.46; N, 10.84. Found for **48**: C, 46.18; H, 5.31; N, 10.77; for **50**: C, 47.09; H, 5.38; N, 10.27.

*1D-2-Acetamido-1,3,4,5-tetra-*O*-acetyl-2-deoxy-6-*O*-methyl-*chiro*-inositol* (**49**). — Compound **48** (147 mg, 0.38 mmol) was hydrogenated and acetylated as for the preparation of **30**. Column chromatography of the product with 1:10 EtOH–toluene gave **49** (89 mg, 60%), $[\alpha]_D^{21}$ +34° (*c* 0.7, $CHCl_3$); ^1H-n.m.r. (270 MHz, $CDCl_3$): δ 5.65 (d, 1 H, $J_{2,NH}$ 8.8 Hz, N*H*), 5.50 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 10 Hz, H-3), 5.26 (t, 1 H, $J_{1,2}$ = $J_{1,6}$ = 3.1 Hz, H-1), 5.13 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.08 (dd, 1 H, $J_{5,6}$ 3.1 Hz, H-5), 4.66 (ddd, 1 H, H-2), 3.74 (t, 1 H, H-6), 3.52 (s, 3 H, OCH_3), 2.18, 2.08, 2.04, 2.01, and 1.93 (5 s, 15 H, 5 CH_3CO).

Anal. Calc. for $C_{17}H_{25}NO_{10}$: C, 50.63; H, 6.25; N, 3.47. Found: C, 50.97; H, 6.18; N, 3.12.

*1L-2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-5-*O*-methyl-*chiro*-inositol* (**51**). — Compound **50** (96 mg, 0.25 mmol) was hydrogenated and acetylated as for the preparation of **30**. Column chromatography of the product with 1:10 EtOH–toluene gave **51** (80 mg, 80%), m.p. 193–194° (from EtOH), $[\alpha]_D^{23}$ −33° (*c* 1.1, $CHCl_3$); ^1H-n.m.r. (90 MHz, $CDCl_3$): δ 5.73 (d, 1 H, $J_{2,NH}$ 9 Hz, N*H*), 5.50 (t, 1 H, $J_{1,6}$ = $J_{5,6}$ = 3.5 Hz, H-6), 5.27 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 5.17 (t, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.12 (t, 1 H, $J_{2,3}$ 9.5 Hz, H-3), 4.77–3.96 (m, 1 H, H-2), 3.47 (dd, 1 H, H-5), 3.35 (s, 3 H, OCH_3), 2.16, 2.06, 2.03, and 1.90 (4 s, 6, 3, 3, and 3 H, 5 CH_3CO).

Anal. Calc. for $C_{17}H_{25}NO_{10}$: C, 50.63; H, 6.25; N, 3.47. Found: C, 50.45; H, 6.15; N, 3.49.

*1L-1,3,4,5-Tetra-*O*-acetyl-6-azido-6-deoxy-2-*O*-methyl-*chiro*-* (**52**) *and 1D-*

1,2,3,4-tetra-O-acetyl-5-azido-5-deoxy-6-O-methyl-scyllo-*inositol* (**54**). — A mixture of **25** (176 mg, 0.34 mmol), sodium azide (111 mg, 1.7 mmol), and aqueous 90% 2-methoxyethanol (2 mL) was stirred for 13 h at 120°, and then evaporated to dryness. The residue was acetylated conventionally. Column chromatography of the products with 1:7 ethyl acetate–toluene gave **52** (69 mg, 52%), $[\alpha]_D^{27}$ −15° (*c* 1, $CHCl_3$), and **54** (37 mg, 28%), m.p. 128–130° (from EtOH); $[\alpha]_D^{27}$ −14° (*c* 0.9, $CHCl_3$). ^{1}H-N.m.r. data (90 MHz, $CDCl_3$): **52**, δ 5.50–5.10 (m, 4 H, H-1,3,4,5), 4.12 (dd, 1 H, *J* 3 and 4 Hz, H-6), 3.65–3.40 (m, 1 H, H-2), 3.35 (s, 3 H, OCH_3), 2.16, 2.09, 2.05, and 2.02 (4 s, 12 H, 4 CH_3CO); **54**, δ 5.25–4.80 (m, 4 H, H-1,2,3,4), 3.70–3.15 (m, 2 H, H-5,6), 3.57 (s, 3 H, OCH_3), 2.10, 2.08, and 1.99 (3 s, 3, 3, and 6 H, 4 CH_3CO).

