BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2593—2597 (1972)

Aminocyclitols. XXVIII. Bromination of Inosamines and Inosadiamines

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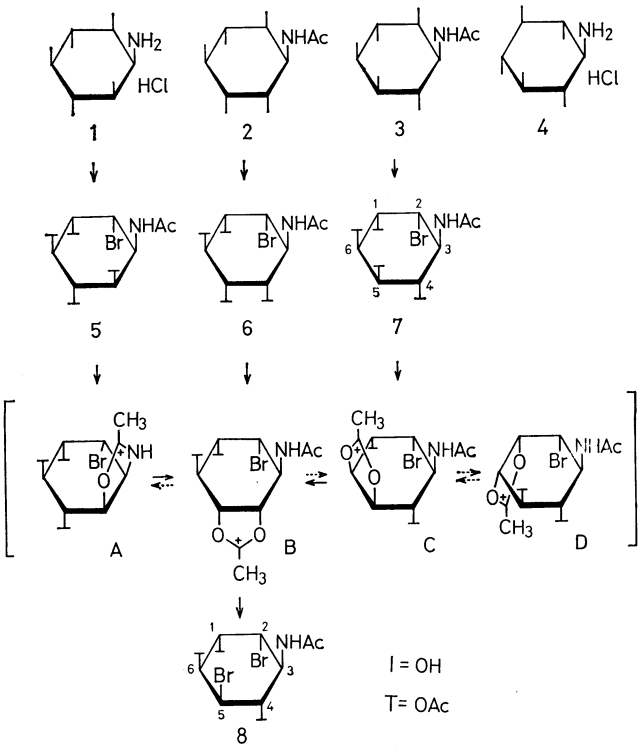
(Received January 22, 1972)

Bromination of four inosamines (*myo*-2 (**1**), *chiro*-1 (**2**), *muco*-1 (**3**), and *scyllo* (**4**)) and three inosadiamines (*neo*-1,4 (**11**), *muco*-1,5 (**14a,b**), and *muco*-1,4 (**19**)) with acetyl bromide and acetic anhydride in a sealed tube at 130—160°C has been studied. 2,5-Dibromo-2,5-dideoxy-*chiro*-inosamine-3 tetraacetate (**8**), was obtained from **1**, **2**, and **3**, and, as a monobromide, only 2-bromo-2-deoxy-*chiro*-inosamine-3 pentaacetate (**7**) could be isolated from the bromination product of **3**. From **11**, monobromide (**12**) and dibromide (**13**) were obtained. From **14a** or **14b**, 2-bromo-2-deoxy-*chiro*-inosadiamine-3,5 pentaacetate (**15**) was obtained, and, under a more drastic condition, **15** was further brominated to afford 1,5-dibromo-1,5-dideoxy-*chiro*-inosadiamine-2,4 tetraacetate (**16**). The bromo compounds so obtained were converted into the corresponding deoxy or dideoxy derivatives by hydrogenolysis. All the structures of the new compounds have been confirmed on the basis of proton magnetic resonance (PMR) spectroscopy using their acetyl derivatives. Considering from the structures of the bromides, a mechanism of a bromination reaction has been proposed.

In connection with the previous paper,[1] we wish to report the bromination of inosamines and inosadiamines with acetyl bromide and acetic anhydride at high temperature. Bromo-deoxyinosamines and -deoxy-inosadiamines are useful precursors for a preparation of the corresponding deoxy derivatives. We had already described the facile synthesis of 2-deoxy-streptamine from the key intermediary compound, 2-bromo-2-deoxystreptamine, which was obtained in a high yield by bromination of *myo*-inosadiamine-1,3.[2] In all the cases studies so far,[1-3] the hydroxyl groups vicinal and in *cis* position to an amino or acetamido group in aminocyclitols are preferentially displaced by bromine in a mixture of acetyl bromide and acetic anhydride. However, in the present report, it has been shown that, when there is a possibility of a displacement of more than one hydroxyl groups by bromine, a bromine atom was previously introduced in aminocyclitols following observed rule, whereas, the displacement of the second hydroxyl group was much influenced by a stereochemical and electronic environments.

