Carbohydrate Research, 52 (1976) 23–29
© Elsevier Scientific Publishing Company, Amsterdam – Printed in Belgium

SYNTHESES OF 2-*O*-METHYL-, 3-*O*-METHYL-, AND 2,3-DI-*O*-METHYL-D-TALOSE AND SOME DERIVATIVES THEREOF

GORDON J. F. CHITTENDEN
Department of Exobiology, The University, Toernooiveld, Nijmegen (The Netherlands)
(Received March 19th, 1976; accepted for publication, April 12th, 1976)

ABSTRACT

The title compounds, and some derivatives thereof, have been synthesised from easily accessible benzyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranoside (**4**). Treatment of **4** with methyl sulphoxide–phosphorus pentaoxide gave the known ketone **5**, which was stereospecifically reduced with neutralised sodium borohydride, without cleavage of the benzoate group, to benzyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-talopyranoside (**6**). Under mild alkaline conditions, **6** was converted into the corresponding 2-benzoate **10**. Debenzoylation of **6** gave the diol **7**. Methylation of **6**, **7**, and **10** with diazomethane in the presence boron trifluoride etherate gave the corresponding methylated products in high yield. Removal of the blocking groups by conventional methods gave 2-*O*-methyl, 3-*O*-methyl-, and 2,3-di-*O*-methyl-D-talose. Methylation of **7** with diazomethane in the presence of a catalytic amount of stannous chloride dihydrate showed high specificity to give benzyl 4,6-*O*-benzylidene-3-*O*-methyl-β-D-talopyranoside (**16**, 89%).

INTRODUCTION

The synthesis of methyl ethers of talose has been hampered by a lack of suitable intermediates. A reducing syrup, presumably 2-*O*-methyl-D-talose (**1**), was obtained by acid hydrolysis of 1,6-anhydro-3,4-*O*-isopropylidene-2-*O*-methyl-β-D-talopyranose[1]. Syrupy 3-*O*-methyl-L-talose has been prepared as an intermediate in the synthesis of 2-*O*-methyl-L-lyxose, by acid hydrolysis of 1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl-L-talofuranose[2,3].

The present report describes the synthesis of **1**, 3-*O*-methyl-D-talose (**2**), 2,3-di-*O*-methyl-D-talose (**3**), and some of their derivatives from readily available benzyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranoside[4] (**4**).

RESULTS AND DISCUSSION

Benzyl 4,6-*O*-benzylidene-β-D-*lyxo*-hexopyranosidulose 3-benzoate (**5**) was prepared, as described earlier[5], by the oxidation of compound **4** with methyl

sulphoxide–phosphorus pentaoxide. Reduction of the ketone **5** with neutralised sodium borohydride[6] in tetrahydrofuran–ethyl acetate–water (9:3:1) gave 89% of benzyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-talopyranoside (**6**). The reduction appeared to be stereospecific, as none of the benzoate **4** was detected (t.l.c.) in the crude reduction product. Debenzoylation of compound **6** with sodium methoxide gave the known benzyl 4,6-*O*-benzylidene-β-D-talopyranoside (**7**).

Treatment of benzoate **6** with methyl sulphoxide–phosphorus pentaoxide yielded the ketone **5**, which was characterised as the *p*-nitrophenylhydrazone[5] **8**. This result showed that the benzoate group in **6** had been retained, and in its original position, during the reduction with the reagent. Sodium borohydride usually causes[7] simultaneous reduction and acyl-ester cleavage. Acyl groups can be retained during borohydride reduction by strict pH control[8]. Treatment[9] of **4** with dilute alkali is known to yield the corresponding 2-benzoate **9** in high yield. 1,3-Diesters of dihydroxyacetone can be reduced[6] to the corresponding acylated derivatives of glycerol with this reagent, without appreciable acyl migration; the reagent should find further application in the carbohydrate field.

Treatment of the 3-benzoate **6** in acetone solution with dilute alkali yielded (t.l.c.) a mixture of unreacted **6**, a monobenzoate with R_F value lower than that of **6**, and a trace of the diol **7**. Column chromatography of the product gave the 3-benzoate **6** (59%) and benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-talopyranoside (**10**, 27%). Examination of the interconversion of **6** and **10** in aqueous acetone under homogeneous conditions[10] showed that these yields represented the approximate equilibrium values. The conversion of **6** into **10** is poor compared with that for the corresponding *galacto* derivatives[9], **4** and **9**. This is probably due to the unfavorable stereochemistry of the β-D-*talo* configuration.

