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## Note

# Synthesis of 1,6-anhydro-1(6)-thio-β-maltotriose*

KEN'ICHI TAKEO* AND TAKASHI KUGE

*Department of Agricultural Chemistry, Kyoto Prefectural University, Shimogamo, Kyoto 606 (Japan)*

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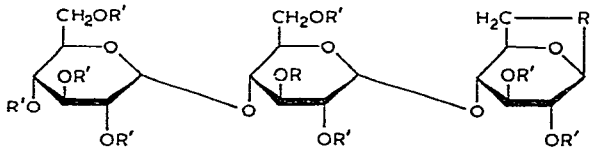
As a part of our studies on the chemical modification of maltotriose[1,2], this paper describes the synthesis of 1,6-anhydro-1(6)-thio-β-maltotriose (**4**) starting from 1,6-anhydro-β-maltotriose nonaacetate[2] (**1**) by use of a reaction sequence analogous to that employed for the preparation of 1,6-anhydro-1(6)-thio-β-D-disaccharides[3–5]. Preparation of several maltotriose derivatives substituted specifically at C-1 and C-6 is also included

Attempts to cleave the 1,6-anhydro ring of **1** with titanium tetrachloride in chloroform under the reaction conditions described for the maltose series[6] led to no reaction and resulted in recovery of the starting material **1**. In contrast, the reaction proceeded smoothly with titanium tetrabromide[5] in place of titanium tetrachloride Subsequent replacement of the acetate group with anomeric inversion of the resulting acetylglycosyl bromide by treatment with mercuric acetate in acetic acid gave a mixture comprising the β-decaacetate **5** having a free hydroxyl group at C-6 and unchanged starting material **1** This mixture could not be separated either by fractional crystallization or by column chromatography on silica gel with a variety of solvents The reaction mixture was treated with trityl chloride in pyridine to yield a mixture composed of the 6-trityl ether **6** and of **1**, from which pure **6** could be readily isolated in 56% yield by column chromatography Detritylation of **6** with aqueous acetic acid followed by column chromatographic purification afforded crystalline **5** in an overall yield of 51% based on **1**. Acetylation of **5** with acetic anhydride and pyridine gave β-maltotriose hendecaacetate[1,2,7].

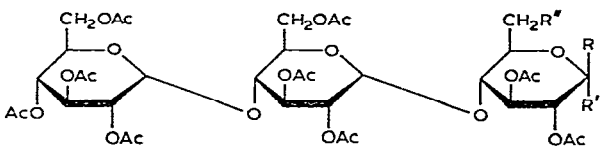
On *p*-toluenesulfonylation and methanesulfonylation, **5** gave the 6-*O*-*p*-toluenesulfonyl and 6-*O*-methylsulfonyl β-decaacetates (**7** and **8**), respectively The displacement reaction of the sulfonates **7** and **8** with sodium iodide in acetonylacetone afforded the 6-deoxy-6-iodo β-decaacetate **9**; this confirmed the location of the sulfonyloxy groups at C-6 in **7** and **8** The replacement of *N*,*N*-dimethylformamide or *N*,*N*,*N'*,*N'*,*N''*,*N''*-hexamethylphosphoric triamide in this replacement reaction was

*Chemical modification of maltotriose Part III. For Part II, see ref 1.
†To whom inquiries should be addressed

ineffective and resulted in an incomplete reaction Reductive removal of iodine from **9** gave the 6-deoxy β-decaacetate **10**, the n m r. spectrum (chloroform-*d*) of which showed the C-5 methyl resonance at τ 8.54 as a doublet (*J* 5 5 Hz). Reaction of **5** with sulfuryl chloride and pyridine in chloroform yielded the 6-chloro-6-deoxy β-decaacetate **11**



