Stereochemistry of Nucleophilic Addition Reactions. 10.[1] Preparation of 2-*C*-Diacetylmethyl and 2-*C*-Acetylmethyl Derivatives with the *Altro*, *Gluco*, and *Manno* Configuration from Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-3-nitro-α-D-*erythro*-hex-2-enopyranoside

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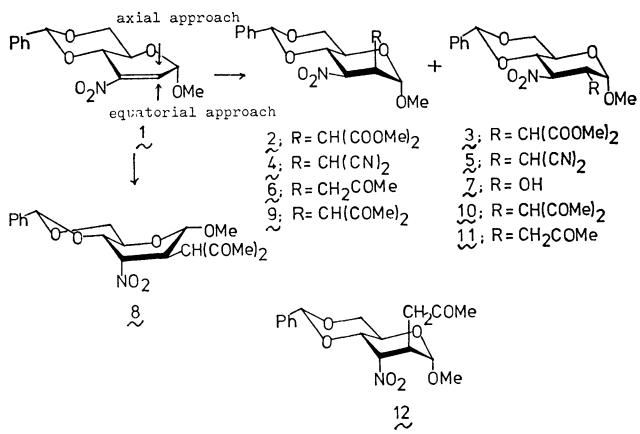
Reaction of the title compound with acetylacetone in the presence of a catalytic amount of sodium hydroxide afforded the 2-*C*-diacetylmethyl and 2-*C*-acetylmethyl derivatives having the *altro*, *gluco*, and *manno* configurations. The 2-*C*-diacetylmethyl derivative with the *altro* configuration exceptionally exists in a skew boat form. The product ratio depends on solvent and the amount of THF.

The reaction of an α-nitro olefin with active methylene compounds predominantly affords a thermodynamically more stable product, because of its reversible character.[2] However, it has been found that phase transfer catalyzed, heterogeneous reactions of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-α-D-*erythro*-hex-2-enopyranoside (**1**) with active methylene compounds give the thermodynamically less stable mannopyranoside in good yields.[3] These results prompted us to investigate a similar reaction in a homogeneous system. In a preliminary communication,[4] we reported the preparation of the altropyranoside **8** from **1** and acetylacetone; in spite of the high tendency of the nitro group to occupy an equatorial orientation in nitro sugars,[5] the nitro group of **8** is orientated axially. Studies have been carried out in order to clarify kinetically controlled protonation. In this paper, we report the preparation of 2-*C*-diacetylmethyl and 2-*C*-acetylmethyl derivatives having the *altro*, *gluco*, and *manno* configuration as well as solvent effects.

Results and Discussion

Treatment of **1** (0.1 mmol) with dimethyl malonate (0.11 mmol) in THF (2 ml) in the presence of 0.05 M (1 M=1 mol dm^{-3}) NaOH (0.2 ml) for 1 h at room temperature resulted in the recovery of **1**, while in the presence of 5.0 M NaOH (0.2 ml) it afforded a complex mixture, from which isolation of the adduct **2** or **3** was unsuccessful. A similar reaction, however, with 0.2 M NaOH (0.1 ml) predominantly afforded the mannopyranoside **2**; similar results were obtained in the reaction with diethyl malonate in the heterogeneous system.[3] A similar reaction of **1** with malononitrile afforded mannopyranoside **4** and glucopyranoside **5** in a 9 : 1 ratio, the highest ratio being 1 : 1.3 in the heterogeneous reaction.[3]

Although in the heterogeneous system the reaction of **1** with acetone resulted in the introduction of a hydroxyl group instead of an acetylmethyl group at the C-2 position, homogeneous reaction afforded the desired