With one equivalent of *N*-benzoylimidazole[4], glycoside **7** yielded a mixture of the dibenzoate **11**, the two monobenzoates (**6** and **10**), and unreacted **7**. No single component preponderated and no attempt was made to fractionate the mixture chromatographically. Treatment of **7** with excess benzoyl chloride in pyridine gave the non-crystalline dibenzoate **11**. The lack of selectivity shown by the secondary hydroxyl groups in diol **7** is presumably due to intramolecular hydrogen-bonding[9]. Both HO-2 and HO-3 in compound **7** can form strong hydrogen-bonds with adjacent oxygen functions. For the methyl 4,6-*O*-benzylidenegalactosides, Reichstein and his co-workers[11–14] found, in most cases, a higher proportion of the 3-ester in the β- than in the α-series in which both HO-2 and HO-3 groups may form a hydrogen bond.

Treatment[15] of the 3-benzoate **6**, in dichloromethane, with excess diazomethane in the presence of boron trifluoride etherate at −15° gave benzyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-*O*-methyl-β-D-talopyranoside (**12**) in good yield (77–83%). The product was debenzoylated with methanolic sodium methoxide to give benzyl 4,6-*O*-benzylidene-2-*O*-methyl-β-D-talopyranoside (**13**). Exhaustive hydrogenation of **13** over a palladium catalyst gave syrupy 2-*O*-methyl-D-talose (**1**), which failed to yield a crystalline derivative. Acetylation, followed by chromatography on silica gel, gave

a pure, syrupy tetra-acetate **14**. Treatment of **1** with phenylhydrazine–acetic acid gave D-*lyxo*-hexose phenylosazone; 2-*O*-methyl sugars yield osazones under these conditions[1].

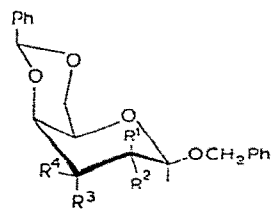
Similar methylation of the 2-benzoate **10** with the diazomethane reagent yielded 76% of benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-methyl-β-D-talopyranoside (**15**). Compound **15** was debenzoylated with sodium methoxide in methanol to give benzyl 4,6-*O*-benzylidene-3-*O*-methyl-β-D-talopyranoside (**16**) which, on catalytic hydrogenation over palladium oxide, yielded 3-*O*-methyl-D-talose (**2**). The syrupy product was characterised as the crystalline tetrakis(*p*-nitrobenzoate).

Oxidative degradation of **2** with active manganese dioxide gave syrupy material having the same chromatographic characteristics as 2-*O*-methyl-L-lyxose, formed in the same manner from 3-*O*-methyl-L-talose[2,3].

Treatment of diol **7** in dichloromethane–methanol solution with excess diazomethane in the presence of a catalytic amount of stannous chloride dihydrate[16,17] gave the 3-methyl ether **16**. Benzoylation of **16** gave compound **15**.

Reaction of **7** with diazomethane in the presence of boron trifluoride etherate gave benzyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-β-D-talopyranoside (**17**) in 71% yield.

No reaction was observed between the diol **7** and diazomethane in the absence of a catalyst[17]. Hydrogenation of **17** over a palladium catalyst yielded syrupy 2,3-di-*O*-methyl-D-talose (**3**), which was characterised as the tris(*p*-nitrobenzoate).