1 R = O, R′ = Ac
2 R = O, R = H
3 R = S R′ = Ac
4 R = S, R′ = H



5 R = OAc, R′ = H, R″ = OH
6 R = OAc, R′ = H, R″ = OTr
7 R = OAc R′ = H R″ = OTs
8 R = OAc, R′ = H, R″ = OMs
9 R = OAc R′ = H, R″ = I
10 R = OAc R′ = H R″ = H
11 R = OAc, R′ = H, R″ = Cl
12 R = $S_2COEt$, R′ = H, R″ = OTs
13 R = $S_2COEt$ R′ = H R″ = OMs
14 R = H R′ = OAc R″ = SAc
15 R = OAc R′ = H, R″ = SAc
16 R = H R′ = Br R″ = OAc
17 R = $S_2COEt$ R′ = H R″ = OAc
18 R = SAc R′ = H, R″ = OAc

Treatment of **7** or **8** with sodium methoxide in methanol followed by acetylation gave **1** in a good yield. By analogy with the results obtained in the disaccharide series[3–5], this result supports the structures assigned to **7** and **8**, in which an acetoxyl group with β-configuration is attached to C-1 and a sulfonyloxy group to C-6

The *p*-toluenesulfonate **7** was converted with hydrogen bromide in acetic acid into the corresponding α-bromide, which was then treated with potassium *O*-ethyl dithiocarbonate in ethanol to give 2,2′,2″,3,3′,3″,4″,6′,6″-nona-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-β-maltotriosyl *O*-ethyl dithiocarbonate (**12**) The mesylate **8** was likewise converted into 2,2′,2″,3,3′,3″,4″,6′,6″-nona-*O*-acetyl-6-*O*-methylsulfonyl-β-maltotriosyl *O*-ethyl dithiocarbonate (**13**). Treatment of **12** or **13** with sodium methoxide in methanol followed by acetylation gave crystalline 1,6-anhydro-1(6)-thio-β-maltotiose nonaacetate (**3**) which on deacetylation furnished 1,6-anhydro-1(6)-thio-β-maltotriose (**4**) in crystalline form

In the n m r spectrum (deuterium oxide) of **4**, the H-1 resonance appeared at a lowest field (τ 4 53) as a broad singlet, in agreement with the previous observation obtained with the corresponding oxygen analog[2] **2**, indicating the $^1C_4$ conformation

of the 1,6-anhydro-1(6)-thio ring of **4** as the favored conformation Comparison of the n m r spectrum of **2** with that of **4** showed a marked difference at high field; in the spectrum of **4**, a two-proton multiplet, which was assigned to the methylene protons at C-6, was observed in the region of $\tau$ 6.78–6 94, whereas in the spectrum of **2** no signal could be detected in this region This indicates the shielding effect of the sulfur atom in the 1,6-anhydro-1(6)-thio ring of **4** A similar observation has been described[3] after comparison of the n m r spectra of 1,6-anhydro- and 1,6-anhydro-1(6)-thio-$\beta$-lactose hexaacetates

Acetolysis of **3** allowed the opening of the 1,6-anhydro-1(6)-thio ring without cleavage of the glycosidic linkages to give 1,2,2′,2″,3,3′,3″,4″,6′,6″-deca-*O*-acetyl-6-*S*-acetyl-6-thio-α-maltotriose (**14**) Compound **15**, the $\beta$ anomer of **14**, was obtained by treatment of 7 with potassium thioacetate in *N*,*N*-dimethylformamide The n m r spectra (chloroform-*d*) of **14** and **15** showed the H-1 resonances at $\tau$ 3 80 and $\tau$ 4 28 as doublets ($J_{1,2}$ 3 8 and 7 5 Hz, respectively), supporting the anomeric configurations assigned to **14** and **15**

