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# Preparation of *p*-Toluenesulfonyl Derivatives of *myo*-Inositol

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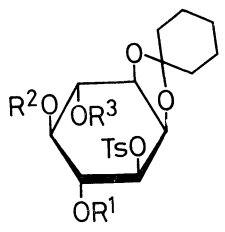
Six *p*-toluenesulfonyl esters of *myo*-inositol, five of which are new, have been prepared by a selective sulfonylation of *myo*-inositol derivatives and the structures of the new compounds were established by means of their proton magnetic resonance (PMR) spectra and the reaction sequences. Preparation of 1,3-di-*O*-*p*-toluenesulfonyl-*myo*-inositol, an useful intermediary compound for synthesizing *myo*-inosadiamine-1,3, has been improved by the present method.

In the preceding paper,[1] we described the preparations of *p*-toluenesulfonyl esters of *myo*-inositol by selective sulfonylation of 1,2-*O*-cyclohexylidene-*myo*-inositol. In this paper, we wish to report the alternative synthetic route to its positional isomers. Six *p*-toluenesulfonyl esters (1,3-, 1,3,4- 1,3,5-, 1,3,4,5-, 1,3,4,6- and 1,3,4,5,6-) have been prepared by selective sulfonylation of *myo*-inositol derivatives. The structures of the new compounds were confirmed by the PMR spectra of their acetyl derivatives or the reaction sequences. Preparation of 1,3-di-*O*-*p*-toluenesulfonyl-*myo*-inositol,[2] an important intermediary compound for *myo*-inosadiamine-1,3,[3] has been much improved by the present method.

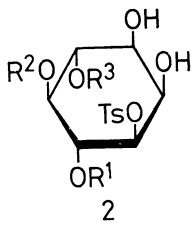
Treatment of 4,5,6-tri-*O*-acetyl-1,2-*O*-cyclohexylidene-3-*O*-*p*-toluenesulfonyl-*myo*-inositol (**1a**)[1] with boiling 80% aqueous acetic acid resulted removal of cyclohexylidene group to give 4,5,6-tri-*O*-acetyl-1-*O*-*p*-toluenesulfonyl-*myo*-inositol (**2a**) in 68% yield. One of the two hydroxyl groups in **2a** was expected to be selectively esterified by *p*-toluenesulfonyl chloride, since they are in an axial and an equatorial orientation, respectively.[4] When **2a** was treated with 2 molar equivalents of *p*-toluenesulfonyl chloride in dry pyridine at 30°C for 4 days, 4,5,6-tri-*O*-acetyl-1,3-di-*O*-*p*-toluenesulfonyl-*myo*-inositol (**3a**) was obtained as a sole product in 88% yield. The structure of **3a** was established by converting it into the known tetraacetyl derivative (**4a**)[2] by the usual manner. Therefore, the equatorial hydroxyl group on C-3 was shown to be selectively esterified. While the axial hydroxyl group on C-2 was found to be extremely unreactive due to being highly sterically hindered by the two vicinal *p*-toluenesulfonyloxy groups in *cis* relationship. Even when the reaction of **2a** with an excess amount of *p*-toluenesulfonyl chloride was carried out over 100°C for prolonged periods, a formation of the tri-ester could not be detected by a thin layer chromatography (tlc).

Similarly, 5,6-di-*O*-acetyl-1,4-di-*O*-*p*-toluenesulfonyl-*myo*-inositol (**2b**) was obtained in 86% yield from 4,5-di-*O*-acetyl-1,2-*O*-cyclohexylidene-3,6-di-*O*-*p*-toluenesulfonyl-*myo*-inositol (**1b**)[1] by refluxing in aqueous acetic acid. Treatment of **2b** with 3 molar equivalents of *p*-toluenesulfonyl chloride gave 5,6-di-*O*-acetyl-1,3,4-tri-*O*-*p*-toluenesulfonyl-*myo*-inositol (**3b**) selectively in 90% yield. Compound **3b** was also obtained from 4,5-di-*O*-acetyl-1,6-di-*O*-*p*-toluenesulfonyl-*myo*-inositol (**2c**) which was derived from 5,6-di-*O*-acetyl-1,2-*O*-cyclo-