4 $R^1 = R^3 = H$; $R^2 = OH$; $R^4 = OBz$
6 $R^1 = OH$; $R^2 = R^3 = H$; $R^4 = OBz$
7 $R^1 = R^4 = OH$; $R^2 = R^3 = H$
9 $R^1 = R^3 = H$; $R^2 = OBz$; $R^4 = OH$
10 $R^1 = OBz$; $R^2 = R^3 = H$; $R^4 = OH$
11 $R^1 = R^4 = OBz$; $R^2 = R^3 = H$
12 $R^1 = OMe$; $R^2 = R^3 = H$; $R^4 = OBz$
13 $R^1 = OMe$; $R^2 = R^3 = H$; $R^4 = OH$
15 $R^1 = OBz$; $R^2 = R^3 = H$; $R^4 = OMe$
16 $R^1 = OH$; $R^2 = R^3 = H$; $R^4 = OMe$
17 $R^1 = R^4 = OMe$; $R^2 = R^3 = H$

Earlier[16,17] studies on the partial methylation of *C*- and *O*-glycosides with diazomethane, in the presence of stannous chloride as catalyst, have shown similar, high specificity. Intramolecular hydrogen-bonding has been suggested[17] as a probable influence. In the diol **7**, both hydroxyl groups are capable of hydrogen-bond formation. The high yield of the 3-*O*-methyl derivative described above is probably due, in part, to steric reasons. The size of the β-D-benzyl glycoside group and the axial disposition of HO-2 favour methylation at HO-3, which is equatorially situated.

EXPERIMENTAL

I.r. spectra were determined for Nujol mulls. Descending paper chromatography was performed as described previously[5]. Keiselgel 60 (Merck) was used for column

chromatography and silica gel (Merck GF) was used for analytical t.l.c.; compounds were detected by charring with sulphuric acid. Dichloromethane was redistilled from phosphorus pentaoxide before use. Evaporations were carried out at 40° *in vacuo*. All melting points are uncorrected.

Benzyl 3-O-benzoyl-4,6-O-benzylidene-β-D-talopyranoside (**6**). — A solution of benzyl 4,6-*O*-benzylidene-β-D-*lyxo*-hexopyranosidulose 3-benzoate[5] (**5**, 2.8 g) in tetrahydrofuran (45 ml), ethyl acetate (15 ml), and water (5 ml) was cooled to 5° and stirred with neutralised[6] sodium borohydride (0.465 g) over 1 h. The excess reagent was then decomposed with 2% aqueous acetic acid, and the mixture was evaporated *in vacuo* to dryness. Methanol was evaporated several times from the residue, which was then diluted with water (20 ml) and extracted with dichloromethane (3 × 25 ml). The combined extracts were washed with water, dried (Na_2SO_4), and concentrated *in vacuo* to give a white residue which, on recrystallization from propan-2-ol, gave compound **6** (2.49 g, 89%), m.p. 187–188°, $[\alpha]_D^{23}$ −15.5° (*c* 1.73, acetone) (Found: C, 69.9; H, 5.5. $C_{27}H_{26}O_7$ calc.: C, 70.1; H, 5.7%).

Benzyl 4,6-O-benzylidene-β-D-talopyranoside (**7**). — A suspension of the 3-benzoate **6** (0.25 g) in methanol (30 ml) was treated with 2M methanolic sodium methoxide (0.6 ml) at room temperature for 36 h with stirring. The homogeneous solution was neutralised with methanol-washed Dowex-50 (H^+) resin, the solid was filtered off and washed with methanol, and the combined filtrate and washings were evaporated. The crystalline residue was recrystallised from propan-2-ol–methanol to give benzyl 4,6-*O*-benzylidene-β-D-talopyranoside (**7**, 151 mg, 77%), m.p. 168–170°, $[\alpha]_D^{24}$ −68.5° (*c* 1.49, dichloromethane); lit.[5] m.p. 171°, $[\alpha]_D^{20}$ −70°.

With benzoyl chloride–pyridine, in the usual manner, **7** gave the dibenzoate **11** as a non-crystalline foam, $[\alpha]_D^{25}$ −24° (*c* 0.83, methanol) (Found: C, 71.5; H, 5.6. $C_{34}H_{30}O_8$ calc.: C, 72.1; H, 5.3%).

Treatment of **6** *with methyl sulphoxide–phosphorus pentaoxide*[5]. — The benzoate **6** (0.4 g) dissolved in *N*,*N*-dimethylformamide (1.25 ml) and methyl sulphoxide (0.2 ml) was stirred with phosphorus pentaoxide (0.2 g) for 21 h at 65°. The mixture was then poured into ice–water (50 ml) containing sodium hydrogen carbonate (0.4 g), and the solid product was collected, washed thoroughly with water, and dried *in vacuo*. The crude product was recrystallised from propan-2-ol–acetone to give **5** (0.24 g, 61%), m.p. 156–159° (dec.), $[\alpha]_D^{24}$ +63° (*c* 0.5, dichloromethane); lit.[5] m.p. 160–162° (dec.), $[\alpha]_D^{21}$ +67°.