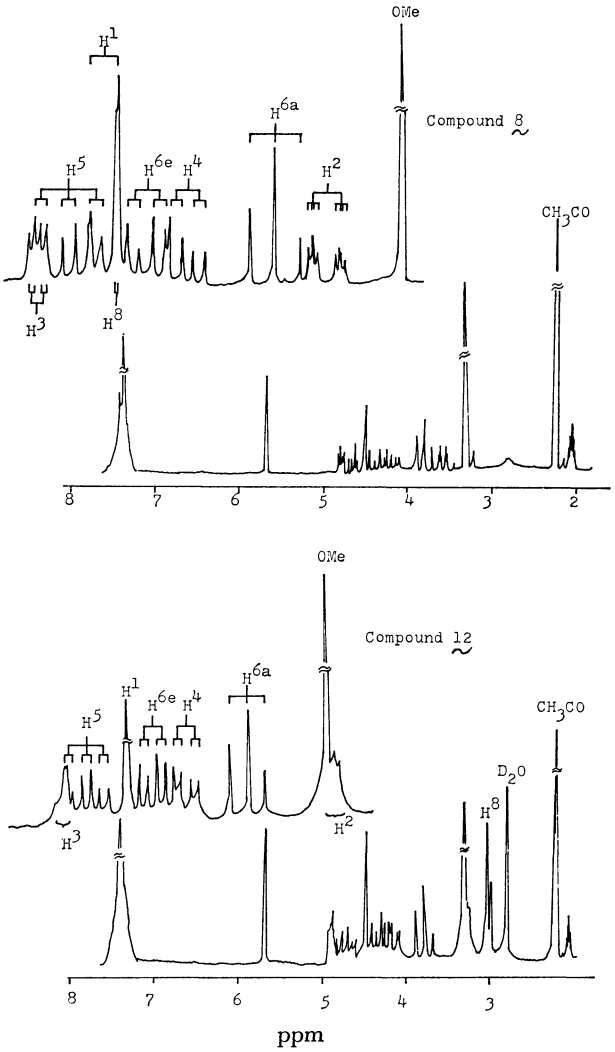


Fig. 1. The NMR spectra of the altropyranoside **8** and **12** (in acetone-d_6, 100 MHz).

TABLE 1. NMR SPECTRA IN $CDCl_3$ (Me_4Si AS INTERNAL STANDARD) AT 100 MHz

Compd	Chemical shifts, δ/ppm						First-order coupling constants, J/Hz				
	H^1	H^2	H^3	H^4	PhCH	H^{6} a)	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{2,8}$
2	4.87	3.56	5.23	?	5.64	~3.86	~1.0	5.2	10.9	?	5.2
3	5.21	3.18	5.27	?	5.56	3.46	3.0	11.0	9.3	?	3.7
8b)	4.46	3.57	4.70	4.14	5.66	4.40	10.5	2.5	4.5	10.0	1.5
10	4.77	3.36	4.87	4.19	5.56	4.04	3.1	11.9	10.0	10.0	6.5
11	4.91	2.96	4.73	4.17	5.57	2.2—3.0	3.0	11.0	10.0	10.0	?
12	4.47	3.22	4.86	4.13	5.67	2.8—3.0	≤1.0	1.9	4.1	10.0	?

a) Methine or methylene proton(s) of the substituent at C-2. b) Recorded in acetone-d_6.

2-*C*-acetylmethyl derivative **6**, together with a small amount of the nitro alcohol **7**.

Reaction of **1** (0.1 mmol) with acetylacetone (0.15 mmol) in THF (2 ml) in the presence of 0.2 M NaOH (0.1 ml) at 21 °C for 1 h afforded a mixture consisting mainly of the altropyranoside **8** and mannopyranoside **9** in an approximately 4: 1 ratio. These compounds were separated by fractional crystallization. The *altro* configuration with a skew boat form was assigned to **8** by NMR data (Fig. 1). The assignment of signals, carried out by INDOR method, was confirmed by comparison with the spectrum of 3-deuterated derivative of **8**; i) $J_{1,2}$=10.5 Hz indicating the diaxial relationship between H-1 and H-2, ii) $J_{2,3}$=2.5 Hz and $J_{3,4}$=4.5 Hz the equatorial orientation of H-3, and iii) $J_{4,5}$=$J_{5,6a}$= 10 and $J_{5,6e}$=5.0 Hz the benzylidene acetal ring with normal chair conformation.