Reaction of the α-bromide **16** with potassium *O*-ethyl dithiocarbonate in ethanol afforded 2,2′,2″,3,3′,3″,4″,6,6′,6″-deca-*O*-acetyl-$\beta$-maltotriosyl *O*-ethyl dithiocarbonate (**17**) which on treatment with sodium methoxide in methanol gave the sodium salt of 1-thiomaltotriose as a hygroscopic powder Subsequent acetylation of this salt **19** furnished crystalline 2,2′,2″,3,3′,3″,4″,6,6′,6″-deca-*O*-acetyl-1-*S*-acetyl-1-thio-$\beta$-maltotriose (**18**) This compound was also obtained in a high yield by condensation of the α-bromide **16** with potassium thioacetate in acetone

## EXPERIMENTAL

*General* — The general conditions are as described[2] in Part I The following solvent systems were used for t l c and column chromatography, (A) 1 1 (v/v) benzene–ethyl acetate and (B) 3 2 (v/v) benzene–ethyl acetate

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1*→*4*)-O-(*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1*→*4*)-*1,2,3-tri*-O-*acetyl*-$\beta$-D-*glucopyranose* (**5**) *and* O-(*2,3,4,6-tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1*→*4*)-O-(*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1*→*4*)-*1,2,3-tri*-O-*acetyl*-*6*-O-*trityl*-$\beta$-D-*glucopyranose* (**6**) — To a solution of **1** (15 g, ref 2) in anhydrous chloroform (270 ml) was added titanium tetrabromide (20 g) and the mixture was heated gently under reflux for 5 h The reaction mixture was cooled and poured into ice–water (500 ml) The organic layer was separated, washed with water (3 × 200 ml), dried ($MgSO_4$), and evaporated to dryness The resulting syrup was dissolved in a solution of mercuric acetate (16 g) in acetic acid (160 ml) The solution was kept at room temperature for 5 h, and then poured into ice–water (800 ml) and extracted with chloroform (3 × 250 ml). The extracts were washed successively with aqueous sodium hydrogencarbonate and water, dried ($Na_2SO_4$), and concentrated to dryness A solution of the residue in pyridine (50 ml) was heated with trityl chloride (6 g) for 3 h at 100°. The cooled solution was poured into ice–water, and the precipitate formed was collected by filtration, washed well with water, and dried T l c

(Solvent A) indicated the presence of the 6-trityl ether **6** ($R_F$ 0 68) and unchanged starting material **1** ($R_F$ 0 29) The mixture was fractionated on a column of silica gel (300 g) with Solvent A The fractions containing **6** were collected and concentrated to a syrup which crystallized from methanol–water (10 6 g, 56%), m p. 112–113°, $[\alpha]_D^{15}$ +65.3° (*c* 1 5, chloroform); u v data· $\lambda_{max}^{MeOH}$ 259 nm ($\varepsilon$ 670)

*Anal* Calc for $C_{57}H_{66}O_{26}$: C, 58 66, H, 5 70. Found· C, 58 44, H, 5.77

A solution of **6** (10 g) in 80% acetic acid (300 ml) was stirred for 3 h at 50° Removal of the solvents by codistillation with toluene gave a syrup which was purified by elution from a column of silica gel (150 g) with Solvent B to yield **5** (7 3 g, 92%), m p 105–106° (from ethanol–water), $[\alpha]_D^{15}$ +92 4° (*c* 1.5, chloroform)

*Anal* Calc for $C_{38}H_{52}O_{26}$· C, 49 35, H, 5 67 Found C, 49 23, H, 5 71.