Anal. Calc. for $C_{15}H_{21}N_3O_9$: C, 46.51; H, 5.46; N, 10.84. Found for **52**: C, 46.56; H, 5.35; N, 10.58; for **54**: C, 46.58; H, 5.22; N, 10.56.

*1*L*-1-Acetamido-2,3,4,6-tetra-O-acetyl-2-deoxy-5-O-methyl*-chiro-*inositol* (**53**). — Compound **52** (27 mg, 0.07 mmol) was hydrogenated and acetylated as for the preparation of **30** to give, after column chromatography with 1:10 EtOH–toluene, **53** (21 mg, 74%), $[\alpha]_D^{32}$ −9° (*c* 1, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 6.00 (d, 1 H, $J_{1,NH}$ 7.5 Hz, N*H*), 5.65 (dd, 1 H, *J* 3 and 5 Hz, H-6), 5.45–5.00 (m, 3 H, H-2,3,4), 4.70–4.45 (m, 1 H, H-1), 3.65–3.40 (m, 1 H, H-5), 3.47 (s, 3 H, OCH_3), 2.15, 2.06, and 2.05 (3 s, 3, 6, and 6 H, 5 CH_3CO).

Anal. Calc. for $C_{17}H_{25}NO_{10}$: C, 50.62; H, 6.25; N, 3.47. Found: C, 50.54; H, 6.19; N, 3.42.

*1*L*-1-Acetamido-2,3,4,5-tetra-O-acetyl-1-deoxy-6-O-methyl*-scyllo-*inositol* (**55**). — Compound **54** (24 mg, 0.06 mmol) was hydrogenated and acetylated as for the preparation of **30**, to give, after column chromatography with 1:10 EtOH–toluene as eluent, **55** (20 mg, 79%), m.p. 215–216° (from $CHCl_3$); $[\alpha]_D^{32}$ −5° (*c* 1, $CHCl_3$); ^{1}H-n.m.r. (270 MHz, $CDCl_3$): δ 6.00 (d, 1 H, $J_{1,NH}$ 10 Hz, N*H*), 5.28–5.12 (m, 4 H, H-2,3,4,5), 4.15 (dt, $J_{1,2} = J_{1,6} =$ 10 Hz, H-1), 3.61 (t, 1 H, $J_{5,6}$ 10 Hz, H-6), 3.42 (s, 3 H, OCH_3), 2.07, 2.04, 2.00, and 1.98 (4 s, 3, 3, 3, and 6 H, 5 CH_3CO).

Anal. Calc. for $C_{17}H_{25}NO_{10}$: C, 50.62; H, 6.25; N, 3.47. Found: C, 50.72; H, 6.16; N, 3.49.

*1*L*-1,2:3,4-Di-O-isopropylidene-5-O-methyl-6-O-*p*-tolylsulfonyl*-chiro-*inositol* (**9**). — A mixture of **6** (ref. 12) (206 mg, 0.75 mmol), *p*-toluenesulfonyl chloride (716 mg, 3.75 mmol), and pyridine (5 mL) was stirred for 23 h at 60°, and then diluted with ethyl acetate (70 mL). The solution was washed with water, dried, and evaporated. Column chromatography of the residue with 1:6 ethyl acetate–hexane as eluent gave **9** (317 mg, 99%), $[\alpha]_D^{22}$ −14° (*c* 1.4, $CHCl_3$); lit.[12] $[\alpha]_D^{20}$ −15.4° ($CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 7.83, 7.34 (2 d, 4 H, *J* 8 Hz, $CH_3C_6H_4$), 5.03 (t, 1 H, $J_{1,6} = J_{5,6} =$ 3.5 Hz, H-6), 4.50–4.20 (m, 2 H, H-1,2), 3.75–3.50 (m, 3 H, H-3,4,5), 3.25 (s, 3 H, OCH_3), 2.44 (s, 3 H, CH_3Ph), 1.42, 1.38, and 1.30 (3 s, 6, 3, and 3 H, 4 CCH_3).

Anal. Calc. for $C_{20}H_{28}O_8S$: C, 56.06; H, 6.59. Found: C, 55.89; H, 6.51.