When *myo*-inosamine-2 hydrochloride (**1**)[4] was treated with acetyl bromide in a sealed tube at 155—160°C for 8 hr, followed by acetylation, dibromo-dideoxyinosamine tetraacetate (**8**) was obtained mainly as a sole crystalline product in 32% yield. On treatment with acetyl bromide similarly as described above, both *N*-acetyl-*chiro*-inosamine-1 (**2**) and *N*-acetyl-*muco*-



1) T. Suami, S. Ogawa, and H. Sano, This Bulletin, **43**, 1843 (1970).

2) T. Suami, F. W. Lichtenthaler, S. Ogawa, Y. Nakashima, and H. Sano, *ibid.*, **41**, 1014 (1968).

3) T. Suami, S. Ogawa, Y. Nakashima, and H. Sano, *ibid.*, **40**, 2958 (1967).

4) H. E. Carter, R. K. Clark, B. Lytle, and G. E. McCasland, *J. Biol. Chem.*, **175**, 684 (1948).

inosamine-1 (**3**)[5] gave **8** in 16 and 11% yield, respectively. While, the reaction of **3** with acetyl bromide at 135—140°C for 4 hr gave bromo-deoxyinosamine pentaacetate (**7**) in 45% yield, along with a small amount of **8**. Hydrogenolysis of **7** and **8** in the presence of Amberlite IR-4B (OH^-) and Raney nickel T-4[6] afforded deoxy- (**9**) and dideoxy-inosamine (**10**) in 65 and 56% yield, respectively.

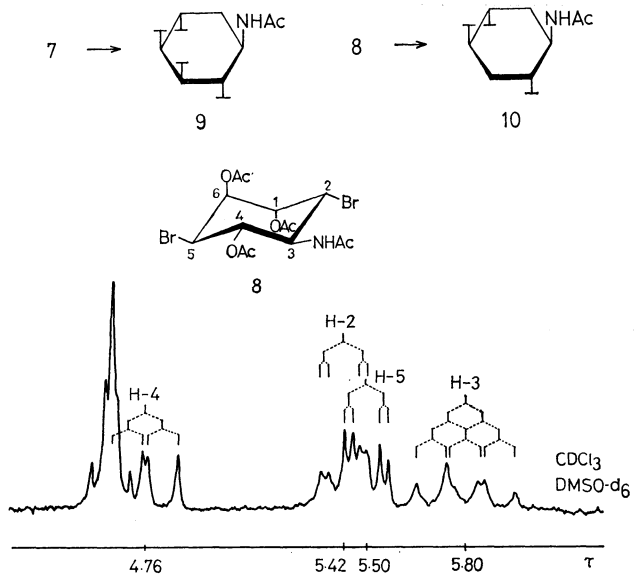


Fig. 1. Partial PMR spectrum of 2,5-dibromo-2,5-dideoxy-*chiro*-inosamine-3 tetraacetate (**8**) in a mixture of $CDCl_3$ and DMSO-d_6 at 100 MHz.