Conventional acetylation of **5** (110 mg) with acetic anhydride and pyridine at room temperature overnight gave $\beta$-maltotriose hendecaacetate[1,2 7] (101 mg, 88%), m p and mixed m p 134–136° (after crystallization from ethanol), $[\alpha]_D^{22}$ +88 0° (*c* 1 4, chloroform)

A solution of **5** (200 mg) in chloroform (3 ml) and pyridine (0 4 ml) was treated at −10° with sulfuryl chloride (0 3 ml), and then stirred at room temperature for 5 h The mixture was diluted with chloroform, washed successively with cold 5% sulfuric acid, aqueous sodium hydrogen carbonate and water, dried ($Na_2SO_4$), and concentrated to dryness The residue was purified by elution from a small column of silica gel with Solvent A to give *O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-1,2,3-tri-*O*-acetyl-6-chloro-6-deoxy-β-D-glucopyranose (**11**) (180 mg, 89%) as a glass that could not be crystallized, $[\alpha]_D^{20}$ +86 2° (*c* 1 2, chloroform), t l c $R_F$ 0 49 (Solvent A)

*Anal* Calc for $C_{38}H_{51}ClO_{25}$ C, 48 39, H, 5 45, Cl, 3 76 Found C, 48 33, H, 5 60, Cl, 3 70

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-*1,2,3-tri*-O-*acetyl*-*6*-O-p-*tolylsulfonyl*-β-D-*glucopyranose* (**7**) — To a cooled solution of the decaacetate **5** (2 7 g) in pyridine (15 ml) was added *p*-toluenesulfonyl chloride (2 9 g) The mixture was stirred at room temperature overnight and then poured into ice–water The resulting precipitate was filtered off, dried, and fractionated on a column of silica gel (80 g) with Solvent B. The first fraction crystallized from ethanol to give **7** (2 9 g, 93%), m p 97–99°, $[\alpha]_D^{15}$ +83 2° (*c* 1 5, chloroform), n m r data (chloroform-*d*) τ 7 53 (s, 3 H, aryl-$CH_3$)

*Anal* Calc for $C_{45}H_{58}SO_{28}$ C, 50 09; H, 5 42; S, 2 97 Found· C, 50 17; H, 5 60, S, 2 89.

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-*1,2,3-tri*-O-*acetyl*-*6*-O-*methylsulfonyl*-β-D-*glucopyranose* (**8**). — Methanesulfonyl chloride (1 4 ml) was added to a cooled solution of **5** (3 2 g) in pyridine (16 ml) and the mixture was kept overnight at 0° Isolation as just described gave a syrup which, on elution from a column of silica gel (100 g) with Solvent B, afforded **8** (3 1 g, 87%), m p 100–102° (from ethanol), $[\alpha]_D^{15}$ +81.1° (*c* 1 5, chloroform), n m r data (chloroform-*d*) τ 6 91 (s, 3 H, $MeSO_2$)

*Anal* Calc for $C_{39}H_{54}SO_{28}$. C, 46.71; H, 5.43; S, 3 20 Found C, 46 50, H, 5.50, S, 3 16.

*Compound* **1** *from* **7** *and* **8** — A solution of **7** (140 mg) in methanolic 0 1M sodium methoxide (5 ml) was stirred for 5 h at room temperature, and then neutralized with acetic acid and evaporated to dryness Acetylation of the residue with acetic anhydride (2 ml) and pyridine (3 ml) overnight at room temperature gave **1** (94 mg, 84%), m p and mixed m p 156–157° (after crystallization from ethanol), $[\alpha]_D^{22}$ +83 0° (*c* 1 5, chloroform) Similar treatment of **8** (160 mg) as just described for **7** also produced **1** (112 mg, 82%)

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-*1,2,3-tri*-O-*acetyl-6-iodo-6-deoxy*-β-D-*glucopyranose* (**9**) — Compound **7** (0 5 g) was heated in dry acetonylacetone (12 ml) with sodium iodide (1 g) for 3 h at 100° The mixture was poured into ice–water and the precipitate was filtered off, washed well with water, and dried. Cyrstallization from ethanol gave **9** (0 4 g, 83%), m p 98–100°, $[\alpha]_D^{15}$ +81 8° (*c* 1 5, chloroform)

*Anal.* Calc. for $C_{38}H_{51}IO_{25}$. C, 44 11, H, 4 97, I, 12 26 Found· C, 44 15, H, 5 14, I, 12 13