When dioxane (12 ml) was used as a solvent instead of THF (2 ml), a similar reaction of **1** (20 mg) with acetylacetone afforded predominantly the glucopyranoside **10**, the configuration of which was determined from the coupling constants; $J_{1,2}$=3.1, $J_{2,3}$=11.9, and $J_{3,4}$= 10 Hz.

Treatment of **1** (20 mg) with acetylacetone (10 mg) in THF (1.3 ml) in the presence of 1 M NaOH (0.1 ml) at 21 °C for 1 h afforded a deacetylated product, methyl 2-*C*-acetylmethyl-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-α-D-mannopyranoside (**6**), in 89% yield. When the reaction was stopped at 15 min, the nitro olefin **1**, mannopyranoside **6**, and altropyranoside **8** were detected in an approximate ratio of 1: 1.2: 14, but only a trace of diacetylmethyl derivative with *manno* configuration **9** was detected by NMR spectroscopy. Under the same conditions, deacetylation of **9** was slow; the ratios of **9** to **6** were 8: 1 and 2.5: 1 after 15 min and 1.5 h, respectively. On the other hand, the altropyranoside **8** was completely converted into **6** within 1.5 h. It is noteworthy that a small amount of **8** was detected during the course of deacetylation of **9**.

A similar treatment of the glucopyranoside **10** with 1 M NaOH for 15 h gave the glucopyranoside **11** in a high yield, structure of which was deduced by coupling constants; $J_{1,2}$=3.0, $J_{2,3}$=11, and $J_{3,4}$=10 Hz. Deacetylation of **10** occurred slowly; the ratios of **10** to **11** were 4: 1 and 1.3: 1 after 40 min and 1.5 h, respectively.

When the mixture of **8** and **9** (*ca.* 5: 1, 200 mg) in THF (2.3 ml) was treated with 0.2 M NaOH (0.7 ml) for 50 h, a complex mixture was formed, from which the mannopyranoside **9** and glucopyranoside **10** were isolated in 75 and 12.5% yield, respectively. In addition to these compounds, a small amount of a new compound **12** was isolated. Elemental analysis and the NMR spectrum show that it was a 2-*C*-acetylmethyl derivative. The possibility of **12** being *allo* configuration was chemically excluded; treatment of **12** with 0.2 M NaOD in acetone-d_6 exclusively afforded the C-3 deuterated derivative of the mannopyranoside **6**.[6] Thus, compound **12** should be the altropyranoside; appearance of the H-5 signal at a low field (δ 4.72) as that of **8** (δ 4.60)[7] supports the axial orientation of the nitro group. However, in contrast to the case of **8**, the NMR data strongly suggest that it has the chair conformation;[8] $J_{1,2}$≤1.0, $J_{2,3}$=1.9, $J_{3,4}$=4.1, $J_{4,5}$=$J_{5,6a}$=10, and $J_{5,6e}$=5.0 Hz (Fig. 1). The reason why compound **8** has a skew boat conformation and compound **12** a chair conformation is not clear. If such assignments were correct, compound **12**, having unfavorable 1,3-diaxial interaction between the nitro and methoxyl group, should be less stable than compound **8**. In fact epimerization of **12** to the mannopyranoside **6** occurred more readily than that of **8** to **9**.

In these reactions no evidence for formation of the allopyranoside was obtained. Attempts for epimerization of the glucopyranoside **10** with 1 M NaOH or sodium hydride in THF failed, only glucopyranosides **10** and **11** being detected.

Re-examination of phase transfer catalyzed, heterogeneous reaction of **1** (benzene–0.2 M NaOH) with acetylacetone showed the formation of a trace of altropyranoside **8** besides the mannopyranoside **9** (main product). In the heterogeneous system, about half the amount of **8** epimerized to **9** within 2 min. In the homogeneous system the epimerization was much slower.