*1*L*-1-Azido-1-deoxy-2,3:4,5-di-O-isopropylidene-6-O-methyl*-myo-*inositol* (**56**) *and 2*L*-(2,4,5/3)-2,3:4,5-di-O-isopropylidene-1-O-methyl-1(6)-cyclohexene-1,2,3,4,5-pentol* (**57**). — A mixture of **9** (120 mg, 0.28 mmol), sodium azide (91 mg, 1.4 mmol), and dimethyl sulfoxide (1 mL) was stirred for 19 h at 120°, and then diluted with ethyl acetate (60 mL). The solution was washed with water, dried, and evaporated. Column chromatography of the residue with 1:12 ethyl acetate–toluene gave **56** (59 mg, 71%). $[\alpha]_D^{19}$ +48° (*c* 1.1, $CHCl_3$); and **57** (12 mg, 17%), m.p. 70–73° (from EtOH); $[\alpha]_D^{20}$ −7.8° (*c* 0.5, $CHCl_3$). ^{1}H-N.m.r. data (90 MHz, $CDCl_3$): **56**, δ 4.60–3.25 (m, 6 H, H-1–6), 3.53 (s, 3 H, OCH_3), 1.59, 1.46, and 1.40 (3 s, 3, 6, and 3 H, 4 CCH_3); **57**, δ 4.95 (ddd, 1 H, $J_{2,5}$ 1, $J_{4,5}$ 7, $J_{5,6}$ 4 Hz, H-5), 4.66 (dd, 1 H, $J_{2,6}$ 2 Hz, H-6), 4.46 (dd, 1 H, $J_{3,4}$ 9.5 Hz, H-4), 4.14 (ddd, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 3.82 (t, 1 H, H-3), 3.67 (s, 3 H, OCH_3), 1.54, 1.50, 1.47, and 1.40 (4 s, 12 H, 4 CCH_3).

Anal. Calc. for $C_{13}H_{21}N_3O_5$: C, 52.16; H, 7.07; N, 14.04. Found for **56**: C, 52.39; H, 6.91; N, 13.78. Calc. for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87. Found for **57**: C, 60.69; H, 7.64.

1D-1,2,5,6-Tetra-O-acetyl-3-azido-3-deoxy-4-O-methyl-myo-inositol (**58**). — A mixture of **56** (60 mg, 0.20 mmol), ethanol (0.5 mL), and 2M hydrochloric acid (1 mL) was stirred for 1 h at 60°, and then evaporated. The residue was acetylated conventionally, and column chromatography of the crude product with 1:8 ethyl acetate–toluene as eluent gave **58** (77 mg, 99%), m.p. 174–174.5° (from EtOH); $[\alpha]_D^{22}$ −39° (*c* 1.2, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 5.55 (t, 1 H, $J_{1,2} = J_{2,3} = 2.5$ Hz, H-2), 5.47 (t, 1 H, $J_{1,6} = J_{5,6} = 10$ Hz, H-6), 5.10 (m, 1 H, H-5), 4.91 (dd, 1 H, H-1), 3.87–3.31 (m, 2 H, H-3,4), 3.57 (s, 3 H, OCH_3), 2.19, 2.11, 2.02, and 1.98 (4 s, 12 H, 4 CH_3CO).

Anal. Calc. for $C_{15}H_{21}N_3O_9$: C, 46.51; H, 5.46; N, 10.84. Found: C, 46.24; H, 5.37; N, 10.81.

1L-1-Acetamido-2,3,4,5-tetra-O-acetyl-1-deoxy-6-O-methyl-myo-inositol (**59**). — Compound **58** (68 mg, 0.2 mmol) was hydrogenated and acetylated as for the preparation of **30**. Column chromatography with 1:8 EtOH–toluene as eluent gave **59** (67 mg, 95%), m.p. 189–190° (from EtOH); $[\alpha]_D^{20}$ +9° (*c* 0.9, $CHCl_3$); ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 5.75–5.45 (m, 1 H, NH), 5.53 (t, 1 H, $J_{1,2} = J_{2,3} = 3$ Hz, H-2), 5.29 (m, 2 H, H-4,5), 5.02 (dd, 1 H, $J_{3,4}$ 9 Hz, H-3), 4.90 (ddd, 1 H, $J_{1,6}$ 11, $J_{1,NH}$ 9 Hz, H-1), 3.64 (dd, 1 H, H-6), 3.45 (s, 3 H, OCH_3), 2.18, 2.08, 2.01, 1.99, and 1.95 (5 s, 15 H, 5 CH_3CO).