Compound **5** in propan-2-ol–dichloromethane was treated[5] with *p*-nitrophenylhydrazine to give the *p*-nitrophenylhydrazone **8**, m.p. 172–174°, $[\alpha]_D^{24}$ +276° (*c* 0.9, dichloromethane); lit.[5] m.p. 174–175°, $[\alpha]_D^{20}$ +273°.

Benzyl 2-O-benzoyl-4,6-O-benzylidene-β-D-talopyranoside (**10**). — A solution of the 3-benzoate **6** (1.0 g) in acetone (50 ml) was treated with 0.05M sodium hydroxide (50 ml). A precipitate formed immediately, and the mixture was kept for a further 3 min at room temperature, whereupon ice–water (50 ml) was added. The product was collected by filtration, washed well with water, and dried *in vacuo*. The crude product contained (t.l.c.; benzene–ether, 4:1), in addition to a trace of the diol **7**, two

compounds, one of which corresponded to the 3-benzoate **6**. Elution of the mixture from silica gel with benzene and benzene–ether (4:1) gave **6** (0.59 g, 59%), m.p. 185–187°, $[\alpha]_D^{24}$ −13.8° (*c* 1.1, dichloromethane), and the 2-benzoate **10** (0.27 g, 27%), m.p. 181–183°, $[\alpha]_D^{25}$ −61° (*c* 0.6, chloroform) (Found: C, 69.9; H, 5.6. $C_{27}H_{26}O_7$ calc.: C, 70.1; H, 5.7%).

Benzyl 3-O-benzoyl-4,6-O-benzylidene-2-O-methyl-β-D-talopyranoside (**12**). — A solution of compound **6** (0.6 g) in dichloromethane (20 ml) at −15° was treated with boron trifluoride etherate (0.03 ml) and, at the same temperature, diazomethane in dichloromethane was then added until a faint yellow colour presisted for 15 sec. After 2 h at 0°, polymethylene was filtered off, and the filtrate was washed successively with saturated, aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and evaporated. The product was recrystallised from propan-2-ol to yield **12** (0.48–0.52 g, 77–83%), m.p. 173–175°, $[\alpha]_D^{24}$ +31° (*c* 8.0, chloroform) (Found: C, 70.7; H, 6.0. $C_{28}H_{28}O_7$ calc.: C, 70.6; H, 5.9%).

Benzyl 4,6-O-benzylidene-2-O-methyl-β-D-talopyranoside (**13**). — A solution of compound **12** (0.7 g) in methanol (85 ml) was treated with 2M methanolic sodium methoxide (1.2 ml) at room temperature for 27 h with stirring. The solution was neutralised with methanol-washed Dowex-50 (H^+) resin, the solids were filtered off and washed with methanol, and the combined filtrate and washings were evaporated. The crystalline residue was recrystallised from propan-2-ol to give **13** (0.46 g, 84%), m.p. 137–139°, $[\alpha]_D^{24}$ −57° (*c* 4, methanol) (Found: C, 67.9; H, 6.8. $C_{21}H_{24}O_6$ calc.: C, 67.7; H, 6.5%).

2-O-Methyl-D-talose (**1**). — Compound **13** (390 mg) in methanol (100 ml) and glacial acetic acid (1 ml) was hydrogenated exhaustively in the presence of palladium (from 1 g of the oxide). The filtered mixture was concentrated in *vacuo* to give syrupy **1** (200 mg), R_{GAL} 1.97, $[\alpha]_D^{23}$ −4.6° (equil.; *c* 4, water); lit.[1] $[\alpha]_D$ −4°.

With acetic anhydride–pyridine in the usual manner, **1** gave a syrupy tetra-acetate, $[\alpha]_D^{23}$ +62° (*c* 1.8, dichloromethane) (Found: C, 50.3; H, 5.7. $C_{15}H_{22}O_{10}$ calc.: C, 49.7; H, 6.1%).