Compound **9** (124 mg, 80%) was also obtained from **8** (150 mg) by a similar procedure

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-*1,2,3-tri*-O-*acetyl-6-deoxy*-β-D-*glucopyranose* (**10**) — A solution of **9** (310 mg) in ethanol (10 ml) and pyridine (0 1 ml) was hydrogenated over 10% paladium-on-charcol (200 mg) under atmospheric pressure for 6 h at 60°. The catalyst was removed by filtration and the filtrate was evaporated to dryness The residue was dissolved in chloroform, and the solution was successively washed with 10% sodium thiosulfate and water, dried ($Na_2SO_4$), and concentrated to a syrup which crystallized from ethanol to give **10** (250 mg, 92%), m p 106–108°, $[\alpha]_D^{15}$ +92 0° (*c* 1 5, chloroform), n m r data (chloroform-*d*) τ 8 54 (d, 3 H, $J_{5,6}$ 5 5 Hz $CH_3$-5)

*Anal.* Calc for $C_{38}H_{52}O_{25}$· C, 50 22, H, 5 77 Found C, 50 15; H, 5 86

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-*2,3-di*-O-*acetyl-6*-O-p-*tolylsulfonyl*-β-D-*glucopyranosyl* O-*ethyl dithiocarbonate* (**12**) — A solution of **7** (1 96 g) in acetic acid (7 ml) was treated with acetic acid (5 ml) saturated with hydrogen bromide at 0°, and then stirred for 1 h at room temperature The reaction mixture was diluted with chloroform, washed successively with cold water, aqueous sodium hydrogencarbonate, and water, dried ($MgSO_4$), and evaporated to give the corresponding α-glycosyl bromide as a glass (1 85 g), $[\alpha]_D^{15}$ +143 3° (*c* 1 0, chloroform), which was used without further purification The α-bromide was added to a solution of potassium *O*-ethyl dithiocarbonate (323 mg) in ethanol (34 ml). The mixture was warmed for a few min on a steam bath and then kept for 1 h at room temperature. The mixture was poured into ice–water and extracted with chloroform The extract was washed well with water, dried ($Na_2SO_4$), and evaporated to a syrup which crystallized from ethanol to give **12** (1 74 g, 84%), m p 83–85°, $[\alpha]_D^{15}$ +106 5° (*c* 1 5, chloroform), u v data· $\lambda_{max}^{MeOH}$

273 nm (ε 10500); n m r. data (chloroform-*d*): τ 7.53 (s, 3 H, aryl-$CH_3$) and 8 56 (t, 3 H, *J* 7 0 Hz, $CH_2CH_3$)

*Anal.* Calc. for $C_{46}H_{60}S_3O_{27}$: C, 48.42, H, 5 30, S, 8 43. Found C, 48 22, H, 5 41; S, 8.59

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-*2,3-di*-O-*acetyl*-*6*-O-*methylsufonyl*-β-D-*glucopyranosyl* O-*ethyl dithiocarbonate* (**13**) — As just described, **8** (2 3 g) was converted into the corresponding α-bromide (2 2 g), $[\alpha]_D^{15}$ +145 8° (*c* 1.5, chloroform), which was treated with potassium *O*-ethyl dithiocarbonate (413 mg) in ethanol (30 ml), as described for the preparation of **12**, to give **13** (1 98 g, 81%), m p. 88–91° (from ethanol), $[\alpha]_D^{15}$ +94 0° (*c* 1 5, chloroform), u v data $\lambda_{max}^{MeOH}$ 273 nm (ε 10300), n m r data (chloroform-*d*) τ 6 91 (s, 3 H, $MeSO_2$) and 8 53 (t, 3 H, *J* 7 0 Hz, $CH_2CH_3$)

*Anal.* Calc for $C_{40}H_{56}S_3O_{27}$ C, 45 11, H, 5 30; S, 9.03 Found C, 45 02, H, 5 41; S, 8 90