The structural elucidation of **7**, **8**, **9**, and **10** was carried out by means of the PMR spectroscopy. The PMR spectrum of **8** in a mixture of $CDCl_3$ and dimethylsulfoxide-d_6 (DMSO-d_6) at 100 MHz (Fig. 1) was in good accord with the structure, 2,5-dibromo-2,5-dideoxy-*chiro*-inosamine-3 tetraacetate. The wide sextet at τ 5.80 (J=9.5, 11.0, and 11.0 Hz) was assigned to C-3 proton that has two vicinal axial protons and indicated an axial-axial-axial arrangement for H-2, H-3, and H-4. Both H-2 and H-5 appeared as a quartet at τ 5.42 and 5.50, showing $J_{2,3}=J_{4,5}=11.0$ Hz and $J_{1,2}=J_{5,6}=2.0$ Hz, which was indicative of an equatorial-equatorial arrangement for H-1 and H-6. The wide doublet of doublet at τ 4.76 (J=9.5 and 11.0 Hz) was attributed to C-4 proton which demonstrated that one of the two bromine atoms is located at C-5. While, in the spectrum measured in $CDCl_3$, four acetyl methyl protons appeared at τ 7.78, 7.80, 7.88, and 8.00, which were assigned to an axial, an axial and an equatorial acetoxy, and an equatorial acetamido group, respectively.[7] Furthermore, the PMR spectrum of **10** in $CDCl_3$ at 100 MHz showed an octet at τ 5.75 which was assignable to H-3, since on deuteration it collapsed to a sextet. This result again indicated a diaxial arrangement for H-3 and H-4 and another bromine atom should attach equatorially to C-2. Therefore, the proposed structure of **8** was confirmed evidently.

In the PMR spectrum of **7** in $CDCl_3$, signals due to two protons attached to the carbon atoms having the acetamido group and bromine atom appeared around τ 5.50 as a complex multiplet, which probably suggested that they are located on a vicinal position. The acetyl methyl protons appeared as fine singlets at τ 7.83, 7.85, 7.92, 7.98, and 8.04, which were attributed to an axial, an axial, an equatorial and an equatorial acetoxy, and an equatorial acetamido group, respectively. Since **7** might be considered as the intermediary compound for **8** in the bromination reaction, its structure, taking an epimerization into account, should be either 2-bromo-2-deoxy-*chiro*-inosamine-3 or -*muco*-inosamine-3 pentaacetate. The latter might be likely the intermediary bromo-deoxy compound (**6**) from **2**, however, the formation of **6** could not be observed on bromination of **2** under a mild condition. Consequently, **7** was assigned to the former structure.

According to the results obtained, the mechanism of the bromination reaction might be proposed as follows. Initially, cyclic oxazolinium ions are formed between *cis* arranged acetamido and acetoxy groups by a front-side participation reaction.[8] Then they are opened by S_N2 attack of bromide ion to produce the bromo-deoxy compound (**5**, **6**, and **7**). Then, cyclic acetoxonium or oxazolinium ions are formed between remaining *cis* arranged groups and the cyclic ions are cleaved by nucleophlic attack of bromide ions or *trans*-situated adjacent groups.[9] The existence of an equilibrium (A⇄B⇄C⇄D) resulted from a rearrangement of a cyclic intermediary ion may be substantiated by the formation of the same dibromide **8** from **1**, **2**, and **3**, which additionally indicated that a bromide ion can only attack them in the most favorable configuration (B) satisfying the stereochemical and electronic requirement to afford one dibromide predominantly. For instance, in the similar halogenation reaction of cyclitols studied so far,[10] a vicinal dihalide has never been obtained.

Attempted bromination of *scyllo*-inosamine hydrochloride (**4**)[4] under a vigorous condition failed. Thus, even though the reaction temperature was raised up to 180°C, **4** was recovered as the hexaacetate from the reaction mixture. This result, like in the case of streptamine,[2] demonstrated that a formation of an intermediary oxazolinium ion initiates a nucleophilic attack of bromide ion.

Then the bromination of readily available *N*,*N*'-diacetyl-*neo*-inosadiamine-1,4 (**11**)[11] was attempted. On similar treatment with acetyl bromide and acetic anhydride (2: 1) at 145—150°C for 7 hr, **11** gave the acetates of bromodeoxyinosadiamine (**12**) and dibromo-

5) T. Suami and S. Ogawa, This Bulletin, **37**, 1238 (1964); T. Suami, F. W. Lichtenthaler, and S. Ogawa, *ibid.*, **39**, 170 (1966).

6) S. Nishimura, *ibid.* **32** 61 (1959).

