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NUCLEOCYCLITOLS. SYNTHESIS OF 3-(ADENIN-9-YL)-3-DEOXY-1,5,6-TRI-*O*-(METHYLSULFONYL)-*muco*-INOSITOL

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ABSTRACT

The reaction of 2,3-di-*O*-acetyl-1,4,5,6-tetra-*O*-(methylsulfonyl)-*myo*-inositol (**1**) with sodio-adenine in $HCONMe_2$ for 24 h at 100° gave, in 53.7% yield, the title compound, whose structure was ascertained by physical methods. Other parallel, secondary reactions were the aromatization of compound **1** to give 2,4-di-*O*-(methylsulfonyl)-1,2,4-benzenetriol (13.8%), and the formation of 1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol (17.8%).

INTRODUCTION

There is a permanent interest in the synthesis of carbohydrates condensed with purine and pyrimidine bases, analogous to the natural nucleosides, that is originated by the diverse physiological activities shown by these synthetic derivatives in such different fields as those of antitumor, antibiotic, or antiviral agents.

However, in the broad group of compounds thus far synthesized, inositol derivatives have received little investigation, the synthesis, by Suami *et al.*[1], of several biologically active adeninyl-cyclitols being the only precedent in the literature. These syntheses were based on the condensation of an aminocyclitol with a conveniently substituted pyrimidine, and subsequent elaboration of the adenine nucleus.

In a strictly structural sense, these compounds are not "nucleoside analogs", as they are devoid of an "oside" structure. This is chemically evidenced by their great stability in boiling acid solutions, which neither hydrolyze the base–inositol linkage nor change the structure of the non-base. The general terms "nucleocyclitol" and "nucleoinositol", while maintaining a useful resemblance to the name of the former compounds, avoid any misleading structural connotation.

RESULTS AND DISCUSSION

We performed the attachment of the adenine base to the inositol by nucleophilic attack of the adeninyl anion upon the previously described[2,3] 2,3-di-*O*-acetyl-1,4,5,6-tetra-*O*-(methylsulfonyl)-*myo*-inositol (**1**) in $HCONMe_2$ at 100°. This

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reaction would be greatly facilitated by the *trans*-vicinal, 3-acetoxyl group, which would anchimerically assist elimination of the mesyloxy group on C-4 through intermediate formation of an acetoxonium ion (see Scheme 1). The attack of the adeninyl nucleophile upon C-3 led to 3-(adenin-9-yl)-3-deoxy-1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol (**2**), whose structure was ascertained from the following evidence.

The ^{1}H-n.m.r.-spectrum (100 MHz, Me_2SO-d_6) of compound **2** showed two peaks (2 H), at δ 8.11 and 8.14, due to the aromatic protons on C-8 and C-2 of the adenine moiety, and a broad peak (2 H) at δ 7.05, due to the amino group.

The protons of the inositol nucleus appeared to be separated into two definite sets of peaks. One of them was assigned to the hydroxyl groups (δ 5.69 and 5.76), as they disappeared on deuterium exchange after the addition of acetic acid-d_4 to the dimethyl sulfoxide-d_6 solution. Likewise, the amino protons at δ 7.05 were also exchanged.