1

| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| a | Ac | Ac | Ac |
| b | Ac | Ac | Ts |
| c | Ts | Ac | Ac |
| d | Ac | Ts | Ac |
| e | Ts | Ac | Ts |
| f | Ac | Ts | Ts |




2

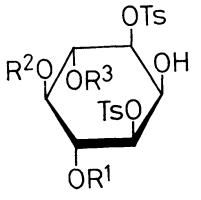
| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| a | Ac | Ac | Ac |
| b | Ac | Ac | Ts |
| c | Ts | Ac | Ac |
| d | Ac | Ts | Ac |
| e | Ts | Ac | Ts |
| f | Ac | Ts | Ts |
| g | Ts | Ts | Ts |

1) T. Suami, S. Ogawa, T. Tanaka, and T. Otake, This Bulletin, **44**, 835 (1971).

2) T. Suami, F. W. Lichtenthaler, and S. Ogawa, *ibid.*, **40**, 1488 (1967); S. J. Angyal, P. T. Gilham, and G. J. H. Melrose, *J. Chem. Soc.*, **1965**, 5252.

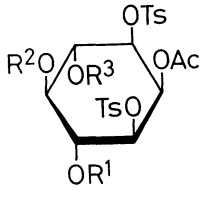
3) T. Suami and S. Ogawa, This Bulletin, **40**, 1295 (1967); T. Suami, S. Ogawa, S. Naito, and H. Sano, *J. Org. Chem.*, **33**, 2831 (1968).

4) T. Suami and S. Ogawa, This Bulletin, **37**, 1238 (1964).




3

| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| a | Ac | Ac | Ac |
| b | Ac | Ac | Ts |
| c | Ac | Ts | Ac |
| d | Ts | Ac | Ts |
| e | Ac | Ts | Ts |
| f | Ts | Ts | Ts |




4

| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| a | Ac | Ac | Ac |
| b | Ac | Ac | Ts |
| c | Ac | Ts | Ac |
| d | Ts | Ac | Ts |
| e | Ac | Ts | Ts |

hexylidene-3,4-di-*O*-*p*-toluenesulfonyl-*myo*-inositol (**1c**).[1] These results confirmed the proposed structure of **3b** unambiguously. Acetylation of **3b** gave the triacetyl derivative (**4b**) which, in PMR spectrum in deuteriochloroform ($CDCl_3$), revealed a narrow triplet ($J$= 3 Hz) at $\tau$ 4.49. Similar triplet was found in the PMR spectrum of **4a** ($\tau$ 4.37), and then it was assigned to the hydrogen atom on C-2 bearing acetoxy group.

Preferential sulfonylation of 4,6-di-*O*-acetyl-1,5-di-*O*-*p*- toluenesulfonyl-*myo*-inositol (**2d**). which was obtained by removal of the cyclohexylidene group of 4,6-di-*O*-acetyl-1,2-*O*-cyclohexylidene-3,5-di-*O*-*p*-toluenesulfonyl-*myo*-inositol (**1d**),[1] afforded 4,6-di-*O*-acetyl-1,3,5-tri-*O*-*p*-toluenesulfonyl-*myo*-inositol (**3c**) exclusively in 95% yield. On acetylation, **3c** gave the triacetyl derivative (**4c**), which revealed two signals of 1 : 2 relative intensities in an acetoxy methyl region[5] in its PMR spectrum