This seems to be the first example to isolate the kinetically controlled product of not only the addition of nucleophile but also the following protonation, in the Michael reaction of nitro olefin derivatives. Then we have studied the reaction in detail and found two remarkable solvent effects.

As seen from Table 2, the relative ratios of the altropyranoside **8** to the mannopyranoside **9** increase with an increase in the amount of THF or acetone. Nearly equal amounts of **8** and **9** are formed, when 0.3 ml of THF is used (Entry 1), whereas a 4.2: 1 ratio is obtained for 3 ml of THF (7). From the fact that all of **9** and most of **8** were recovered under the same conditions (2 and 3), the formation of nearly equal

TABLE 2. EFFECTS OF AMOUNT OF THF OR ACETONE IN THE REACTION OF **1** WITH ACETYLACETONE[a]

Entry	Starting material	Solvent (ml)	Reaction time/min	Product ratio[b] 1 : 8 : 9 : 10
1	**1**	THF(0.3)	10	— : 1 : 1 : —
2	**8**[c]	THF(0.3)	10	— : 9 : 1 : —
3	**9**[c]	THF(0.3)	10	— : — : 1 : —
4	**1**	THF(0.8)	30	1.7 : 2.2 : 1 : —
5	**1**	THF(1.3)	10	2.3 : 3.4 : 1 : t
6	**1**	THF(2.0)	30	1 : 3.8 : 1 : t
7	**1**	THF(3.0)	30	0.8 : 4.2 : 1 : 0.8
8	**1**	THF(6.0)	60	0.8 : 3.1 : 1 : 1.5
9	**1**	THF(6.0)+H_2O(0.03)	40	3.2 : 5.7 : 1 : t
10	**1**	THF(6.0)+H_2O(0.03)	180	— : 2 : 1 : t
11	**8**[c,d]	THF(6.0)	60	— : 5[e] : 1[e] : —
12	**9**[c,d]	THF(6.0)	60	— : — : 1 : —
13	**1**	THF(12)	60	t : 3 : 1 : 3.3
14	**1**	THF(12)	140	t : 1.2 : 1 : 1.8
15	**1**[f]	THF(12)	240	1 : 3 : 1 : 7
16	**1**	Acetone(0.3)	10	— : 1.3 : 1 : —
17	**1**	Acetone(1.3)	10	0.4 : 2.9 : 1 : —
18	**1**	Acetone(3.0)	10	0.7 : 3.2 : 1 : —

a) A solution of the nitro olefin **1** (20 mg, 0.068 mmol) in the solvent indicated was stirred at 21 °C with acetylacetone (10 mg, 0.1 mmol) in the presence of 0.2 M NaOH (0.1 ml). b) Determined by NMR spectroscopy: —, product not detected; t, trace. c) Twenty-six mg (0.066 mmol) of starting material used. The same results were obtained in the absence of acetylacetone. d) Instead of 0.2 M NaOH, 0.2 M NaOD used. e) The C-3 position completely deuterated. f) Amount of sodium hydroxide (0.2 M) reduced to 0.03 ml.

amounts of **8** and **9** reflected, at least mostly, kinetically controlled reaction. Treatment of **9** with 0.2 M NaOD for 1 h at 21 °C gave undeuterated **9**, whereas the same treatment of **8** afforded a mixture of **8** and **9** in a 5: 1 ratio, where the C-3 position of both compounds was completely deuterated. This suggests that the protonation at C-3 of the intermediary nitronate derived from **8** is more favorable from the face *cis* to the C-2 substituent, giving the altropyranoside **8**.

Epimerization of **8** to **9** in acetone-d_6 in the presence of 0.2 M NaOD was monitored by NMR spectroscopy. As shown in Fig. 2, epimerization of the mannopyranoside **9** to the altropyranoside **8** occurred more slowly than that of **8** to **9**.