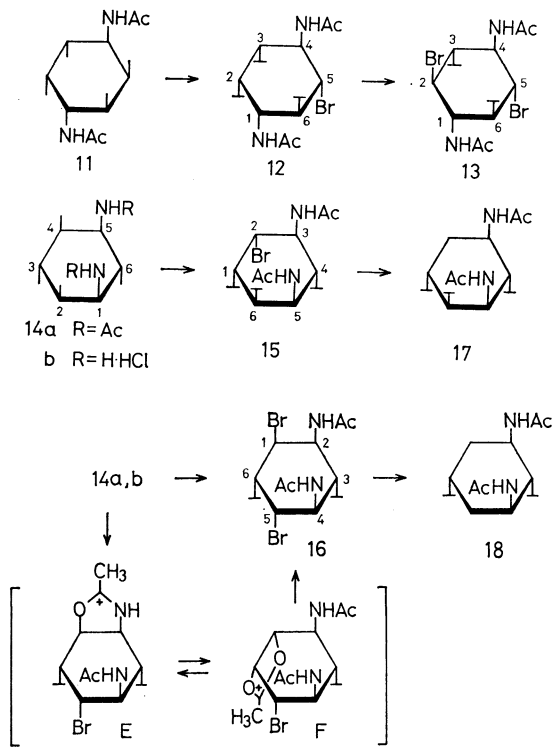
7) F. W. Lichtenthaler and P. Emig, *Carbohyd. Res.*, **7**, 121 (1968).

8) R. Boschan and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 4921 (1956).

9) S. J. Angyal, P. A. J. Gorin, and M. E. Pitman, *J. Chem. Soc.*, **1965**, 1807; H, Paulsen and C-P. Herold, *Chem. Ber.*, **104**, 1311 (1971).

10) G. E. McCasland, *Advans. Carbohyd. Chem.*, **20**, 11 (1965).

11) F. W. Lichtenthaler and H. O. L. Fischer, *J. Amer. Chem. Soc.*, **83**, 2005 (1961).



dideoxyinosadiamine (**13**) in a yield of 29 and 14%, respectively. By analogy with the proposed reaction mechanism, the structure of **12** and **13** may be deduced to be 5-bromo-5-deoxy-*myo*-inosadiamine-1,4 pentaacetate and 2,5-dibromo-2,5-dideoxy-*scyllo*-inosadiamine-1,4 tetraacetate, respectively. In the PMR spectrum of **12**, the signal due to one axial acetoxy group diminished and this accounted for one of the axial hydroxyl groups in **11** being replaced by bromine atom. The PMR spectrum of **13** gave two singlets in τ 8 region, indicating the symmetrical configuration of **13**. These PMR spectroscopic evidences are consistent with the proposed structures of **12** and **13**.

Secondarily, *N,N'*-diacetyl-*muco*-inosadiamine-1,5 (**14a**)[5] was subjected to the bromination reaction. It gave the bromo-deoxyinosadiamine pentaacetate (**15**) in 33% yield, on treatment with acetyl bromide and acetic anhydride (2: 1) at 140°C for 3 hr. While, when the same reaction was conducted at 145—150°C for 6 hr, the dibromo-dideoxyinosadiamine tetraacetate (**16**) was obtained mainly in 32% yield. From *muco*-inosadiamine-1,5 dihydrochloride (**14b**),[5] **16** was also obtained in 31% yield by a drastic condition. Hydrogenolysis of **15** and **16** afforded the corresponding deoxy- (**17**) and dideoxy-derivative (**18**) in 85 and 72% yield, respectively.