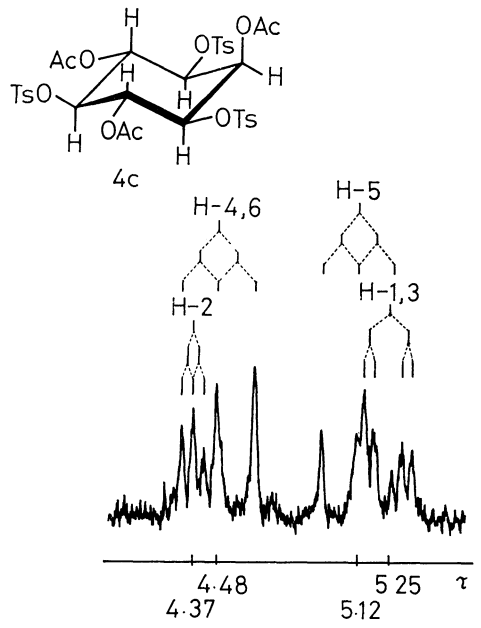



Fig. 1. Partial PMR spectrum of 2,4,6-tri-*O*-acetyl-1,3,5-tri-*O*-*p*-toluenesulfonyl-*myo*-inositol (**4c**) in $CDCl_3$ at 60 MHz: $J_{ae}$=3 Hz, $J_{aa}$=10 Hz.

5) F. W. Lichtenthaler and P. Emig, *Carbohyd. Res.*, **7**, 121 (1968).

Table 1. Chemical shifts of methyl protons[a]

| Compd. No. | Acetoxy | *p*-Toluenesulfonyloxy |
|---|---|---|
| **4a** | 7.95 (1) | 7.54 (2) |
| | 8.01 (1) | |
| | 8.10 (2) | |
| **4b** | 7.93 (1) | 7.54 (3) |
| | 8.00 (1) | |
| | 8.12 (1) | |
| **4c** | 7.97 (1) | 7.53 (3) |
| | 8.17 (2) | |
| **4d** | 7.92 (1) | 7.56 (4) |
| | 8.02 (1) | |
| **4e** | 8.00 (1) | 7.56 (4) |
| | 8.15 (1) | |

a) Measured at 60 MHz in $CDCl_3$. Values in parenthesis show number of methyl groups. Chemical shifts are expressed in $\tau$-values.

in $CDCl_3$. This result supported the proposed structure of **4c**, because it has a symmetrical structure and the signals due to two acetoxy groups on C-4 and C-6 should be overlapped each other (Table. 1). Furthermore, the signals of the ring protons could be resolved by first-order method and assigned unambiguously to each proton, as shown in Fig. 1.

By the same reaction sequences, 5-*O*-acetyl-1,4,6-tri-*O*-*p*-toluenesulfonyl-*myo*-inositol. (**2e**) and 6-*O*-acetyl-1, 4,5-tri-*O*-*p*-toluenesulfonyl-*myo*-inositol (**2f**) were obtained from 5-*O*-acetyl-1,2-*O*-cyclohexylidene-3,4,6-tri-*O*-*p*-toluenesulfonyl-*myo*-inositol (**1e**)[1] and 4-*O*-acetyl-1,2-*O*-cyclohexylidene-3,5,6-tri-*O*-*p*-toluenesulfonyl-*myo*-inositol (**1f**)[1] in 90 and 93% yield, respectively. On sulfonylation with 5 molar equivalents of *p*-toluenesulfonyl chloride, **2e** and **2f** afforded 5-*O*-acetyl-1,3,4,6-tetra-*O*-*p*-toluenesulfonyl-*myo*-inositol (**3d**) and 6-*O*-acetyl-1,3-4,5-tetra-*O*-*p*-toluenesulfonyl-*myo*-inositol (**3e**) predominantly in 42[6] and 99% yield, respectively. Compound **3d** and **3e** were converted into the diacetyl derivative (**4d**) and (**4e**), respectively, which showed the narrow triplets ($J$=3 Hz) at $\tau$ 4.55 and 4.58, supporting the location of the acetoxy group at C-2.

Sulfonylation of 1,4,5,6-tetra-*O*-*p*-toluenesulfonyl-*myo*-inositol (**2g**)[1] produced 1,3,4,5,6-penta-*O*-*p*-toluenesulfonyl-*myo*-inositol (**3f**) as a sole product in 63% yield. Attempt of acetylation of **3f** by the usual manner failed. Introduction of five *p*-toluenesulfonyl group into all the equatorially orientated hydroxyl groups in *myo*-inositol seemed to make the remaining axial hydroxyl group on C-2 extremely unreactive. Therefore, the structure of **3g** was substantially established by an analogy.