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-*2,3-di*-O-*acetyl*-*1,6-anhydro*-*1*(*6*)-*thio*-β-D-*glucopyranose* (**3**). — A solution of **12** (1 6 g) in dry methanol (20 ml) was treated with 2 6M sodium methoxide in methanol (10 ml) The solution was kept overnight at room temperature, and then neutralized with acetic acid and evaporated to dryness The resulting syrup was acetylated with acetic anhydride (15 ml) and pyridine (15 ml) overnight at 0° Isolation, in the usual way by pouring the mixture into ice–water, gave **3** (1 2 g, 81%), m p 160–161° (from methanol), $[\alpha]_D^{15}$ +92 5° (*c* 1 5, chloroform)

*Anal* Calc for $C_{36}H_{48}SO_{23}$: C, 49 09, H, 5 49, S, 3 64 Found C, 49 12, H, 5 53, S, 3 55

Compound **3** (942 mg, 76%) was also obtained from **13** (1 5 g) by an analogous procedure

O-α-D-*Glucopyranosyl*-(*1→4*)-O-α-D-*glucopyranosyl*-(*1→4*)-*1,6-anhydro*-*1*(*6*)-*thio*-β-D-*glucopyranose* (**4**) — A solution of **3** (1 16 g) in anhydrous methanol (10 ml) was treated with methanolic M sodium methoxide (1 ml) The solution was stirred for 2 h at room temperature, neutralized with Amberlite IR-120 ($H^+$) ion-exchange resin, filtered, and evaporated to give a crystalline mass which on recrystallization from ethanol gave **4** (571 mg, 91%), m p 203–204 5°, $[\alpha]_D^{15}$ +136 2° (*c* 1 1, water), n m r data (deuterium oxide) τ 4 53 (s, 1 H, H-1), 4 61 (d, 1 H, $J_{1'',2''}$ 3.5 Hz, H-1''), 4 88 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1'), and 6 78–6 94 (m, 2 H, $CH_2$-6)

*Anal* Calc for $C_{18}H_{30}SO_{14}$ C, 43 03; H, 6 02, S, 6 38 Found C, 42 95, H, 6 10, S, 6 33.

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-*1,2,3-tri*-O-*acetyl*-*6*-S-*acetyl*-*6*-*thio*-α-D-*glucopyranose* (**14**) — Compound **3** (300 mg) was dissolved in the acetolysis mixture[8] (15 ml, acetic anhydride–acetic acid–sulfuric acid, 70 30 1) After stirring for 3 h at room temperature, the solution was poured into ice–water. The precipitate formed was filtered off, washed with water, and dried Crystallization from methanol gave **14** (288 mg, 86%),

m.p. 99–101°, $[\alpha]_D^{15}$ +121 5° (*c* 1.6, chloroform); n m r. data (chloroform-*d*)· $\tau$ 3.80 (d, 1 H, $J_{1,2}$ 3 8 Hz, H-1), 7.63 (s, 3 H, SAc).

*Anal* Calc for $C_{40}H_{54}SO_{26}$: C, 48 88, H, 5 54, S, 3 26 Found. C, 48.99, H, 5 41; S, 3 15

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1*→*4*)-O-(*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*-(*1*→*4*)-*1,2,3-tri*-O-*acetyl-6*-S-*acetyl-6-thio*-β-D-*glucopyranose* (**15**) — Compound **7** (270 mg) was heated in *N,N*-dimethylformamide (4 5 ml) containing potassium thioacetate (60 mg) for 1 h at 100°. Isolation, in the usual way, gave **15** (192 mg, 78%), m.p 125–126°, $[\alpha]_D^{20}$ +85 1° (*c* 1 0, chloroform), n m r. data (chloroform-*d*) $\tau$ 4 28 (d, 1 H, $J_{1,2}$ 7 5 Hz, H-1) and 7 63 (s, 3 H, SAc)