On the basis of the following PMR spectroscopic data, the structures of **15** and **16** were assigned to 2-bromo-2-deoxy-*chiro*-inosadiamine-3,5 pentaacetate and 1,5-dibromo-1,5-dideoxy-*chiro*-inosadiamine-2,4 tetraacetate, respectively, and **17** and **18** were assigned to the corresponding deoxy- and dideoxy-compound. The PMR spectrum of **15** in DMSO-d_6 revealed two singlets in an axial region of an acetoxy group, hence, one axial hydroxyl group in **14** must be replaced by bromine atom. Had the bromine atom been located at

Table 1. Chemical shifts of acetyl methyl protons[a]

Compound	Solvent	Acetoxy ax.	Acetoxy eq.	Acetamido eq.
7	A	7.75 7.83	7.93 7.99	8.00
	B	7.80 7.85	8.05 8.09	8.20
8[c]	A	7.78 7.80	7.88	8.00
	B	7.82[b]	7.98	8.20
9	A	7.83 7.85	7.92 7.98	8.04
10[c]	A	7.89 7.92	7.93	8.05
12	B	7.82	7.96 8.13	8.16 8.20
13	B		8.00[b]	8.20[b]
15	B	7.81 7.85	8.08	8.21[b]
16	B	7.80	8.07	8.13 8.20
17	B	7.85[b]	8.08	8.18 8.23
18	B	7.91	8.10	8.25[b]
neo-Inosadiamine-1,4 hexaacetate	B	7.89[b]	8.11[b]	8.25[b]
muco-Inosadiamine-1,5 hexaacetate[5]	B	7.87 7.90[b]	8.08	8.21[b]

a) PMR spectra were measured at 60 MHz, unless otherwise noted. Solvents were: A $CDCl_3$, B DMSO-d_6. The peak positions are given in τ-values.
b) Signal due to two equivalent methyl protons.
c) Measured at 100 MHz.

C-3, both **15** and **17** should have a symmetrical structure and their PMR spectra had to be simpler than those observed herein. Nonequivalence of the signals due to two axial acetoxy groups in **15** and two acetamido groups in **17** evidently indicated their unsymmetrical structures and the location of the bromine atom at C-2 (C-4) of **14**. The PMR spectrum of **18** showed three singlets (1: 1: 2) at τ 8 region, that were assigned to an axial and an equatorial acetoxy, and two equatorial acetamido groups, respectively. The signals due to ring protons were amenable to the first order analysis, that is, a narrow quintet at τ 4.97 (J=2.5 Hz) and a wide triplet at τ 5.93 (J=10.0 Hz) were readily assigned to H-6 and H-3 proton, respectively. A two protons octet at τ 5.73 (J=11.5, 10.0, 10.0, and 6.5 Hz) assignable to two equivalent protons at C-2 and C-4 showed that two acetamido groups were equivalent each other and adjacent to the equatorial acetoxy group and methylene protons. On the other hand, in the PMR spectrum of **16**, two singlets at τ 8.13 and 8.20 were assigned to the equatorial two acetamido groups. The presence of nonequivalent acetamido groups indicated that the arrangement of two bromine atoms adjacent to them should be 1,3-*trans* position. Therefore, the configuration of the bromine atom in **15** only remained equivocal. Since, in the PMR spectrum of **15** in DMSO-d_6, the signals corresponding to the ring protons attached to the carbon atoms having the acetamido groups and bromine atom appeared as a complex multiplet at τ 5.5—6.0, the configuration of the bromine

atom could not be determined by the first order analysis of them. However, by analogy with the proposed reaction mechanism of the bromination reaction, it might be reasonable that the cyclic oxazolinium ion initially formed is opened by a rearside attack of bromide ion and therefore the bromine atom in **15** is in *trans* configuration to the neighboring acetamido group. Then the second oxazolinium ion (E) seemed to be attacked by the adjacent *trans*-situated acetoxy group to produce another ion (F), which only undergoes nucleophilic attack of bromide ion to give **16**.

Bromination of *muco*-inosadiamine-1,4 dihydrochloride (**19**)[12] gave a complex mixture (at least four components were detected by tlc analysis) and no further isolation has been attempted.