Anal. Calc. for $C_{17}H_{25}NO_{10}$: C, 50.62; H, 6.25; N, 3.47. Found: C, 50.67; H, 6.11; N, 3.45.

1L-1,2,3,4-Tetra-O-acetyl-6-azido-6-deoxy-5-O-methyl-chiro- (**60**) *and 1D-1,2,3,5-tetra-O-acetyl-4-azido-4-deoxy-6-O-methyl-scyllo-inositol* (**62**). — A mixture of **27** (485 mg, 1.1 mmol), sodium azide (345 mg, 5.45 mmol), and aqueous 90% 2-methoxyethanol (5 mL) was refluxed overnight, and then evaporated. The residue was acetylated conventionally and the products were chromatographed on a column of silica gel with 1:6 ethyl acetate–toluene as eluent to give **60** (290 mg, 69%), $[\alpha]_D^{21}$ −14.4 (*c* 0.4, $CHCl_3$); and **62** (16 mg, 5%), m.p. 144–145° (from EtOH); $[\alpha]_D^{26}$ −9° (*c* 0.8, $CHCl_3$). ^{1}H-N.m.r. data (90 MHz, $CDCl_3$): **60**, δ 5.55–5.00 (m, 4 H, H-1,2,3,4), 4.12 (t, 1 H, $J_{1,2} = J_{1,6} = 4$ Hz, H-6), 3.61 (dd, 1 H, $J_{4,5}$ 9 Hz, H-5), 3.49 (s, 3 H, OCH_3), 2.16, 2.07, 2.02, and 1.97 (4 s, 12 H, 4 CH_3CO); **62**, δ 5.23–4.93 (m, 4 H, H-1,2,3,5), 3.73–3.30 (m, 2 H, H-4,6), 3.42 (s, 3 H, OCH_3), 2.17, 2.08, 2.06, and 2.00 (4 s, 12 H, 4 CH_3CO).

Anal. Calc. for $C_{15}H_{21}N_3O_9$: C, 46.51; H, 5.46; N, 10.84. Found for **60**: C, 46.73; H, 5.45; N, 10.47; for **62**: C, 46.49; H, 5.17; N, 10.61.

*1*L-*1-Acetamido-3,4,5,6-tetra*-O-*acetyl-1-deoxy-2*-O-*methyl*-chiro-*inositol* (**61**). — Compound **60** (157 mg, 0.41 mmol) was hydrogenated and acetylated as described for the preparation of **30** to give, after column chromatography with 1:5 EtOH–toluene as eluent, **61** (152 mg, 93%), m.p. 183–184° (from CHCl$_3$); $[\alpha]_D^{21}$ −10.5° (*c* 1, CHCl$_3$); ^{1}H-n.m.r. (90 MHz, CDCl$_3$): δ 6.09 (d, 1 H, $J_{1,NH}$ 8 Hz, N*H*), 5.65–5.50 (m, 1 H, H-6), 5.38–5.06 (m, 3 H, H-3,4,5), 4.73–4.48 (m, 1 H, H-1), 3.80–3.60 (m, 1 H, H-2), 3.47 (s, 3 H, OC*H*$_3$), 2.12, 2.10, 2.04, and 2.03 (4 s, 3, 3, 3, and 6 H, 5 C*H*$_3$CO).

Anal. Calc. for $C_{17}H_{25}NO_{10}$: C, 50.62; H, 6.25; N, 3.47. Found: C, 50.40; H, 5.93; N, 3.48.