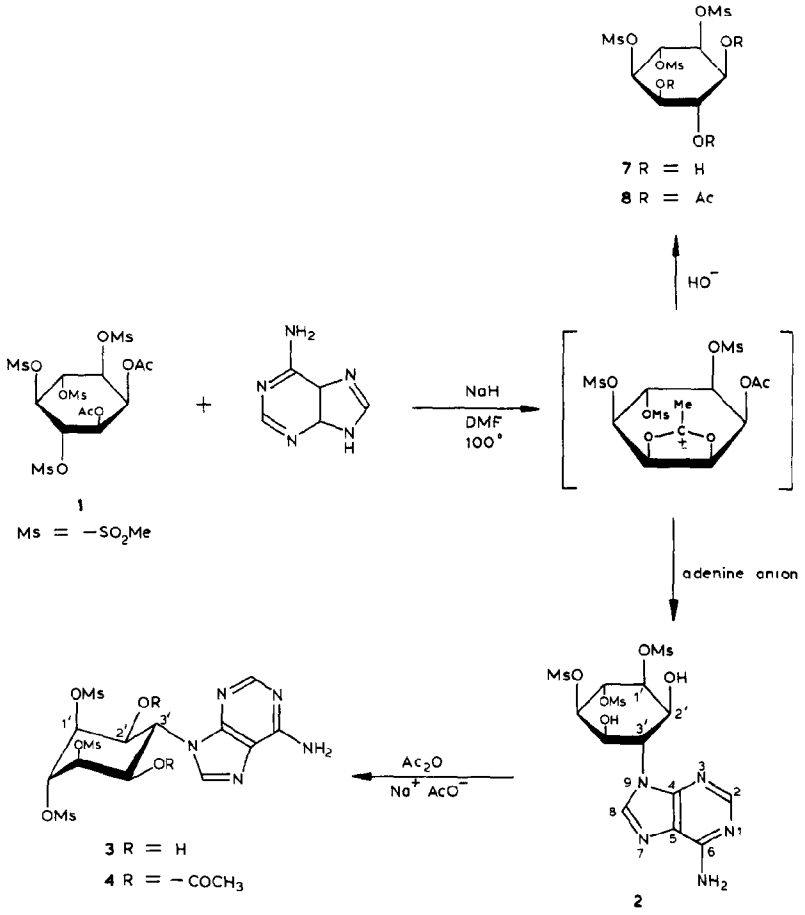
The remaining six protons appeared to be distributed as follows: at δ 5.20–4.96, a narrow multiplet attributable to the three equatorially oriented protons H-1′, H-5′, and H-6′ (see conformational formula **3**); at δ 4.94–4.60, a broader multiplet due to the two axially disposed H-2′ and H-4′; and, emerging from that multiplet, at δ 4.45, a triplet was clearly discernible, attributable to the axial H-3′, with spacings of 11 Hz due to coupling to H-2′ and H-4′. The methylsulfonyl group appeared as a six-proton singlet at δ 3.26, corresponding to the 1-*O*- and 5-*O*-mesyl groups on the basis of their symmetrical environment, and a three-proton singlet at δ 3.40 due to the 6-*O*-mesyl group. This n.m.r. spectrum clarified the main structural features of **2**, but that of the di-*O*-acetyl derivative **4** was more useful for ascertaining the conformational and other structural aspects.

Acetylation of **2**, even under vigorous conditions, gave a mixture from which the di-*O*-acetyl derivative **4** was isolated in pure state, for n.m.r.- and mass-spectral study, by preparative t.l.c. The ^{1}H-n.m.r. spectrum of **4** (100 MHz, C_5H_5N-d_5) showed two sharp singlets, at δ 8.65 and 8.60, due to H-2 and H-8, and a broad singlet (2 H), at δ 8.40, due to the amino group. A pair of doublets centered at δ 7.06, corresponding to two protons, was assigned to superimposed signals for H-2′ and H-4′, which, on the basis of the resonances of the 2′- and 4′-acetoxyl groups (see later), would both be in axial orientation. The spacings for these signals were 10 and 3 Hz, and their symmetrical surrounding explains their similar spectroscopic behavior. The remaining four protons of the inositol nucleus appeared as a multiplet at δ 6.24–5.72. In this multiplet, there could be clearly discerned a triplet at δ 5.87, with spacings of 10 Hz, ascribable to axial H-3′, coupled with H-2′ and H-4′. The mesyl groups, in a symmetrical environment, appeared as a six-proton singlet at δ 3.54, displaced 0.28 p.p.m. to lower field with respect to the same groups in **2**, whereas the signal of the third mesyloxy group, on C-6′, remained at δ 3.40.

The resonances of the acetyl groups were important to structural and conformational diagnostics. Both acetyl groups resonated as a six-proton singlet at δ 1.85,

indicating a symmetrical structure, which could only be formed by opening of the hypothetical, acetoxonium intermediate in the way depicted in Scheme 1. The alternative attack at C-4 by the adeninyl nucleophile should have afforded two differently oriented hydroxyl groups, leading to different resonances for the corresponding acetyl groups. On the other hand, nucleophilic attack with direct SN2 displacement of any of the mesyloxy groups of **1** should leave two hydroxyl groups in a *cis*, equatorial–axial relationship, leading to two different resonances for the corresponding diacetyl derivative. The fact that, in this reaction, no other compound with a nucleoinositol structure was detected indicated that a direct SN2 displacement was very difficult, despite the fact that $HCONMe_2$ was employed as the solvent. The resonances at δ 1.85 (τ 8.15) for both acetyl groups fall in the range described[4] for equatorial ones, supporting conformation **3** depicted in Scheme 1.