## Experimental

Melting points were determined on a Mitamura Riken micro hot stage and are uncorrected. PMR spectra were measured on a Varian Associate A-60D (60 MHz) spectrometer at a concentration of *ca.* 10% deuteriochloroform with tetramethylsilane as an internal standard. Chemical shifts are expressed in $\tau$-values and signals are described as

6) The low yield of **3d** may be due to a partial de-*O*-acetylation of **2d** and/or **3d** during a sulfonylation reaction.

s (singlet), t (triplet), q (quartet), or m (complex multiplet). Values given for coupling constants are first-order. Thin layer chromatography was done with silica gel (Wakogel B-10, Wako pure chemical industries Ltd.) using toluene-methyl ethyl ketone (4:1 or 3:1 volume) as the solvent system. The compounds were detected by exposing the plates to iodine vapor or by heating after spraying 50% sulfuric acid. All solutions were concentrated by a rotary evaporator at 40—50°C under reduced pressure. All the compounds described in this paper are racemic.

*4,5,6-Tri*-O-*acetyl-1*-O-p-*toluenesulfonyl*-myo-*inositol (2a).* A mixture of 4,5,6-tri-*O*-acetyl-1,2-*O*-cyclohexylidene-3-*O*-*p*-toluenesulfonyl-*myo*-inositol (**1a**)[1] (1.0 g) and 80% aqueous acetic acid (20 m*l*) was refluxed for 2 hr. The reaction mixture was evaporated to give an oily product which crystallized by trituration with ethanol to afford crystals (0.54 g, 68%) of **2a**, mp 202—204°C. Recrystallization from ethanol gave colorless prisms which showed the same melting point.

Found: C, 50.14; H, 5.26; S, 7.12%. Calcd for $C_{19}H_{24}O_{11}S$: C, 49.55; H, 5.25; S, 6.96%.

*4,5,6-Tri*-O-*acetyl-1,3-di*-O-p-*toluenesulfonyl*-myo-*inositol (3a).* To a solution of **2a** (0.46 g) in dry pyridine (5 m*l*) was added *p*-toluenesulfonyl chloride (0.29 g) under ice cooling. The reaction mixture was allowed to stand at 30°C for 4 days, till when the tlc showed the disappearance of **2a**. Poured into ice and water (100 m*l*), the crude crystals (0.64 g) were collected by filtration. A 0.44 g portion of the crude product was recrystallized from ethanol to give colorless needles (0.38 g, 88%) of **3a** monohydrate, mp 207—208.5°C (after melting and resolidifying to plates at 117—125°C).

Found: C, 49.55; H, 5.20; S, 9.62%. Calcd for $C_{26}H_{30}O_{13}S_2 \cdot H_2O$: C, 49.37; H, 5.10; S, 10.14%.

The monohydrate lost water of crystallization when it was dried over phosphorus pentoxide under vacuum at 120°C for 24 hr, mp 207.5—208.5°C.

Found: C, 50.94; H, 4.88; S, 10.46%. Calcd for $C_{26}H_{30}O_{13}S_2$: C, 50.80; H, 4.92; S, 10.43%.

*2,4,5,6-Tetra*-O-*acetyl-1,3-di*-O-p-*toluenesulfonyl*-myo-*inositol (4a).* A 0.21 g portion of the crude **3a** monohydrate was treated with a mixture of acetic anhydride (2 m*l*) and pyridine (2 m*l*) at 80°C for 1 hr. Then the mixture was poured into ice and water and the crystals were collected by filtration; yield 0.19 g (90%), mp 220—223°C (lit,[2] mp 220—222°C). This compound was identified with an authentic sample by comparing with IR spectra.

*5,6-Di*-O-*acetyl-1,4-di*-O-p-*toluenesulfonyl*-myo-*inositol (2b).* A mixture of 4,5-di-*O*-acetyl-1,2-*O*-cyclohexylidene-3,6-di-*O*-*p*-toluenesulfonyl-*myo*-inositol (**1b**)[1] (1.27 g) and 80% aqueous acetic acid (25 m*l*) was refluxed for 2 hr. Then the mixture was evaporated and the crystalline residue was triturated with ethanol to afford colorless crystals (0.97 g, 86%) of **2b**, mp 201.5—203.5°C. Recrystallization from ethanol gave an analytical sample, colorless needles, mp 207.5—209°C.