*Anal* Calc for $C_{40}H_{54}SO_{26}$: C, 48 88, H, 5.54, S, 3 26 Found C, 48 80, H, 5 60, S, 3 19

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1*→*4*)-O-(*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1*→*4*)-*2,3,6-tri*-O-*acetyl*-β-D-*glucopyranosyl* O-*ethyl dithiocarbonate* (**17**). — To a solution of potassium *O*-ethyl dithiocarbonate (390 mg) in ethanol (8 ml) was added the α-bromide[2] **16** (2 g) The mixture was heated for 5 min at 85°, kept for 15 min at room temperature, and was poured into ice–water The precipitate was filtered off and dried. Crystallization from ethanol gave **17**, (1 8 g, 86%), m p 92–94°, $[\alpha]_D^{15}$ +94 5° (*c* 1 5, chloroform), u v. data: $\lambda_{max}^{MeOH}$ 274 nm ($\varepsilon$ 11500), n m r. data (chloroform-*d*)· $\tau$ 8 55 (t, 3 H, *J* 7 0 Hz, $CH_2CH_3$)

*Anal* Calc for $C_{41}H_{56}S_2O_{56}$ C, 47 86, H, 5 49, S, 6 23 Found C, 47 95; H, 5 31, S, 6 29

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1*→*4*)-O-(*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1*→*4*)-*2,3,6-tri*-O-*acetyl-1*-S-*acetyl-1-thio*-β-D-*glucopyranose* (**18**) — (*a*) A solution of **17** (1.3 g) in chloroform (5 ml) was cooled to −20° and treated with methanolic M sodium methoxide (1 ml) under stirring for 1 h at this temperature The precipitated solid was filtered off, washed with chloroform, and dried to give 1-thiomaltotriose sodium salt (**19**) as a hygroscopic powder (620 mg, 90%), $[\alpha]_D^{20}$ +102 8° (*c* 1 1, water) The sodium salt **19** was acetylated with acetic anhydride (3 ml) and pyridine (4 ml) overnight at 0° Isolation, in the usual manner, gave **18** (630 mg, 51%), m p. 139–140° (from methanol), $[\alpha]_D^{20}$ +93 3° (*c* 1.3, chloroform), n m r. data (chloroform-*d*) $\tau$ 7 62 (s, 3 H, SAc).

*Anal* Calc for $C_{40}H_{54}SO_{26}$· C, 48 88, H, 5 54, S, 3 26. Found C, 48.72, H, 5 60; S, 3 29

(*b*). A mixture of the α-bromide **16** (1 5 g) and potassium thioacetate (210 mg) in acetone (15 ml) was boiled for 5 min and then kept at room temperature for 2 h. Isolation, in the usual way, gave **18** (1 35 g, 90%), m p and mixed m p. 139–140° (after crystallization from methanol), $[\alpha]_D^{20}$ +92.7° (*c* 1 2, chloroform), the n m r spectrum was identical with that of the compound obtained in (*a*)

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## REFERENCES

1 K TAKEO AND T KUGE, *Staerke* (1976), in press
2 K TAKEO, K MINE, AND T. KUGE, *Carbohydr Res*, 48 (1976) 197–208.
3 S TEJIMA, *Carbohydr Res*, 20 (1971) 123–132
4 S TEJIMA AND Y OKAMORI, *Chem Pharm Bull*, 20 (1972) 2036–2041
5 M MORI, M HAGA, AND S TEJIMA, *Chem Pharm Bull*, 22 (1974) 1331–1338
6 L ASP AND B LINDBERG, *Acta Chem Scand*, 6 (1952) 941–946
7 A THOMPSON AND M L WOLFROM, *J Am Chem Soc*, 74 (1952) 3612–3614
8 G G S DUTTON AND K N SLESSOR, *Can J. Chem*, 44 (1966) 1069–1074