The ^{13}C-n.m.r.-spectrum of **2** in Me_2SO-d_6 at 25° showed the regions corresponding to the base and the sugar well separated. The scheme of resonances for the



Scheme 1

adenine portion correlated well with that published for adenosine[5] (in D_2O) and for the cyclitol antibiotic Neplanocin[6] A (in Me_2SO-d_6), and, on this basis, the signals were straightforwardly assignable.

The inositol portion showed four peaks for the six carbon atoms of the ring, two of these peaks being of double intensity. The higher-field, single-intensity resonance (δ 57.4) can be attributed to the point of insertion (C-3′) of the base.

The bulky adenine moiety imposes on compound **2** a strong limitation to the conformational mobility of the inositol ring, leading to an almost exclusive preponderance of the conformation depicted as **3** in Scheme 1. Assuming that *O*-mesylation could exert steric effects comparable to those of *O*-sulfation[7] and *O*-methylation[8,9] in sugars, the ^{13}C resonances for the inositol portion could be assigned by considering that the axial substituents on C-1′ and C-5′, would, through a strong, downfield α-effect on these magnetically equivalent carbon atoms, give rise to the doubly intense, downfield peak at δ 77.4. A concomitant, usually small, upfield β-effect on the symmetrically equivalent C-2′ and C-4′ would, in part, justify the high field (δ 64.2) of the other, doubly intense peak. However, this value suggests an additional, stronger effect; an upfield γ-effect of the axial, 6′-mesyloxy group upon C-2′ and C-4′ appears dubious if facts known about *O*-methyl substituents[9] are considered, but it could be operative in the case of *O*-mesyl ones. On the other hand, an influence of the adeninyl portion, of unknown magnitude on these vicinal carbon atoms, cannot be discarded. At present, there are available no systematic data to clarify these uncertainties. The last signal, at δ 73.6, can be assigned to C-6′. The symmetrical pattern of ^{13}C-resonances for the inositol moiety of **2** supports the postulated insertion of the purine at C-3′.

The point of attachment of C-3′ of the inositol moiety to N-9 of the purine ring can be postulated on the basis of the u.v. spectrum of **2**. Whereas substitution at N-7 of the adenine ring is usually evidenced[10] by u.v. maxima at 272–276 nm, coupling at N-9 showed[10] maxima at 260–262 nm. The u.v. spectrum of **2** in ethanol showed the maximum at 260 nm (pH 7), which correlates with attachment at N-9, previously also observed for (adenin-9-yl)inositols[1].

On the other hand, the known sensitivity of ^{13}C-n.m.r. parameters to structural changes further supports the assignment of the coupling site as N-9 in **2**, in view of the aforementioned close analogy of our ^{13}C-n.m.r. data for the adenine portion to those for adenin-9-yl derivatives[5,6]. This can be more specifically related to a ^{13}C-n.m.r. method for assignment of the site of glycosylation of the nitrogen heterocycles that had been reported[11], the pattern of the purinyl resonances for **2** being similar to that of the 9-purinyl derivatives described[11], which differ markedly from that of 7-purinyl compounds.