Found: C, 50.52; H, 4.86; S, 11.05%. Calcd for $C_{24}H_{28}O_{12}S_2$: C, 50.33; H, 4.94; S, 11.20%.

*5,6-Di*-O-*acetyl-1,3,4-tri*-O-p-*toluenesulfonyl*-myo-*inositol (3b).* To a solution of **2b** (0.19 g) in dry pyridine (2 m*l*) was added *p*-toluenesulfonyl chloride (0.18 g, 2.8 molar equiv.) and the reaction mixture was kept at 30°C for 4 days, followed at 85°C for 1 hr. Then the mixture was poured into ice and water (25 m*l*) and the resulting oily product was extracted with chloroform (25 m*l*), washed with water (3×20 m*l*) and dried over anhydrous sodium sulfate. Evaporation gave a colorless oil, which crystallized on treatment with chloroform and ethanol to give crystals (0.21 g, 90%) of **3b**, mp 201—203°C. Recrystallization from chloroform and ethanol afforded an analytical sample, colorless plates, mp 204.5—206°C.

Found: C, 51.32; H, 4.82; S, 13.14%. Calcd for $C_{31}H_{34}O_{14}S_3$: C, 51.23; H, 4.72; S, 13.23%.

*2,5,6-Tri*-O-*acetyl-1,3,4-tri*-O-p-*toluenesulfonyl*-myo-*inositol (4b).* A 100 mg portion of **3b** was treated with acetic anhydride (1 m*l*) and pyridine (1 m*l*) at room temperature overnight. The reaction mixture was poured into ice and water and the resulting crystals were collected by filtration. The crude crystals of **4b** weighed 100 mg (96%), mp 147—150.5°C. An analytical sample was obtained by recrystallization from chloroform and ethanol, mp 166—167.5°C. PMR: $\tau$ 4.49 (1, t, H-2, $J$=2.8 Hz).

Found: C, 51.60; H, 4.65; S, 12.72%. Calcd for $C_{33}H_{36}O_{15}S_3$: C, 51.56; H, 4.72; S, 12.49%.

*4,5-Di*-O-*acetyl-1,6-di*-O-p-*toluenesulfonyl*-myo-*inositol (2c).* A mixture of 5,6-di-*O*-acetyl-1,2-*O*-cyclohexylidene-3,4-di-*O*-*p*-toluenesulfonyl-*myo*-inositol (**1c**)[1] (0.19 g) and 80% aqueous acetic acid (10 m*l*) was refluxed for 2 hr. Then the reaction mixture was evaporated to give a colorless oil which was induced crystallization on addition of aqueous ethanol to afford crystals (0.15 g) of **2c**. Recrystallization from ethanol gave colorless prisms (0.10 g, 58%), mp 184.5—185°C.

Found: C, 50.42; H, 5.17; S, 11.08%. Calcd for $C_{24}H_{28}O_{12}S_2$: C, 50.33; H, 4.94; S, 11.20%.

*Selective* p-*Toluenesulfonylation of 2c.* To a solution of **2c** (61 mg) in dry pyridine (0.6 m*l*) was added *p*-toluenesulfonyl chloride (0.10 g, 4.9 molar equiv.) and the reaction mixture was kept at 30°C for 70 hr. Then the mixture was processed similarly as described in **3b** to give colorless crystals (63 mg, 81%) of **3b**, mp 206—207°C, which was identified with the compound derived from **2b** by the mixed melting point and comparing with IR spectra.

*4,6-Di*-O-*acetyl-1,5-di*-O-p-*toluenesulfonyl*-myo-*inositol (2d).* A mixture of 4,6-di-*O*-acetyl-1,2-*O*-cyclohexylidene-3,5-di-*O*-*p*-toluenesulfonyl-*myo*-inositol (**1d**)[1] (1.04 g) and 80% aqueous acetic acid (20 m*l*) was refluxed for 2 hr. The mixture was evaporated to give a slightly yellow oil, which crystallized on addition of water to give crude crystals (0.89 g). It was shown to be contaminated with the partly de-*O*-acetylated product by a tlc, then, the crude product was recrystallized two times from ethanol to afford chromatographically pure crystals (0.57 g, 63%) of **2d**, mp 178.5—180.5°C.