*1*D-*1-Acetamido-2,3,4,6-tetra*-O-*acetyl-1-deoxy-5*-O-*methyl*-scyllo-*inositol* (**63**). — Compound **62** (12 mg, 0.03 mmol) was hydrogenated and acetylated similarly, and the product was purified by column chromatography with 1:5 EtOH–toluene as eluent to give **63** (8 mg, 64%), m.p. 206–208° (from CHCl$_3$); $[\alpha]_D^{21}$ +3.4° (*c* 0.26, CHCl$_3$); ^{1}H-n.m.r. (90 MHz, CDCl$_3$): δ 5.66 (d, 1 H, $J_{1,NH}$ 10 Hz, NH), 5.25–4.83 (m, 4 H, H-2,3,4,6), 4.31 (q, 1 H, $J_{1,2}$ = $J_{1,6}$ = 10 Hz, H-1), 3.62–3.46 (m, 1 H, H-5), 3.45 (s, 3 H, OC*H*$_3$), 2.09, 2.07, 2.01, 2.00, and 1.88 (5 s, 15 H, 5 C*H*$_3$CO).

Anal. Calc. for $C_{17}H_{25}NO_{10}$: C, 50.62; H, 6.25; N, 3.47. Found: C, 50.84; H, 6.25; N, 3.46.

*1*D-*1,3,5-Tri*-O-*acetyl-2,4-diazido-2,4-dideoxy-6*-O-*methyl-* (**65**) *and 1*D-*1,2,3-tri*-O-*acetyl-5,6-diazido-5,6-dideoxy-4*-O-*methyl*-chiro-*inositol* (**67**), *and 1*D-*1,2,3,5-tetra*-O-*acetyl-6-azido-6-deoxy-4*-O-*methyl*-muco-*inositol* (**69**). — A mixture of **25** (505 mg, 1.06 mmol), sodium azide (690 mg, 10.6 mmol), and aqueous 90% 2-methoxyethanol (5 mL) was refluxed for 6 h, and then evaporated. The residue was acetylated, and the products were chromatographed on a column of silica gel with 1:4→1:3 ethyl acetate–hexane as eluent to give in turn **65** (165 mg, 42%) as a syrup, $[\alpha]_D^{25}$ +22° (*c* 0.9, CHCl$_3$); **67** (48 mg, 14%), $[\alpha]_D^{21}$ −23° (*c* 1.8, CHCl$_3$); and **69** (25 mg, 6%), m.p. 76–80° (from EtOH); $[\alpha]_D^{27}$ +12° (*c* 1, CHCl$_3$). ^{1}H-N.m.r. data (90 MHz, CDCl$_3$): **65**, 5.48 (t, 1 H, $J_{1,2}$ = $J_{1,6}$ = 3.8 Hz, H-1), 5.22 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 10 Hz, H-3), 4.97 (dd, 1 H, $J_{5,6}$ 3, $J_{4,5}$ 10 Hz, H-5), 3.92 (t, 1 H, H-4), 3.75 (dd, 1 H, H-2), 3.72 (dd, 1 H, H-6), 3.50 (s, 3 H, OC*H*$_3$), 2.19, and 2.15 (2 s, 3 and 6 H, 3 C*H*$_3$CO); (270 MHz, CDCl$_3$): **67**, δ 5.32 (t, 1 H, $J_{1,2}$ = $J_{1,6}$ = 3.3 Hz, H-1), 5.30 (dd, 1 H, $J_{2,3}$ 10.3, $J_{3,4}$ 9.5 Hz, H-3), 5.09 (dd, 1 H, H-2), 3.90 (t, 1 H, $J_{5,6}$ 3.3 Hz, H-6), 3.87 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-5), 3.60 (t, 1 H, H-4), 3.60 (s, 3 H, OC*H*$_3$), 2.15, 2.10, and 1.98 (3 s, 9 H, 3 C*H*$_3$CO); (90 MHz, CDCl$_3$): **69**, δ 5.40–4.90 (m, 4 H, H-1,2,3,5), 4.20 (t, 1 H, $J_{1,6}$ = $J_{5,6}$ = 9 Hz, H-6), 3.60 (td, 1 H, $J_{3,4}$ = $J_{4,5}$ = 3.5, $J_{2,4}$ 1.5 Hz, H-4), 3.44 (s, 3 H, OC*H*$_3$), 2.19, 2.15, 2.12, and 2.08 (4 s, 12 H, 4 C*H*$_3$CO).

Anal. Calc. for $C_{13}H_{18}N_6O_7$: C, 42.16; H, 4.90; N, 22.69. Found for **65**: C, 41.99; H, 4.91; N, 23.01; for **67**: C, 41.96; H, 4.76; N, 22.65. Calc. for $C_{15}H_{21}N_3O_9$: C, 46.51; H, 5.46; N, 10.84. Found for **69**: C, 46.13; H, 5.32; N, 11.08.