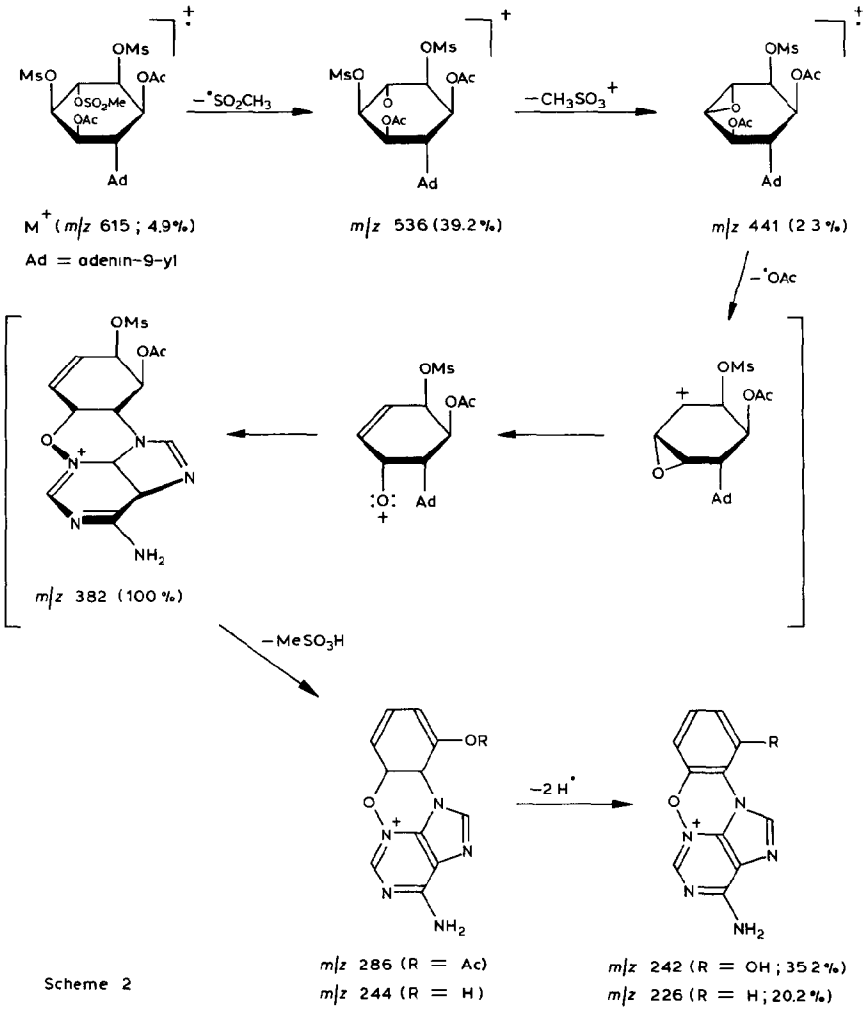
The results reported[11] were based on the fact that, when the free pair of electrons on the nitrogen atom in the anion is protonated, an upfield shift for the carbon atom α to the protonated nitrogen atom and a downfield shift for the β- and γ-carbon atoms were observed[12]. These "protonation parameters" were also observed[13] for several nucleosides of fused nitrogen heterocycles when compared with their base anion.

TABLE I

^{13}C-N.M R. CHEMICAL-SHIFTS FOR ADENINE ANION AND COMPOUND **2**

Compound	*Chemical shifts*[a]										
	C-2	*C-4*	*C-5*	*C-6*	*C-8*	*C-1'*	*C-2'*	*C-3'*	*C-4'*	*C-5'*	*C-6'*
Adenine anion (I)	149.19	159.16	120.08	148.25	153.66						
Compound **2**	151.63	149.46	119.22	155.56	142.15	77.45	64.20	57.44	64.20	77.45	73.74
$\Delta\delta$ I − **2**	−2.44	+9.70	+0.86	−7.31	+11.51						

[a]Shifts given in p.p.m. downfield from Me_4Si, for solutions in Me_2SO-d_6.



Scheme 2

To determine whether the effect of *N*-substitution in the inositol–purine system **2** is similar to that in the aforementioned examples[11–13], the ^{13}C chemical-shifts of **2** were compared with those of the adenine anion, formed by treatment of adenine with lithium hydroxide in Me_2SO-d_6. In compound **2**, C-4 and C-8 are α to the substituted nitrogen atom (N-9) and C-5 is β- and C-6 γ-disposed. Large upfield shifts of 9.70 p.p.m. for C-4, and 11.51 p.p.m. for C-8, were observed. An upfield shift of 0.86 p.p.m. was observed for C-5, which is a reversal from the downfield β-shift predicted, but expected[13] for bridgehead carbon atoms (see Table I).

The mass spectrum of the diacetyl derivative **4** showed the molecular ion (*m/z* 615, 4.9%) and a group of ions closely related thereto. Thus, by successive loss of an acetyl group and ketene from M^+, peaks at *m/z* 572 (1.5%) and 530 (0.7%) were formed; the loss of the CH_3SO_3 group led to *m/z* 520 (1.8%), which, in turn, would afford *m/z* 328 (0.4%) by loss of two molecules of CH_3SO_3H. However, three peaks, at *m/z* 382 (100%), 242 (35.2%), and 226 (20.2%), appear relevant, their formation and stability being attributable to the particular arrangement of substituents around the cyclohexane ring, which led us to postulate the structures shown in Scheme 2, related to coupling at N-9.