A solution of **1** (35 mg) in water (1 ml) containing phenylhydrazine (0.1 ml), acetic acid (0.5 ml), and sodium metabisulphite (3 mg) was kept for 2 h at 100°. The yellow, crystalline product was filtered off, and washed successively with 10% acetic acid, water, ethanol, and ether to give D-*lyxo*-hexose phenylosazone (11 mg), m.p. and mixture m.p. 178–183°; the infrared spectrum was identical with that of an authentic sample.

Benzyl 2-O-benzoyl-4,6-O-benzylidene-3-O-methyl-β-D-talopyranoside (**15**). — A solution of compound **10** (1.0 g) in dichloromethane (40 ml) at −15° was treated with diazomethane–boron trifluoride etherate and processed as described for compound **6**. The product was recrystallised from propan-2-ol to yield **15** (0.783 g, 76%), m.p. 164–166°, $[\alpha]_D^{23}$ −47° (*c* 0.72, chloroform) (Found: C, 70.5; H, 6.1. $C_{28}H_{28}O_7$ calc.: C, 70.6; H, 5.9).

Benzyl 4,6-O-benzylidene-3-O-methyl-β-D-talopyranoside (**16**). — Compound **15** was treated with 2M methanolic sodium methoxide, as described above for **12**. The

crystalline residue was recrystallised from ethanol to give **16** (82%), m.p. 134–137°, $[\alpha]_D^{23}$ −77.5° (*c* 2, chloroform) (Found: C, 67.9; H, 6.4. $C_{21}H_{24}O_6$ calc.: C, 67.7; H, 6.5%).

3-O-Methyl-D-talose (**2**). — Exhaustive hydrogenation of **16** (0.4 g), as described above for **13**, gave syrupy **2** (190 mg, 91%), R_{GAL} 2.04, $[\alpha]_D^{24}$ +13°; lit.[3] $[\alpha]_D$ (L isomer) −13.5°.

A portion of the product (100 mg) was dissolved in pyridine (5 ml), treated with *p*-nitrobenzoyl chloride (0.5 g), and kept for 4 days at room temperature and then at 80° for 1 h. Work-up in the usual way gave a tetrakis(*p*-nitrobenzoate), m.p. 246–247° (from propan-2-ol–acetone), $[\alpha]_D^{22}$ +50.5° (*c* 1.2, dichloromethane) (Found: C, 52.6; H, 3.4; N, 6.9. $C_{35}H_{26}N_4O_{18}$ calc.: C, 53.1; H, 3.3; N, 7.1%).

Oxidation of **2** *with manganese dioxide.* — An aliquot part (55 mg) of **2** in water (10 ml) was treated[3] with manganese dioxide and then processed to yield, after chromatography [elution with acetone–ethyl acetate (1:2)], 2-*O*-methyl-D-lyxose (13 mg, 15%) as a gum, $[\alpha]_D^{22}$ −5.8° (equil.; *c* 0.65, water); lit.[3] m.p. 118–119°, $[\alpha]_D$ −6.5°. The product was indistinguishable [t.l.c., butanone–ethyl acetate (1:2)] from an authentic sample of the L isomer.

Treatment of benzyl 4,6-O-benzylidene-β-D-talopyranoside (**7**) *with diazomethane.* — (*a*) *With stannous chloride dihydrate as catalyst.* A solution of compound **7** (0.4 g) in methanol (20 ml) and dichloromethane (20 ml) containing stannous chloride dihydrate (1.5 mg) was cooled to −5° and treated with a solution of diazomethane in dichloromethane. The mixture was stirred at room temperature for 5–7 h; t.l.c. then indicated complete reaction. The solvents were evaporated, and a solution of the residue in chloroform (50 ml) was washed with water (50 ml), dried (Na_2SO_4), and evaporated. The crystalline product was recrystallised from propan-2-ol to give compound **16** (0.37 g, 89%), m.p. and mixture m.p. 133–135°, $[\alpha]_D^{22}$ −76° (*c* 2.4, chloroform).

Benzoylation of **16** gave **15**, which was identical to that prepared earlier.