Found: C, 49.99; H, 4.95; S, 11.27%. Calcd for $C_{24}H_{28}O_{12}S_2$: C, 50.33; H, 4.94; S, 11.20%.

*4,6-Di*-O-*acetyl-1,3,5-tri*-O-p-*toluenesulfonyl*-myo-*inositol (3c).* To a solution of **2d** (155 mg) in dry pyridine (1.5 m*l*) was added *p*-toluenesulfonyl chloride (250 mg, 4.9 molar equiv.) and the mixture was kept at 30°C for 70 hr. Then the reaction mixture was processed similarly as described in **3b** to give crude crystals, which were recrystallized from chloroform and ethanol to afford colorless needles (187 mg, 95%) of **3c**, mp 165—167°C (after sintering at 147°C). Recrystallization from the same solvents gave an analytical sample which showed the same melting point.

Found: C, 51.28; H, 4.72; S, 12.95%. Calcd for $C_{31}H_{34}O_{14}S_3$: C, 51.23; H, 4.72; S, 13.23%.

*2,4,6-Tri*-O-*acetyl-1,3,5-tri*-O-p-*toluenesulfonyl*-myo-*inositol (4c).* A 101 mg portion of **3c** was treated with acetic anhydride (1 m*l*) and pyridine (1 m*l*) at room temperature overnight. Then the mixture was poured into ice and water to give crystals (106 mg, 99%) of **4c**, mp 178—185°C. An analytical sample was obtained by recrystallization from ethanol, colorless tiny needles, mp 181.5—183°C (after sintering at 175°C).

Found: C, 51.75; H, 4.73; S, 12.41%. Calcd for $C_{33}H_{36}O_{15}S_3$: C, 51.54; H, 4.72; S, 12.49%.

*5-O-Acetyl-1,4,6-tri*-O-p-*toluenesulfonyl*-myo-*inositol (2e).* A mixture of 5-*O*-acetyl-1,2-*O*-cyclohexylidene-3,4,6-tri-*O*-*p*-

toluenesulfonyl-*myo*-inositol (**1e**)[1] (1.0 g) and 80% aqueous acetic acid (50 m*l*) was refluxed for 2 hr. After cooling, the resulting crystals were collected by filtration and washed with ethanol to yield colorless granular crystals (0.79 g, 85%) of **2e**, mp 222.5—224.5°C. Recrystallization from pyridine and ethanol gave an analytical sample, colorless prisms, mp 223—225°C.

Found: C, 51.30; H, 5.19; S, 14.58%. Calcd for $C_{29}H_{32}O_{13}S_3$: C, 50.86; H, 4.72; S, 14.04%.

*5*-O-*Acetyl-1,3,4,6-tetra*-O-p-*toluenesulfonyl*-myo-*inositol (3d)*. To a solution of **2e** (0.25 g) in dry pyridine (3 m*l*) was added *p*-toluenesulfonyl chloride (0.20 g, 3 molar equiv.) and the mixture was kept at 30°C for 4 days. After heating at 80°C for 1 hr, the reaction mixture was poured into ice and water and the resulting oily product was extracted with chloroform (25 m*l*). The extract was washed with water, dried over anhydrous sodium sulfate and then, evaporated to give a colorless oil which crystallized on addition of ethanol. The crude crystals were shown to be consisted of two major components by a tlc: **3d** and de-*O*-acetylated product, probably 1,3,4,6-tetra-*O*-*p*-toluenesulfonyl-*myo*-inositol. Fractional crystallization from ethanol afforded colorless plates (0.13 g, 42%) of **3d**, mp 194.5—199.5°C. An analytical sample was obtained by recrystallization from chloroform and ethanol, mp 200—201°C.

Found: C, 51.67; H, 4.62; S, 15.33%. Calcd for $C_{36}H_{38}O_{15}S_4$: C, 51.53; H, 4.57; S, 15.29%.