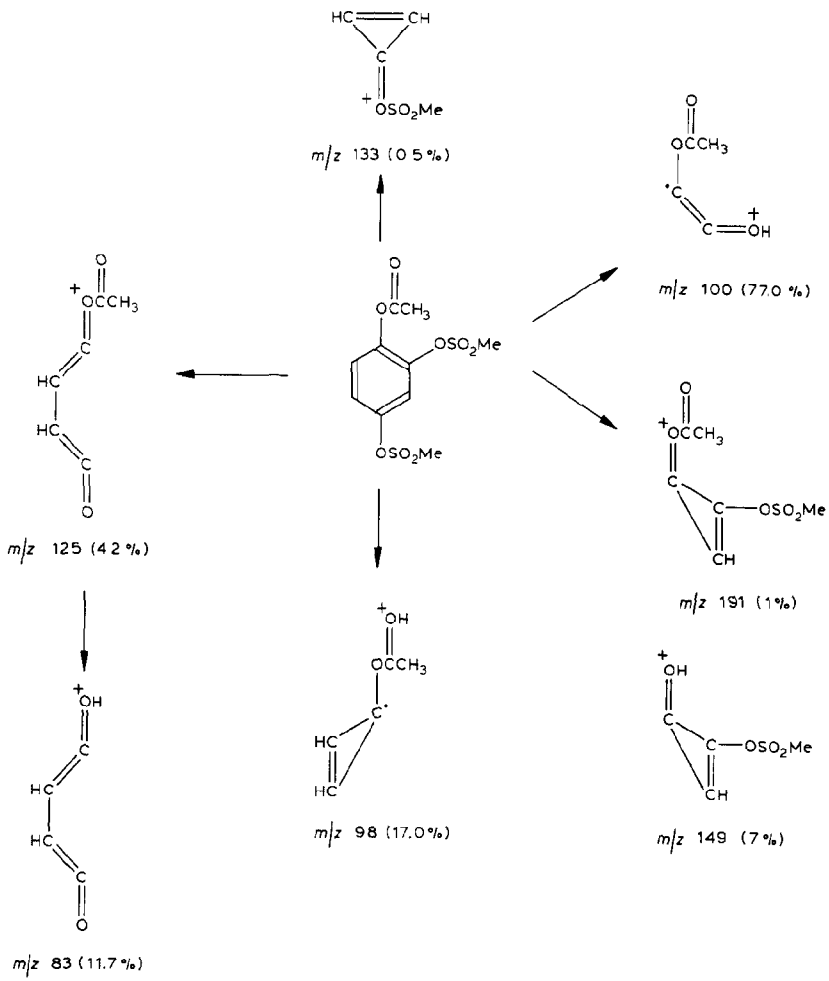
From *m/z* 382, the subsequent loss of CH_3–SO_3H and ketene would lead to *m/z* 286 (6.0%) and 244 (11.7%). The highly favored aromatization of the cyclohexadiene structures (*m/z* 286 and 244) would give rise to the peaks at *m/z* 242 and 226.

The inositol series of ions, afforded by splitting of the base, and protonation, led to *m/z* 398 (2.9%), whose loss of CH_3SO_3H gave *m/z* 302 (15.7%). The presence of other, minor, peaks was predictable, *i.e.*, Ad-C≡C-OAc (*m/z* 218, 1.3%), MsO-C≡C-OMs (*m/z* 214, 8.2%), and MsO-C≡C-OAc (*m/z* 178, 11.7%). Such as Ac-C≡C-OMs or Ad-C≡C-OMs, foreseeable if a structure having two vicinal acetoxyl groups or a vicinal adeninyl–mesyl grouping were present, were not detected.

Cleavage of the C–N inositol–base bond is accompanied by transfer of hydrogen, to yield base + H (*m/z* 135, 41.1%) or[14] base + 2H (*m/z* 136, 63.0%).

Compound **2** was isolated from the reaction mixture by evaporation of the solution, and extraction of the dried residue with 1:4 methanol–chloroform; the insoluble portion contained almost all of the nucleoinositol. By chromatographic separation, the extract afforded two new compounds, produced by transformations of the starting inositol **1** under the influence of the alkaline medium and the drastic conditions employed.