*1*D-*2,4-Diacetamido-1,3,5-tri*-O-*acetyl-2,4-dideoxy-6*-O-*methyl*-chiro-*inositol* (**66**). — Compound **65** (209 mg, 0.56 mmol) was hydrogenated and acetylated as described above, and column chromatography of the product with 1:4 ethanol–toluene as eluent gave **66** (159 mg, 66%), m.p. 243–245° (from EtOH); $[\alpha]_D^{24}$ +25° (*c* 1.3, CH$_3$OH); ^{1}H-n.m.r. (90 MHz, CDCl$_3$): δ 5.77, 5.58 (2 d, 2 H, *J* 9 Hz, 2 N*H*), 5.25 (t, 1 H,

$J_{1,2} = J_{1,6} = 3.5$ Hz, H-1), 5.17–4.88 (m, 2 H, H-3,5), 4.83–4.53 (m, 2 H, H-2,4), 3.67 (dd, 1 H, $J_{5,6}$ 3 Hz, H-6), 3.55 (s, 3 H, OCH_3), 2.16, 2.10, 2.05, 1.93, and 1.90 (5 s, 15 H, 5 CH_3CO).

Anal. Calc. for $C_{17}H_{26}N_2O_9 \cdot H_2O$: C, 49.63; H, 6.62; N, 6.81. Found: C, 49.96; H, 6.50; N, 6.73.

*1*D*-1,2-Diacetamido-4,5,6-tri-*O*-acetyl-1,2-dideoxy-3-*O*-methyl-*chiro*-inositol* (**68**). — Compound **67** (107 mg, 0.29 mmol) was hydrogenated and acetylated as described above to give **68** (84 mg, 72%), m.p. 137–140° (from CHCl$_3$–EtOH); $[\alpha]_D^{24}$ +17° (*c* 0.8, MeOH); ^{1}H-n.m.r. (270 MHz, CD$_3$OD): δ 5.35 (dd, 1 H, $J_{3,4}$ 9.9, $J_{4,5}$ 9.2 Hz, H-4), 5.23 (dd, 1 H, $J_{5,6}$ 3.3 Hz, H-5), 5.19 (t, 1 H, $J_{1,6}$ 3.3 Hz, H-6), 4.45 (dd, 1 H, $J_{1,2}$ 4.8 Hz, H-1), 4.41 (dd, 1 H, $J_{2,3}$ 11 Hz, H-2), 3.56 (dd, 1 H, H-3), 3.42 (s, 3 H, OCH_3), 2.16, 2.08, 2.05, and 1.94 (4 s, 3, 3, 3, and 6 H, 5 CH_3CO).

Anal. Calc. for $C_{17}H_{26}N_2O_9 \cdot H_2O$: C, 49.63; H, 6.62; N, 6.81. Found: C, 50.07; H, 6.28; N, 6.96.

*1*L*-3-Acetamido-1,2,4,6-tetra-*O*-acetyl-3-deoxy-5-*O*-methyl-*muco*-inositol* (**70**). — Compound **69** (120 mg, 0.31 mmol) was hydrogenated and acetylated as described above to give **70** (114 mg, 91%), m.p. 161–162° (from EtOH), $[\alpha]_D^{21}$ +5.4° (*c* 1.5, CHCl$_3$); ^{1}H-n.m.r. (270 MHz, CDCl$_3$): δ 5.40 (br. d, 1 H, J 10 Hz, NH), 5.30, 5.17 (2 t, 2 H, $J_{1,2} = J_{1,6} = J_{5,6} = 3.4$ Hz, H-1,6), 5.13, 5.06 (2 dd, 2 H, $J_{2,3} = J_{3,4} = 10.3$, $J_{4,5}$ 3.2 Hz, H-2,4), 4.86 (dt, 1 H, H-3), 3.47 (s, 3 H, OCH_3), 3.30 (dd, 1 H, H-5), 2.13, 2.11, 2.03, and 1.92 (4 s, 6, 3, 3, and 3H, 5 CH_3CO).

Anal. Calc. for $C_{17}H_{25}NO_{10}$: C, 50.63; H, 6.25; N, 3.47. Found: C, 50.69; H, 6.08; N, 3.30.

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