The proportion of axial and equatorial approach of the nucleophile to the nitro olefin **1** varies with solvent. In such a polar solvent as DMSO and acetone, no glucopyranoside **10** was detected, whereas in a less polar solvent such as dioxane, **10** became the major product. Under the conditions for formation of **10** (23), epimerization of **8** or **9** to **10** was negligible as judged from NMR spectroscopy. When the amount of dioxane was decreased to 1.3 ml or a small amount of water was added, the ratio of **10** considerably decreased (Table 3).

A similar but not conspicuous trend was observed in

TABLE 3. REACTION OF **1** WITH ACETYLACETONE IN VARIOUS SOLVENTS[a]

Entry	Solvent (ml)	Reaction time	Product ratio[b] 1 : 8 : 9 : 10
19	DMSO(12)	1h	— : 1 : 2.6 : —
20	Acetone(12)	1h	— : 1 : 1 : —
21	Acetone(12)	2h	— : 1 : 4 : —
22	THF(12)	1h	— : 3 : 1 : 3.3
23	Dioxane (12)	1h	— : 1 : 2 : 13
24	Dioxane (12)+H_2O(0.3)	3h 40 min	t : 1 : t : 1.4
25	Dioxane (1.3)	30 min	— : 4.2 : 1 : 1.2
26	Diethyl ether (12)	3h 20 min	2.5 : 2 : 1 : 3.7
27	Isopropyl alcohol(1.3)	10 min	8 : 2 : 1 : —
28	Benzene (6)[c]	1h	2 : t : 3.5 : 1
29	Benzene (6)[d]	10 min	— : 1 : 8 : t

a) The nitro olefin (20 mg, 0.068 mmol) was treated with acetylacetone (10 mg, 0.1 mmol) in the presence of 0.2 M NaOH (0.1 ml) at 21 °C with stirring. b) Determined by NMR spectro scopy: —, product not detected; t, trace. c) Powdered KOH (13 mg) used instead of 0.2 M NaOH. d) Crushed KOH (*ca.* 3 mg) used instead of 0.2 M NaOH in the presence of 18-crown-6 (5 mg).

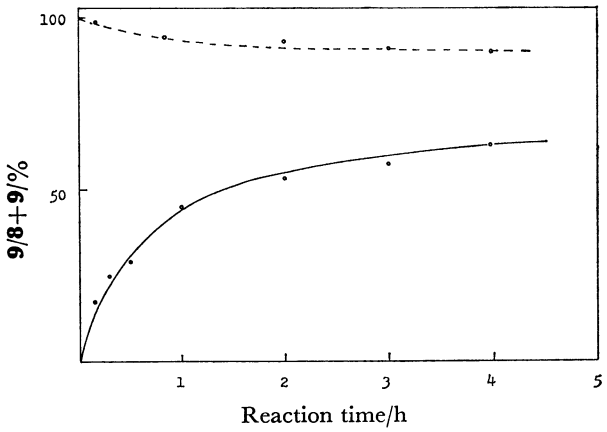


Fig. 2. Epimerization of **8** and **9**.
Compounds **8** and **9** (26 mg, each, 0.66 mmol) in acetone-d_6 (0.25 ml) were treated with 0.2 M NaOD (0.05 ml) in an NMR sample tube at *ca.* 21 °C, and the product ratios were calculated on the basis of integration of the signals due to the benzylidene methine proton at δ 5.78 (**9**) and 5.72 (**8**) and methoxyl group at δ 3.40 (**9**) and 3.30 (**8**). ——: from **8**, ------: from **9**.

Table 4. Reaction of **1** with dimethyl malonate in various solvents[a)]

Solvent (ml)	Reaction time	Product ratio[b)] **1** : **2** : **3**
DMF(12)	2h 40 min	— : 1 : —
Acetone(12)	2h 40 min	— : 1 : —
THF(12)	2h 40 min	— : 10 : 1
THF(6.0)	2h 40 min	— : 15 : 1
THF(0.3)	45 min	— : 1 : —
Dioxane(12)	2h 40 min	1.1 : 1.5 : 1

a) A solution of **1** (20 mg, 0.068 mmol) in the solvent indicated was stirred at 21 °C with dimethyl malonate (13.2 mg, 0.1 mmol) in the presence of 0.2 M NaOH (0.1 ml). b) Determined by NMR spectroscopy; —, product not detected.

the reaction of **1** with dimethyl malonate (Table 4).