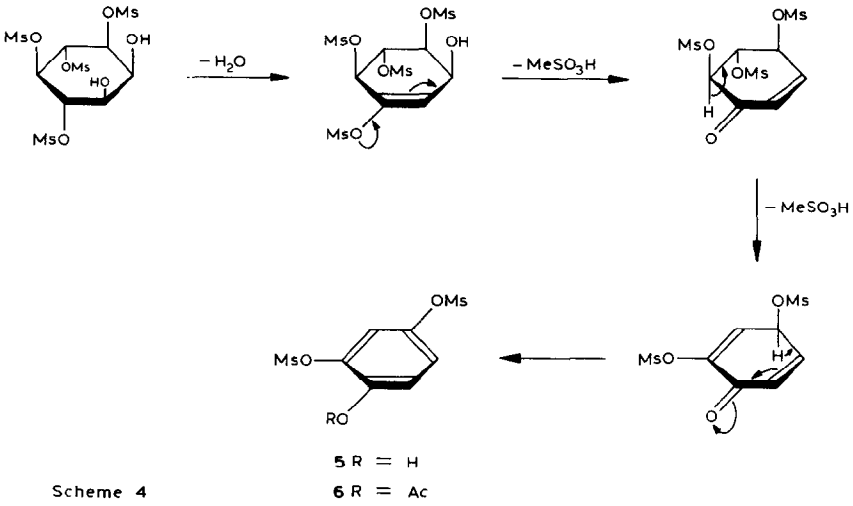
One of these compounds, 2,4-di-*O*-(methylsulfonyl)-1,2,4-benzenetriol (**5**), was eluted from the column with 3:37 absolute ethanol–benzene, and isolated in 13.8% yield; it was purified, and studied structurally, through its acetate (**6**). The 100-MHz, n.m.r. spectrum of **5** in acetone-d_6 showed resonances for two mesyl groups, at δ 3.32 and 3.29, and a hydroxyl proton at δ 3.26. The signals shown by the aromatic protons are characteristic for the substitution pattern present in **5**. At δ 7.33, there appears a doublet ($J_{5,6}$ 8 Hz) corresponding to H-6, and at δ 6.86, a



Scheme 3

pair of doublets correspond to H-5, with $J_{5,6}$ 8 and $J_{3,5}$ 2 Hz. This distribution of signals and coupling constants is usual for a pattern of three protons in 1,2,4 relationship on the benzene ring[3,15,16]. The n.m.r. spectrum of the corresponding acetate (**6**) showed the 1:2 relationship of acetyl to mesyl groups, and its mass spectrum confirmed the structure proposed, and ascertained the relative position of each substituent. The highest mass peak (*m/z* 282, 1.5%) was assigned to the molecular ion of **5**, produced by loss of ketene from **6**. Scheme 3 shows the ruptures that support the structure proposed, the pattern of substitution being defined by the peaks at *m/z* 125, 100, and 98.

The rearrangements of the starting inositol **1** that led to **5** can be rationalized on the basis of similar reactions of other inositol derivatives[17], which, for this particular case, are shown in Scheme 4.



5 R = H
6 R = Ac

Scheme 4

The third product, isolated from the reaction in 17.8% yield after chromatography on a column of silica gel by elution with 1:9 to 3:17 absolute ethanol–benzene, was 1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol (**7**). This compound probably originated from opening of the acetoxonium intermediate (see Scheme 1) by attack, competitive with that of adenine, of a hydroxyl anion, produced in the rearrangements already described, or in destruction processes that took place partially owing to the drastic, alkaline conditions employed.

EXPERIMENTAL

General procedures. — Melting points (Kofler hot-stage) are uncorrected. T.l.c. was conducted on Silica Gel G (Merck) plates (0.25 mm layer thickness) with the following solvents: (*A*) 1:4 (v/v) methanol–chloroform, and (*B*) 1:9 (v/v) methanol–chloroform. The spots were detected with (*1*) iodine vapor, and (*2*) alkaline hydroxylamine–ferric nitrate (for esters[18]). I.r. spectra were recorded, for Nujol mulls, with a Perkin–Elmer 710 B spectrophotometer. N.m.r. spectra were recorded at 20–25° with a Varian XL-100 spectrophotometer at 100 (^{1}H) and 25.00 (^{13}C) MHz, with Me_4Si as the internal reference-standard. Mass spectra were recorded with a Varian-Mat CH-7 spectrometer commanded by a Varian-Mat data-system 166 computer at an ionizing potential of 70 eV; the temperature of the direct-insertion probe was 190°.

*2,3-Di-*O*-acetyl-1,4,5,6-tetra-*O*-(methylsulfonyl)-*myo*-inositol* (**1**). — This compound was synthesized as previously described[2,3].

