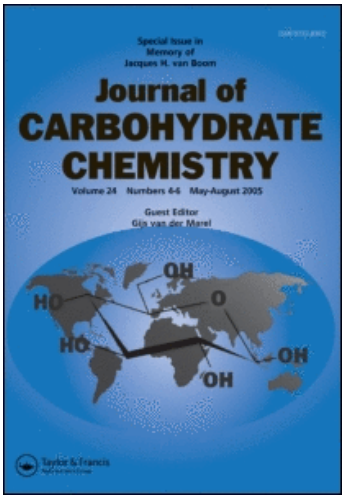

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Accessibility of D-Mannopyranoside Glycosylating Synthons by Acetolysis for Preparations of Oligosaccharide Moieties of N-Linked Glycoproteins

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To cite this Article Shah, Rajan N. , Baptista, José , Perdomo, Guillermo R. , Carver, Jeremy P. and Krepinsky, Jiri J.(1987) 'Accessibility of D-Mannopyranoside Glycosylating Synthons by Acetolysis for Preparations of Oligosaccharide Moieties of N-Linked Glycoproteins', Journal of Carbohydrate Chemistry, 6: 4, 645 — 660
To link to this Article: DOI: 10.1080/07328308708058894
URL: http://dx.doi.org/10.1080/07328308708058894

J. CARBOHYDRATE CHEMISTRY, 6(4), 645-660 (1987)

ACCESSIBILITY OF D-MANNOPYRANOSIDE GLYCOSYLATING SYNTHONS BY ACETOLYSIS FOR PREPARATIONS OF OLIGOSACCHARIDE MOIETIES OF N-LINKED GLYCOPROTEINS

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Received February 19, 1987 - Final Form September 10, 1987

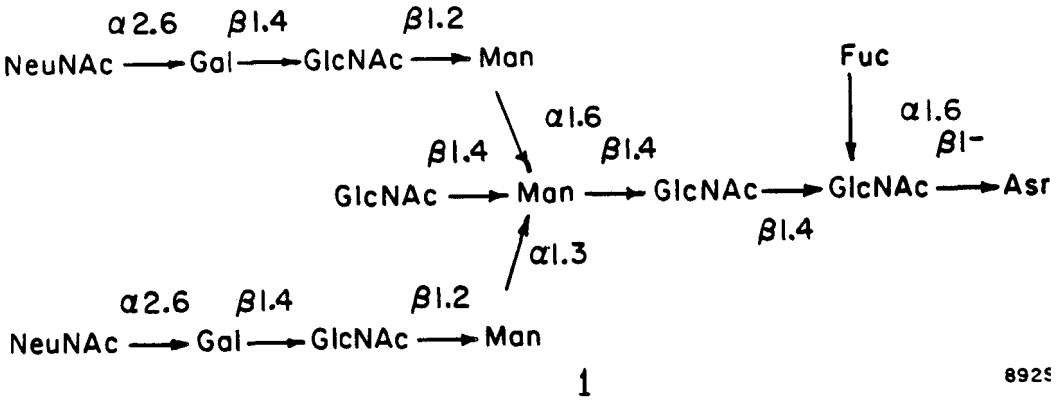
ABSTRACT

Selective acetolysis of methyl 2,3,4,6-tetra-O-benzyl-α-D-mannopyranoside (**2**) allows for easy preparation of 1-acetates of 2,3,4,6-tetra-O-benzyl (**5**), 6-O-acetyl-2,3,4,-tri-O-benzyl-(**6**), 4,6-di-O-acetyl-2,3-di-O-benzyl- (**7**), 3,4,6-tri-O-acetyl-2-O-benzyl- (**8**), and 2,4,6-tri-O-acetyl-3-O-benzyl-D-mannopyranoside (**9**). **8** and **9** formed are separated by preparative HPLC in 30-60g scale. The time course of previously described acetolyses of 3,4,6-tri-O-benzyl- 1,2-O-(1-methoxyethylidene)-β-D-mannopyranose (**3**), and methyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (**4**) giving **9**, 1,2,6-tri-O-acetyl-3,4-di-O-benzyl- (**10**), and 1,2-di-O-acetyl- 3,4,6-tri-O-benzyl- (**11**) α-D-mannopyranose as well **7** have been studied.

INTRODUCTION

Our program, whose objective is a synthesis of a neoantigen carrying oligosaccharide **1**,[2] as well as our NMR studies of conformations of the oligosaccharide moieties of N-linked glycoproteins,[3] depend on the avail-

ability of simpler model oligosaccharides representing fragments of the structure **1** . Any efficient design for syntheses of such fragments requires a number of readily available and appropriately protected derivatives of **D**-mannose and 2-acetamido-2-deoxy-**D**-glucose. In this communication we describe the easy preparation, starting from methyl 2,3,4,6-tetra--O-benzyl-α-**D**-mannopyranoside (**2**), of various combinations of acetyl and benzyl groups on **D**-mannopyranose to be used as glycosylating agents.