In the nucleophilic addition reaction to **1**, previous examples always showed a favorable axial approach under kinetically controlled conditions. This was explained in terms of steric hindrance and stereoelectronic control.[9)] However, predominant equatorial approach in less polar medium is not explained in terms of these factors. Abramovitch and Struble found that such a bulky nucleophile as anion of diethyl malonate exceptionally approaches from the equatorial side of 4-*t*-butyl-1-cyanocyclohexene[10)] and ethyl 4-*t*-butylcyclohexene-1-carboxylate.[11)] They explained the results on the basis of 1,3-interaction between the axial hydrogen atom and an approaching nucleophile. The explanation is not applicable to the present reaction; steric hindrance due to the methoxyl group is apparently more serious than that due to the lone pair on the ring oxygen atom.

Experimental

Melting points were determined in capillaries and are uncorrected. IR spectra were recorded for KBr discs and NMR spectra were determined in chloroform-*d* and/or acetone-d_6 with tetramethylsilane as an internal standard on either a Varian XL-100-15 or a JEOL-PS-100 spectrometer. Column chromatography was carried out on silica gel (C-300, Wakogel). TLC was performed using Merck (Darmstadt) silica gel GF 254. Solutions were concentrated under reduced pressure.

Methyl 4,6-O-Benzylidene-2,3-dideoxy-2-C-[bis(methoxycarbonyl)-methyl]-3-nitro-α-D-mannopyranoside (2). To a solution of **1**[12)] (29.3 mg, 0.1 mmol) and dimethyl malonate (13.8 mg, 0.11 mmol) in THF (2 ml) was added 0.2 M NaOH (0.1 ml) at 21 °C. The mixture was stirred for 2 h and then deionized with cation exchange resin (Amberlite IR-120, H^+). After removal of the resin, the filtrate was concentrated to yield a syrup (42 mg), its NMR spectrum showing it to be almost pure **2**. The syrup (42 +40 mg) was chromatographed on silica gel eluted with benzene–ethyl acetate (20 : 1, v/v) to afford 70 mg of **2** (82%), $[\alpha]_D^{31}$ −30.2° (*c* 1, $CHCl_3$); IR 1750, 1740 (COOMe), and 1560 cm^{-1} (NO_2).

Found: C, 54.02; H, 5.62; N, 3.01%. Calcd for $C_{19}H_{23}NO_{10}$: C, 53.64; H, 5.45; N, 3.29%.

Methyl 4,6-O-Benzylidene-2,3-dideoxy-2-C-[bis(methoxycarbonyl)-methyl]-3-nitro-α-D-glucopyranoside (3). To a solution of **1** (60 mg, *ca.* 0.2 mmol) and dimethyl malonate (42 mg, 0.32 mmol) in dioxane (36 ml) was added 0.2 M NaOH (0.3 ml) at 21 °C, and the mixture was stirred for 6 h. Similar work-up to that for **2** afforded a residue consisting of **2** and **3** in a 1.5: 1 ratio as shown by NMR spectroscopy. The residue (85 +87 mg) was chromatographed on silica gel eluted with benzene–ethyl acetate (20: 1, v/v). The fast running fraction was 83.5 mg of **2** (48%), which was found to be identical with an authentic sample by NMR spectroscopy. The slow running fraction was 57 mg of **3**, which was recrystallized from ethanol to give 52.2 mg of **3** (30%), mp 133—134 °C; $[\alpha]_D^{22}$ +126° (*c* 1, $CHCl_3$); IR 1742, 1722 (COOMe), and 1558 cm^{-1} (NO_2).

Found: C, 53.86; H, 5.50; N, 3.26%. Calcd for $C_{19}H_{23}NO_{10}$: C, 53.64; H, 5.45; N, 3.29%.