*2,5-Di*-O-*acetyl-1,3,4,6-tetra*-O-p-*toluenesulfonyl*-myo-*inositol (4d)*. Acetylation of **3d** (33 mg) with acetic anhydride (1 m*l*) and pyridine (1 m*l*) at room temperature gave colorless crystals (28 mg, 74%) of **4d**, mp 205—207°C. Recrystallization from chloroform and ethanol afforded an analytical sample, mp 207—209°C. PMR: $\tau$ 5.55 (2, q, H-1,3, $J$=3 and 8 Hz), $\tau$ 4.55 (1, t, H-2, $J$=3 Hz).

Found: C, 51.75; H, 4.75; S, 14.31%. Calcd for $C_{38}H_{40}O_{16}S_4$: C, 51.82; H, 4.58; S, 14.57%.

*6*-O-*Acetyl-1,4,5-tri*-O-p-*toluenesulfonyl*-myo-*inositol (2f)*. A mixture of 4-*O*-acetyl-1,2-*O*-cyclohexylidene-3,5,6-tri-*O*-*p*-toluenesulfonyl-*myo*-inositol (**1f**)[1] (1.39 g) and 80% aqueous acetic acid (100 m*l*) was refluxed for 2.5 hr. Then the solution was evaporated to give a crystalline residue. Trituration with ethanol gave crystals (1.16 g, 93%) of **2f**, mp 197—200°C (after melting and resolidifying at 162—168°C). Recrystallization from chloroform and ethanol afforded an analytical sample colorless, needles, mp 202—204°C.

Found: C, 50.90; H, 4.70; S, 13.58%. Calcd for $C_{29}H_{32}O_{13}S_3$: C, 50.86; H, 4.72; S, 14.04%.

*6*-O-*Acetyl-1,3,4,5-tetra*-O-p-*toluenesulfonyl*-myo-*inositol (3e)*. To a solution of **2f** (0.30 g) in dry pyridine (3 m*l*) was added *p*-toluenesulfonyl chloride (0.27 g, 3.4 molar equiv.) and the mixture was kept at 30°C for 4 days. Then the reaction mixture was processed similarly as described in **3a** to give crude crystals (0.37 g, 99%) of **3e**, mp 197—203°C (after sintering and resolidifying at 170—180°C). Recrystallization from chloroform and ethanol afforded an analytical sample, colorless rods, mp 208—210.5°C.

Found: C, 51.30; H, 4.53; S, 15.55%. Calcd for $C_{36}H_{38}O_{15}S_4$: C, 51.53; H, 4.57; S, 15.29%.

*2,6-Di*-O-*acetyl-1,3,4,5-tetra*-O-p-*toluenesulfonyl*-myo-*inositol (4e)*. A 0.15 g portion of **3e** was treated with acetic anhydride (1 m*l*) and pyridine (1 m*l*) at room temperature gave crystals (0.15 g, 95%) of **4e**, mp 99—112°C. Recrystallization from ethyl acetate and ethanol gave an analytical sample, colorless needles (0.09 g), mp 180—194°C (after melting and resolidifying at 130—140°C). PMR $\tau$: 4.58 (1, t, H-2, $J$=3 Hz), $\tau$ 4.54 (1, t, H-6, $J$=9 Hz).

Found: C, 51.92; H, 4.46; S, 15.48%. Calcd for $C_{38}H_{40}O_{16}S_4$: C, 51.82; H, 4.58; S, 14.57%.

*1,3,4,5,6-Penta*-O-p-*toluenesulfonyl*-myo-*inositol (3f)*. To a solution of 1,4,5,6-tetra-*O*-*p*-toluenesulfonyl-*myo*-inositol (**2g**)[1] (0.15 g) in dry pyridine (1.5 m*l*) was added *p*-toluenesulfonyl chloride (0.25 g, *ca.* 7 molar equiv.) and the mixture was kept at 30°C for 2 weeks. Then the reaction mixture was processed similarly as described in **3d** to give colorless crystals (0.12 g, 63%) of **3f**, mp 184—185°C. An analytical sample was obtained by recrystallization from chloroform and ethanol, colorless granular crystals, which showed the same melting point.

Found: C, 51.79; H, 4.53; S, 17.06%. Calcd for $C_{41}H_{42}O_{16}S_5$: C, 51.77; H, 4.46; S, 16.85%.

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