Sodium salt of adenine. — Sodium hydride (from a 50% oil dispersion) was rinsed twice with light petroleum and dried under diminished pressure. This powder (150 mg, 6.25 mmol) was suspended in $HCONMe_2$ (15 mL), and adenine (704 mg, 5.22 mmol) was added. The suspension was stirred for 1 h at 30° and subsequently for 1 h at 50°.

*Synthesis of 3-(adenin-9-yl)-3-deoxy-1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol* (**2**). — A solution of compound **1** (500 mg, 0.86 mmol) in $HCONMe_2$ (5 mL) was added to the suspension of sodium-adenine, and the mixture was stirred for 24 h at 100°. The dark mixture finally obtained was cooled and filtered; a water-soluble, brown solid (353 mg) was separated which, in t.l.c., remained at the starting point (solvent *A*, reagent *1*), and was mainly sodium mesylate.

The solution was evaporated to dryness, and the syrup obtained (1.38 g) was repeatedly extracted with 1:4 (v/v) methanol–chloroform (see later). The insoluble residue contained mainly the nucleoinositol **2**, and, in t.l.c. (solvent *A*, reagent *1*), showed two principal spots, R_F 0.15 (compound **2**), and 0.21 (adenine). On recrystallization from hot water, this powder (600 mg) gave compound **2** as rectangular plates (230 mg); m.p. 248–250°; insoluble in ethanol, acetone, and chloroform, slightly soluble in methanol, and fairly soluble in acetonitrile and in dimethyl sulfoxide. It had R_F 0.15 (solvent *A*, reagent *1*); λ_{max}^{EtOH} (pH 7) 260 (ε_{mM} 0.67), (at pH 1) 257 (0.89), and (at pH 11) 258 nm (1.73); ν_{max}^{Nujol} 3450 (NH), 3350 (OH), 1660 (NH_2), 1630, 1595 (C=C, C=N), 1400–1320, and 1140 cm^{-1} (sulfonyl group); ^{1}H-n.m.r. data (Me_2SO-d_6): δ 3.40 (9 H, 3 CH_3SO_2), 4.32–5.68 (8 H, ring and HO protons), 7.05 (2 H, amino group), and 8.08 (2 H, H-2,8).

Anal. Calc. for $C_{14}H_{21}N_5O_{11}S_3$: C, 31.63; H, 3.98; N, 13.18; S, 18.01. Found: C, 31.10; H, 4.05; N, 12.85; S, 17.61.

Compound **2** (50 mg) was suspended in boiling water (2 mL), and concentrated hydrochloric acid was added to dissolution; then 2-propanol was added to incipient turbidity, and the solution was kept for 24 h at 0°. The solid obtained was filtered off, and recrystallized from methanol containing a few drops of concentrated hydrochloric acid. The hydrochloride of **2** had m.p. 220–225°; R_F 0.18 (solvent *A*, reagent *1*).

Anal. Calc. for $C_{14}H_{21}N_5O_{11}S_3 \cdot HCl$: C, 29.63; H, 3.88; N, 12.34; S, 16.93. Found: C, 29.76; H, 4.14; N, 12.30; S, 16.87.

*2,4-Di-*O*-acetyl-3-(adenin-9-yl)-3-deoxy-1,5,6-tri-*O*-(methylsulfonyl)-muco-inositol* (**4**). — Compound **2** (1 g) was mixed with anhydrous sodium acetate (0.5 g) and acetic anhydride (40 mL). The suspension was boiled under reflux for 5 h and the solution evaporated to dryness. The residue was washed with ethyl acetate (4 × 25 mL), and then crystallized from methanol, giving a mixture of three compounds that, in t.l.c., showed R_F 0.35, 0.25, and 0.19 (solvent *B*, reagent *1*). Only the first two compounds gave a positive test with the reagent for esters (reagent *2*). Repeated recrystallization from methanol, ethanol, or 2-propanol did not afford any of these compounds in pure state; other methods or conditions of acetylation also led to a mixture of acetates.