Methyl 4,6-O-Benzylidene-2-C-dicyanomethyl-2,3-dideoxy-3-nitro-α-D-mannopyranoside (4). To a solution of **1** (29.3 mg) and malononitrile (7.9 mg, 0.12 mmol) in THF (2 ml) was added 0.2 M NaOH (0.1 ml). The mixture was stirred for 2 h and deionized in a similar way to that for **2**. After removal of the resin, the filtrate was concentrated to give a syrup (34 mg), NMR spectrum of which revealed the presence of **4** and **5** in a ratio of 9 : 1. The same reaction was performed three more times and the combined residue was chromatographed on silica gel.[3)] The mannopyranoside **4** and the glucopyranoside **5** isolated were identical with respective authentic samples in IR and NMR spectra.

Methyl 2-C-Acetylmethyl-4,6-O-benzylidene-2,3-dideoxy-3-nitro-α-D-mannopyranoside (6). To a solution of **1** (29.3 mg) in acetone (2 ml) was added 1 M NaOH (0.2 ml) at 21 °C. The mixture was stirred for 2 h and subjected to a similar work-up to that for **2**, giving a residue (32 mg). Recrystallization of the residue (32 +30 mg) from ethanol afforded 53 mg of **6** (75%), which was identical with an authentic sample by IR and NMR spectroscopy.[3)]

The mother liquor mainly consists of **11** and 3-nitro alcohol **7**, as judged from NMR spectroscopy and TLC.

A similar reaction of **1** (20 mg, 0.068 mmol) with acetylacetone (10 mg, 0.1 mmol) in THF (1.3 ml) in the presence of 1 M NaOH (0.1 ml) at 21 °C for 1 h afforded a residue (24 mg). Recrystallization of the residue (24 +26 mg) from ethanol gave 47.7mg of **6** (89%).

Methyl 4,6-O-Benzylidene-2-C-diacetylmethyl-2,3-dideoxy-3-nitro-α-D-altropyranoside (8). To a solution of **1** (29.3

mg) and acetylacetone (15 mg, 0.15 mmol) in THF (2 ml) was added 0.2 M NaOH (0.1 ml) at 21 °C. The mixture was stirred for 20 min and then deionized with cation exchange resin. After removal of the resin, the filtrate was concentrated to give a white powder (36 mg). The powder (36 +35 mg) was recrystallized from isopropyl alcohol to give 55.8 mg of **8** (71%), mp 163—164 °C; $[\alpha]_D^{22}$ +26.8° (*c* 1, acetone); IR 1725, 1700 (CO), and 1555 cm^{-1} (NO_2).

Found: C, 57.91; H, 5.87; N, 3.62%. Calcd for $C_{19}H_{23}NO_8$: C, 58.01; H, 5.89; N, 3.56%.

The mother liquor mainly consists of the mannopyranoside **9**, which was isolated as a second crop (10.2 mg, 13%).

*Methyl 4,6-O-Benzylidene-2-C-diacetylmethyl-2,3-dideoxy-3-nitro-α-D-glucopyranoside (**10**).* To a solution of **1** (20 mg, 0.068 mmol) and acetylacetone (10 mg, 0.1 mmol) in dioxane (12 ml) was added 0.2 M NaOH (0.1 ml) at 21 °C. After the solution had been stirred for 1 h, the mixture was treated in a similar way to that for **8**, giving a crystalline residue. The same reaction was carried out two more times and the combined residues were recrystallized from ethanol to afford 60 mg of **10** (75%), mp 198—199 °C; $[\alpha]_D^{22}$ +30.2° (*c* 0.5, DMSO); IR 1730, 1700 (CO), and 1555 cm^{-1} (NO_2).

Found: C, 57.74; H, 5.88; N, 3.72%. Calcd for $C_{19}H_{23}NO_8$: C, 58.01; H, 5.89; N, 3.56%.