Experimental

Melting points were determined on a Mitamura Riken micro hot stage and are uncorrected. PMR spectra were measured with a Varian A-60D (60 MHz) or HA-100D (100 MHz) spectrometer with tetramethylsilane as internal standard. IR spectra were recorded in KBr disks with Jasco IR-E infrared spectrophotometer. Tlc was performed on silica gel plates (Wakogel B-10) using methyl ethyl ketone–toluene (1 : 5 or 1 : 10) as the solvent system. The compounds were detected by heating with 30% sulfric acid. Evaporations were performed below 50°C under diminished pressure. Whenever pyridine was employed in a reaction, the residual pyridine was removed by repeated codistillation with dry toluene. All the compounds described in this paper are racemic.

N-*Acetyl*-chiro-*inosamine-1 (2).* *chiro*-Inosamine-1 hexaacetate[13] (3.0 g) was treated with methanol (20 m*l*), saturated with ammonia at 0—5°C, overnight at room temperature. Then the mixture was evaporated and the residue was recrystallized from 80% aqueous methanol to give colorless prisms (1.42 g, 41%) of **2**, mp 225—226°C (a transition was observed at 168—169°C). IR: 1640 and 1560 cm^{-1} (NHAc).

Found: C, 43.43; H, 6.84; N, 6.33%. Calcd for $C_8H_{15}NO_6$: C, 43.56; H, 7.06; N, 6.17%.

2-Bromo-2-deoxy-chiro-*inosamine-3 Pentaacetate (7).* A mixture of *N*-acetyl-*muco*-inosamine-1 (**3**)[5] (100 mg) and acetyl bromide (5 m*l*) was heated in a sealed tube at 135—140°C for 4 hr. After cooling to room temperature, the reaction mixture obtained from six sealed tubes was poured into ethanol (200 m*l*) and evaporated to dryness. The residue was treated with acetic anhydride (15 m*l*) and pyridine (15 m*l*) overnight at room temperature. Then an insoluble material was filtered off and the filtrate was evaporated to give crude crystals, which was recrystallized from ethanol to give crystals (602 mg, 45%) of **7**, mp 188—189°C. IR: 1750 (OAc), 1660 and 1575 cm^{-1} (NHAc).

Found: C, 42.73; H, 5.17; N, 3.45; Br, 18.04%. Calcd for $C_{16}H_{22}NO_9Br$: C, 42.50; H, 4.87; N, 3.10; Br, 17.70%.

2,5-Dibromo-2,5-dideoxy-chiro-*inosamine-3 Tetraacetate (8).* (a) A mixture of *myo*-inosamine-2 hydrochloride (**1**)[4] (150mg) and acetyl bromide (5 m*l*) was heated in a sealed tube at 155—160°C for 8 hr. The reaction mixture obtained from five sealed tubes was processed similarly as described under the preparation of **7**. The crude product was chromatographed on a column of activated aluminum oxide with chloroform. The eluates were evaporated to give an oily product which crystallized upon addition of ethanol to give crystals (615 mg, 32%) of **8**, mp 240—245°C. Recrystallization from ethanol afforded colorless needles (590 mg), mp 247—248°C. IR: 3240 (NH), 1755 (OAc), 1660 and 1580 cm^{-1} (NHAc).

Found: C, 35.72; H, 4.43; N, 3.08; Br, 33.52%. Calcd for $C_{14}H_{19}NO_7Br_2$: C, 35.56; H, 4.02; N, 2.96; Br, 33.90%.

(b) A mixture of **2** (220 mg) and acetyl bromide (4 m*l*) was heated in a sealed tube at 145—150°C for 6 hr. The reaction mixture obtained from three sealed tubes was processed as described in (a) to give crystals (223 mg, 16%) of **8**, mp 243—244°C.

(c) A mixture of **3** (100 mg) and acetyl bromide (5 m*l*) was heated in a sealed tube at 155—160°C for 8 hr. The reaction mixture obtained from ten sealed tubes was processed as described in (a) to give crystals (113 mg, 11%) of **8**, mp 244—245°C.

(d) Compound **2** was treated with acetyl bromide similarly as described under the preparation of **7**. *chiro*-Inosamine-1 hexaacetate was obtained in a high yield and tlc of the resulting reaction product showed one main component (*chiro*-inosamine-1 hexaacetate) along with two minor ones, one of which was shown to be corresponding to a reference sample of **8**. The unidentified component was considered to be the bromo-deoxy compound probably.