Preparative t.l.c. on Silica Gel G (1 mm thickness), with solvent *B* as developer, gave, in two successive runs, pure **4** (R_F 0.25, solvent *B*; reagent *1*) as rectangular plates; m.p. 189–190°; n.m.r. data ($C_5H_5N_5$-d_5): δ 1.85 (s, 6 H, acetyl groups), 3.40 (s, 3 H, CH_3SO_2), 3.54 (s, 6 H, 2 CH_3SO_2), 5.76–6.13 (m, 4 H, ring protons), 8.40 (2 H, amino group), and 8.60 and 8.65 (H-2,8); *m/z* (intensity, as

percent of base peak, and then assignments): 615 (4.9, M^+), 572 (1.5, $M^+ - CH_3CO$), 530 (0.7, $M^+ - CH_3CO - CH_2CO$), 536 (39.2, $M^+ - CH_3SO_2$), 520 (1.8, $M^+ - CH_3SO_3$); *m/z* 441, 382, 286, 244, 242, and 226 (see Scheme 2).

Anal. Calc. for $C_{16}H_{19}N_5O_{12}S_3$: C, 35.12; H, 4.09; N, 11.38; S, 15.60. Found: C, 34.85; H, 4.28; N, 11.46; S, 15.47.

The remaining mixtures of acetates were not further separated. *O*-Deacetylation of **4** with sodium methoxide afforded, quantitatively, the starting compound **2**.

Chromatography of the methanol–chloroform extract. — This extract (from the preparation of **2**) was evaporated, and the residue (760 mg) was chromatographed on a column (30 × 340 mm) of Silica Gel (Baker, 60–200 mesh). Elution was successively conducted with benzene, chloroform, increasing concentrations of ethanol in chloroform, and, finally, ethanol. A significant amount of material (412 mg) consisted of brown degradation products that could not be eluted from the column. With 3:17 absolute ethanol–benzene, a further 17 mg of compound **2** was obtained (total yield, 53.7%).

*Isolation of 2,4-di-*O*-(methylsulfonyl)-1,2,4-benzenetriol* (**5**). — The fractions eluted with 3:37 ethanol–benzene gave **5** (39 mg, 13.8% yield) as a wax; t.l.c., one spot R_F 0.50 (solvent *A*, reagent *1*); ^{1}H-n.m.r. data (acetone-d_6): δ 3.26 (OH), 3.29 (OMs), 3.32 (OMs), 7.33 (d, H-6, $J_{5,6}$ 8 Hz), 6.86 (dd, H-5, $J_{3,5}$ 2 Hz), and 7.02 (d, H-3, $J_{3,5}$ 2 Hz).

The acetate (**6**) was obtained by heating **5** with 1:1 acetic anhydride–pyridine; prisms m.p. 82–84°; t.l.c., R_F 0.77 (solvent *B*, reagent *1*); ^{1}H-n.m.r. data ($CDCl_3$): δ 2.34 (s, OAc), 3.18 (s, 6 H, 2 OMs), 7.46 (dd, H-5, $J_{5,6}$ 9, $J_{3,5}$ 3 Hz), and 7.14–7.30 (H-6 and H-3, distorted, partially superimposed pair of doublets); for mass spectrum, see Scheme 3.

Anal. Calc. for $C_{10}H_{12}O_8S_2$: C, 37.03; H, 3.70; S, 19.75. Found: C, 36.81; H, 3.94; S, 20.02.

*Isolation of 1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol* (**7**). — The fractions eluted with 3:27 to 3:17 ethanol–benzene gave compound **7** (64 mg, 17.8% yield), which crystallized and was recrystallized from ethanol; m.p. 184°; ^{1}H-n.m.r. data ($C_5H_5N_5$-d_5): δ 3.48 (2 OMs), 3.52 (OMs), and 5.58–6.24 (6 H, ring protons). This compound, previously synthesized unambiguously[19], was better identified as its tri-*O*-acetyl derivative, which was obtained by heating **7** (30 mg) with 1:1 acetic anhydride–pyridine. The resulting 2,3,4-tri-*O*-acetyl-1,5,6-tri-*O*-(methylsulfonyl)-*muco*-inositol (**8**; 35 mg) was recrystallized from ethanol; m.p. 172–173°; t.l.c. R_F 0.27 (solvent *B*, reagents *1* and *2*); ^{1}H-n.m.r. data ($C_5H_5N_5$-d_5): δ 1.76 (OAc), 2.07 (2 OAc), 3.53 (2 OMs), 3.58 (OMs), and 5.75–6.16 (6 H, ring protons).

Anal. Calc. for $C_{15}H_{24}O_{15}S_3$: C, 33.33; H, 4.44; S, 17.78. Found: C, 33.48; H, 4.54; S, 17.72.

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