*Methyl 2-C-Acetylmethyl-4,6-O-benzylidene-2,3-dideoxy-3-nitro-α-D-glucopyranoside (**11**).* To a solution of **10** (26 mg, 0.066 mmol) in THF (1.3 ml) was added 1 M NaOH (0.1 ml) at 21 °C. The mixture was stirred for 15 h and deionized in a similar way to that for **8**. After removal of the resin, the filtrate was concentrated to give a pure powder by NMR spectroscopy. Recrystallization from ethanol afforded 21 mg of **11** (91%), mp 187—188 °C; $[\alpha]_D^{22}$ +84.3° (*c* 0.5, $CHCl_3$); IR 1710 (CO) and 1545 cm^{-1} (NO_2).

Found: C, 57.95; H, 6.00; N, 4.02%. Calcd for $C_{17}H_{21}NO_7$: C, 58.11; H, 6.02; N, 3.99%.

*Methyl 2-C-Acetylmethyl-4,6-O-benzylidene-2,3-dideoxy-3-nitro-α-D-altropyranoside (**12**).* A mixture of **8** and **9** (in a ratio of *ca.* 5: 1, 200 mg, 0.51 mmol) was dissolved in THF (2.3 ml). To this solution was added 0.2 M NaOH (0.7 ml). The resulting solution was stirred at 21 °C for 50 h and worked up in a similar way to that for **8**, affording a powder. Recrystallization from ethanol gave 150 mg (75%) of platelet crystals of **9** as the first crop, 25 mg (12.5%) of needles of **10** as the second crop, and 23 mg of granular crystals as the third crop. A small amount of chloroform was added to the last crystals and the insoluble material was filtered and recrystallized from ethanol to give 10 mg of **12** as needles (5.6%), mp 204—205 °C; $[\alpha]_D^{22}$ +15.4° (*c* 0.5, acetone); IR 1717 (CO) and 1560 cm^{-1} (NO_2).

Found: C, 58.39; H, 6.00; N, 4.05%. Calcd for $C_{17}H_{21}NO_7$: C, 58.11; H, 6.02; N, 3.99%.

*Attempts for Epimerization of **10**.* To a solution of **10** (26 mg, 0.066 mmol) in THF (1.3 ml) was added *ca.* two equiv NaH (6.4 mg, purity *ca.* 50%) at 21 °C. The mixture was stirred for 1.5 h and worked up in a similar way used for **8** to give a residue, NMR spectrum of which showed the presence of **11** and **10** in a ratio of 2 : 1, but no evidence for formation of the allopyranoside.

A similar treatment of **10** (26 mg) with 1 M NaOH (0.1 ml) in THF (1.3 ml) at 21 °C for 1.5 h also gave a mixture of **11** and **10** in a 1: 1.3 ratio. No evidence was again obtained for formation of the allopyranoside.

*Epimerization of **12** to **6**.* To an acetone-d_6 solution of **12** (13 mg, 0.033 mmol) was added 0.2 M NaOD (0.05 ml). Within 20 min, **12** was completely epimerized to give the 3-deuterated derivative of **6**, the C-2 position of which was not deuterated.

Under the same conditions, epimerization of the altropyranoside **8** was much slower; even after 45 min *ca.* 16% of **8** was epimerized to the mannopyranoside **9**, revealing that compound **12** is much less stable than **8**.

References

1) Part 9 of this series; T. Sakakibara and R. Sudoh, *Carbohydr. Res.*, in press.

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6) If the epimerization occurred *via* the nitro olefin intermediate, the possibility of **12** as being an allopyranoside was not excluded. However, this is not likely since no acetylmethyl group of the product was completely deuterated, *i.e.*, this group did not come from the solvent, and the nitro alcohol **7**, formed (**6** : **7**=3 : 1) by the reaction of the nitro olefin **1** with acetone-d_6 under the same conditions, was not detected by NMR spectroscopy.

7) The H-5 signal of 3-nitro sugar with the *gluco* and *manno* configuration resonated at around δ 3.6.

8) A strongly distorted chair conformation like $^4H_5$ form is also possible from the NMR data.

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