2-Deoxy-chiro-*inosamine-3 Pentaacetate (9).* A solution of **7** (350 mg) in 50% aqueous ethanol (20 m*l*) was catalytically hydrogenated in a Parr shaker type apparatus (4 kg/cm^2 of the initial hydrogen pressure) in the presence of Raney nickel T-4[6] and Amberlite IR-4B (OH^-) at 40—45°C for 20 hr. The catalyst and resin were removed by filtration and the filtrate was evaporated to give crude crystals (206 mg) which was recrystallized from ethanol to afford colorless needles (189 mg, 65%) of **9**, mp 208—209°C. IR: 1750 (OAc), 1660, 1640, and 1585 cm^{-1} (NHAc).

Found: C, 51.80; H, 6.29; N, 3.84%. Calcd for $C_{16}H_{23}NO_9$: C, 51.47; H, 6.21; N, 3.75%.

2,5-Dideoxy-chiro-*inosamine-3 Tetraacetate (10).* Compound **8** (297 mg) was hydrogenated similarly as described under the preparation of **9**. The crude crystals were recrystallized from ethanol to afford colorless crystals (110 mg 56%) of **10**, mp 149—151°C. IR: 1745 (OAc), 1640, and 1570 cm^{-1} (NHAc).

Found: C, 53.55; H, 7.24; N, 4.49%. Calcd for $C_{14}H_{23}NO_7$: C, 53.10; H, 7.26; N, 4.42%.

5-Bromo-5-deoxy-myo-*inosadiamine-1,4 Pentaacetate (12) and 2,5-Dibromo-2,5-dideoxy*-scyllo-*inosadiamine-1,4 Tetraacetate (13).* A mixture of *N,N'*-diacetyl-*neo*-inosadiamine-1,4 (**11**) (mp 324—326°C, lit,[11] 325—328°C) (104 mg), acetyl bromide (5 m*l*) and acetic anhydride (2 m*l*) was heated in a sealed tube at 145—150°C for 7 hr. Then the brown reaction mixture obtained from two sealed tubes was poured into cold ethanol (50 m*l*) and allowed to stand at room temperature overnight. The resulting precipitates were collected, dried and treated with acetic anhydride (3 m*l*) and pyridine (3 m*l*) overnight at room temperature. The acetate (13 mg) so obtained was identified with an authentic sample of *neo*-inosadiamine-1,4 hexaacetate[11] by IR spectral comparison. The alcoholic mother liquor was evaporated to dryness and the residue was acetylated as described above to give an oily product which crystallized upon addition of ethanol to afford crystals (54 mg, 15%) of **13**, mp 268—269°C. Recrystallization from ethanol gave an analytical sample of **13**, mp 272—273°C (decomp.). IR: 1750 (OAc), 1660, and 1540 cm^{-1} (NHAc).

Found: C, 35.78; H, 4.51; N, 6.11; Br, 33.31%. Calcd

12) T. Suami, F. W. Lichtenthaler, and S. Ogawa, This Bulletin, **40**, 1488 (1967).

13) T. Suami, S. Ogawa, and M. Uchida, *ibid.*, **43**, 3577 (1970).

for $C_{14}H_{20}N_2O_6Br_2$: C, 35.62; H, 4.27; N, 5.94; Br, 33.85%.

The mother liquor of **13** was condensed to a small volume and settled in a refrigerator overnight to give crystals (101 mg, 29%) of **12**, mp 257—259°C (decomp.). Recrystallization from ethanol gave colorless plates of **12**, mp 261—262°C (decomp.). IR: 1760 (OAc), 1655 and 1555 cm^{-1} (NHAc).

Found: C, 43.05; H, 5.64; N, 6.07; Br, 17.44%. Calcd for $C_{16}H_{23}N_2O_8Br$: C, 42.59; H, 5.14; N, 6.21; Br, 17.71%.