(*b*) *With boron trifluoride etherate as catalyst.* A solution of compound **7** (0.8 g) in dichloromethane (85 ml) at −15° was treated with boron trifluoride etherate (0.08 ml) and diazomethane, as described above for compound **6**, to yield, after recrystallization (ether–hexane), benzyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-β-D-talopyranoside (**17**; 0.61 g, 71%), m.p. 155–157°, $[\alpha]_D^{23}$ −4.5° (*c* 1, methanol) (Found: C, 67.7; H, 6.9. $C_{22}H_{26}O_6$ calc.: C, 68.4; H, 6.8%).

2,3-Di-O-methyl-D-talose (**3**). — Compound **17** (500 mg) was hydrogenolysed, in the manner described for compound **13**, to give syrupy **3** (250 mg), $[\alpha]_D^{23}$ −9.1° (*c* 4.1, methanol).

To a solution of **3** (200 mg) in pyridine (10 ml) was added freshly recrystallised *p*-nitrobenzoyl chloride (0.75 g). After 78 h at 37°, the product was isolated in the usual manner, and purified by chromatography with butanone–chloroform (4:1) to yield a pale-yellow foam that could not be crystallised; m.p. 85–91°, $[\alpha]_D^{22}$ −5.1° (*c* 0.96, dichloromethane) (Found: C, 53.2; H, 4.2; N, 5.9. $C_{29}H_{35}N_3O_{15}$ calc.: C, 53.1; H, 3.8; N, 6.4%).

ACKNOWLEDGMENTS

The author thanks Professor J. S. Brimacombe for a sample of 2-*O*-methyl-L-talose; Mr. J. Diersmann, Laboratory of Organic Chemistry, University of Nijmegen, for the elemental analyses; and G. Veeneman for technical assistance.

REFERENCES

1 N. A. HUGHES, *Carbohydr. Res.*, 7 (1968) 474–479.
2 J. S. BRIMACOMBE AND A. M. MOFTI, *Chem. Commun.*, (1971) 241–242.
3 J. S. BRIMACOMBE, A. M. MOFTI, AND L. C. N. TUCKER, *J. Chem. Soc., C*, (1971) 2911–2915.
4 G. J. F. CHITTENDEN, *Carbohydr. Res.*, 16 (1971) 495–496.
5 G. J. F. CHITTENDEN, *Carbohydr. Res.*, 15 (1970) 101–109.
6 P. H. BENTLEY AND W. MCCRAE, *J. Org. Chem.*, 35 (1970) 2082–2083.
7 Y. KONDO, *Carbohydr. Res.*, 30 (1973) 386–389.
8 H. HÖNIG AND H. WEIDMANN, *Carbohydr. Res.*, 39 (1975) 374–378.
9 G. J. F. CHITTENDEN AND J. G. BUCHANAN, *Carbohydr. Res.*, 11 (1969) 379–385.
10 S. J. ANGYAL AND G. J. H. MELROSE, *J. Chem. Soc.*, (1965) 6494–6500.
11 E. SORKIN AND T. REICHSTEIN, *Helv. Chim. Acta*, 28 (1945) 1–17.
12 M. GYR AND T. REICHSTEIN, *Helv. Chim. Acta*, 28 (1945) 226–233.
13 R. REBER AND T. REICHSTEIN, *Helv. Chim. Acta*, 28 (1945) 1164–1176.
14 A. C. MAEHLY AND T. REICHSTEIN, *Helv. Chim. Acta*, 30 (1947) 496–507.
15 I. O. MASTRONARDI, S. M. FLEMATTI, J. O. DEFERRARI, AND E. G. GROS, *Carbohydr. Res.*, 3 (1966) 177–183; J. O. DEFERRARI, E. G. GROS, AND I. O. MASTRONARDI, *ibid.*, 4 (1967) 432–434; E. G. GROS AND I. O. MASTRONARDI, *ibid.*, 10 (1969) 318–321; J. O. DEFERRARI, E. G. GROS, AND I. M. E. THIEL, *Methods Carbohydr. Chem.*, 6 (1972) 365–367.
16 M. ARITOMI AND T. KAWASAKI, *Chem. Pharm. Bull.*, 18 (1970) 677–686.
17 G. J. F. CHITTENDEN, *Carbohydr. Res.*, 43 (1975) 366–370.