1,5-Dibromo-1,5-dideoxy-chiro-*inosadiamine-2,4 Tetraacetate (16).* (a) A mixture of *N,N'*-diacetyl-*muco*-inosadiamine-1,5 (**14a**)[5] (250 mg), acetyl bromide (4 m*l*) and acetic anhydride (2 m*l*) was heated in a sealed tube at 145—150°C for 6.5 hr. After keeping in a refrigerator overnight, the tube was opened carefully and the resulting precipitates were collected by filtration. The crude crystals were recrystallized from ethanol to afford crystals (420 mg, 32%) of **16**, mp 228—229°C (decomp.). IR: 1755 (OAc), 1660 and 1540 cm^{-1} (NHAc).

Found: C, 35.85; H, 4.53; N, 5.96; Br, 33.75%. Calcd for $C_{14}H_{20}N_2O_6Br_2$: C, 35.62; H, 4.27; N, 5.94; Br, 33.85%.

The filtrate of the reaction mixture was processed similarly as described under the preparation of **7** to give an oily product. Tlc showed a small proportion of a faster moving component along with **16** and *muco*-inosadiamine hexaacetate.[5]

(b) A mixture of *muco*-inosadiamine-1,5 dihydrochloride (**14b**)[5] (391 mg), acetyl bromide (4 m*l*) and acetic anhydride (2 m*l*) was heated in a sealed tube at 145—150°C for 6.5 hr. Then the reaction mixture was processed similarly as described in (a) to give crystals (226 mg, 31%) of **16**, mp 227—231°C (decomp.).

2-Bromo-2-deoxy-chiro-*inosadiamine-3,5 Pentaacetate (15).* A mixture of **14a** (209 mg), acetyl bromide (4 m*l*) and acetic anhydride (2 m*l*) was heated in a sealed tube at 140°C for 3 hr. After cooling to room temperature, the tube was opened and the precipitates were collected by filtration. Tlc of the reaction solution showed one main component along with one minor one, corresponding to a reference sample of **16**. The crude crystals were fractionally crystallized from ethanol to give crystals (104 mg, 29%) of **15**, mp 235—236°C, and crystals (15 mg, 4%) of **16**.

Found: C, 42.53; H, 5.30; N, 6.24; Br, 18.05%. Calcd for $C_{16}H_{23}N_2O_8Br$: C, 42.59; H, 5.14; N, 6.21; Br, 17.71%.

2-Deoxy-chiro-*inosadiamine-3,5 Pentaacetate (17).* Compound **15** (152 mg) was hydrogenated in 90% aqueous ethanol (30 m*l*) similarly as described under the preparation of **9**. The crude product was recrystallized from aqueous ethanol to give crystals (90 mg, 72%) of **17**, mp 290—293°C. IR: 1755 (OAc), 1650 and 1555 cm^{-1} (NHAc).

Found: C, 51.68; H, 6.74; N, 7.37%. Calcd for $C_{16}H_{24}N_2O_8$: C, 51.60; H, 6.50; N, 7.52%.

1,5-Dideoxy-chiro-*inosadiamine-2,4 Tetraacetate (18).* Compound **16** (675 mg) was hydrogenated similarly as described under the preparation of **17**. The crude crystals were recrystallized from ethanol to give colorless crystals (381 mg, 85%) of **18**, mp 260—262°C. IR: 1745 (OAc), 1660 and 1560 cm^{-1} (NHAc).

Found: C, 53.60; H, 7.29; N, 9.24%. Calcd for $C_{14}H_{22}N_2O_6$: C, 53.49; H, 7.05; N, 8.91%.

The authors are grateful to Professor Sumio Umezawa for his kind advice, to Mr. Saburo Nakada for his elementary analyses, and to Messrs. Hayashi Uchino, Yasutaro Yasuda, and Toshihide Ikeda for their assistance in the preparative experiments. The financial support from the Ministry of Education for this work is gratefully acknowledged.