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It has been recognized previously[4-6] that mild acidic treatment of methyl glycosides, when O-benzyl groups are present in the molecule, results in the hydrolysis of the 1-O-methyl group, leaving the benzyl groups mostly intact. Acetolysis, on the other hand, causes some benzyl groups (in particular those on primary hydroxyls) to be removed more easily than others,[4-14] thus giving rise to precursors of a variety of potential glycosylating agents. Assuming good control of reaction conditions during acetolysis, the starting benzylated D-mannopyranoside derivatives **2-4** could provide easy access to compounds **5-11**, which find immediate use in oligosaccharide synthesis. In fact, compounds **7**, **9**, and **10** have already been prepared by this approach[6-12] and a generalized acetolysis of benzylated mannosides starting from **3** has been described (e.g.[7] cf Scheme II). Regioselective alkylations[16-21] and reductions of benzylidene acetals[22-24] were also used for preparations of some of the above synthons but they are generally more difficult to scale-up. It is the purpose of this communication to show that the

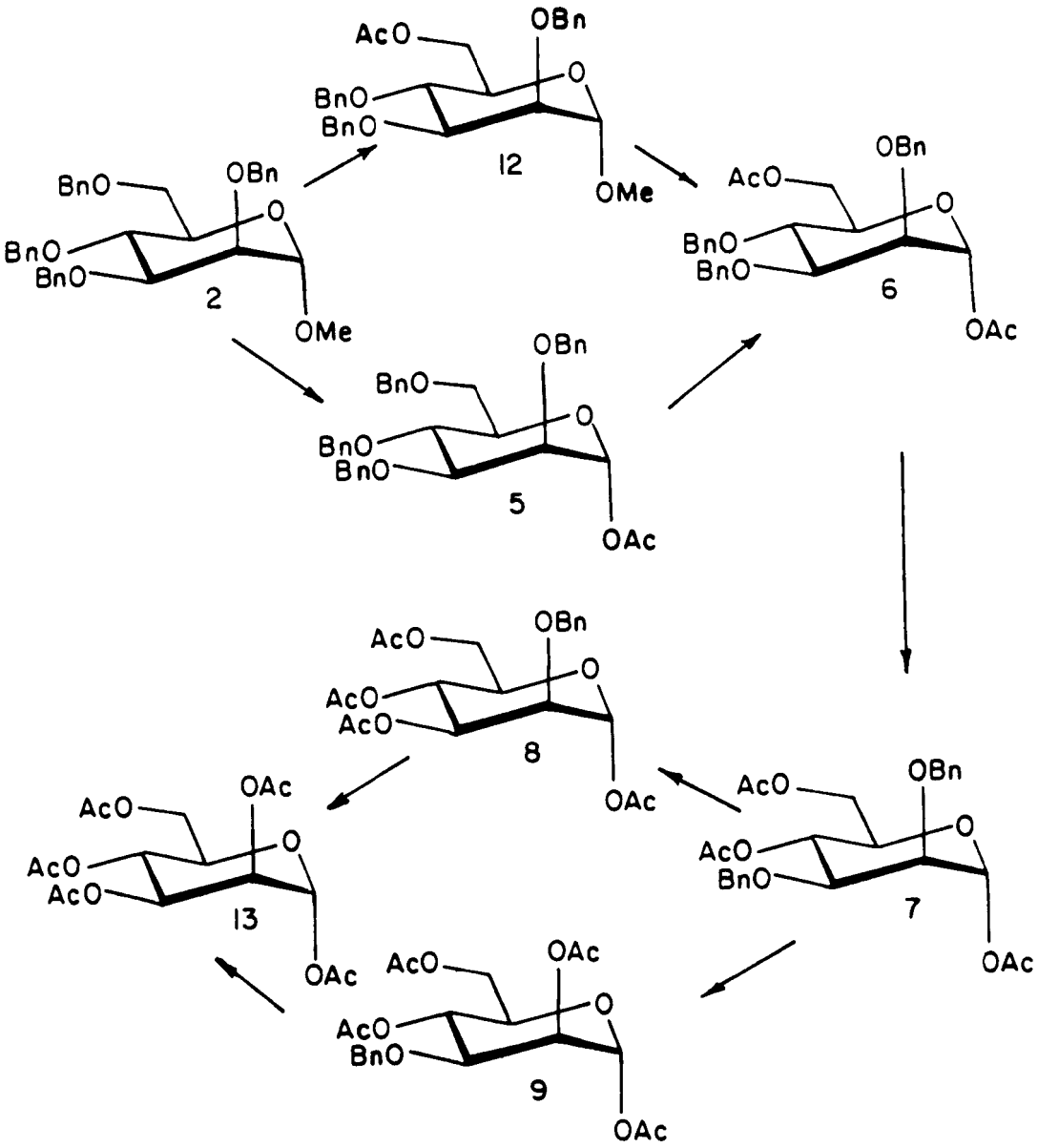
acetolytic conditions can be varied in such a way that the selective formation of a certain product is achieved.

RESULTS AND DISCUSSION

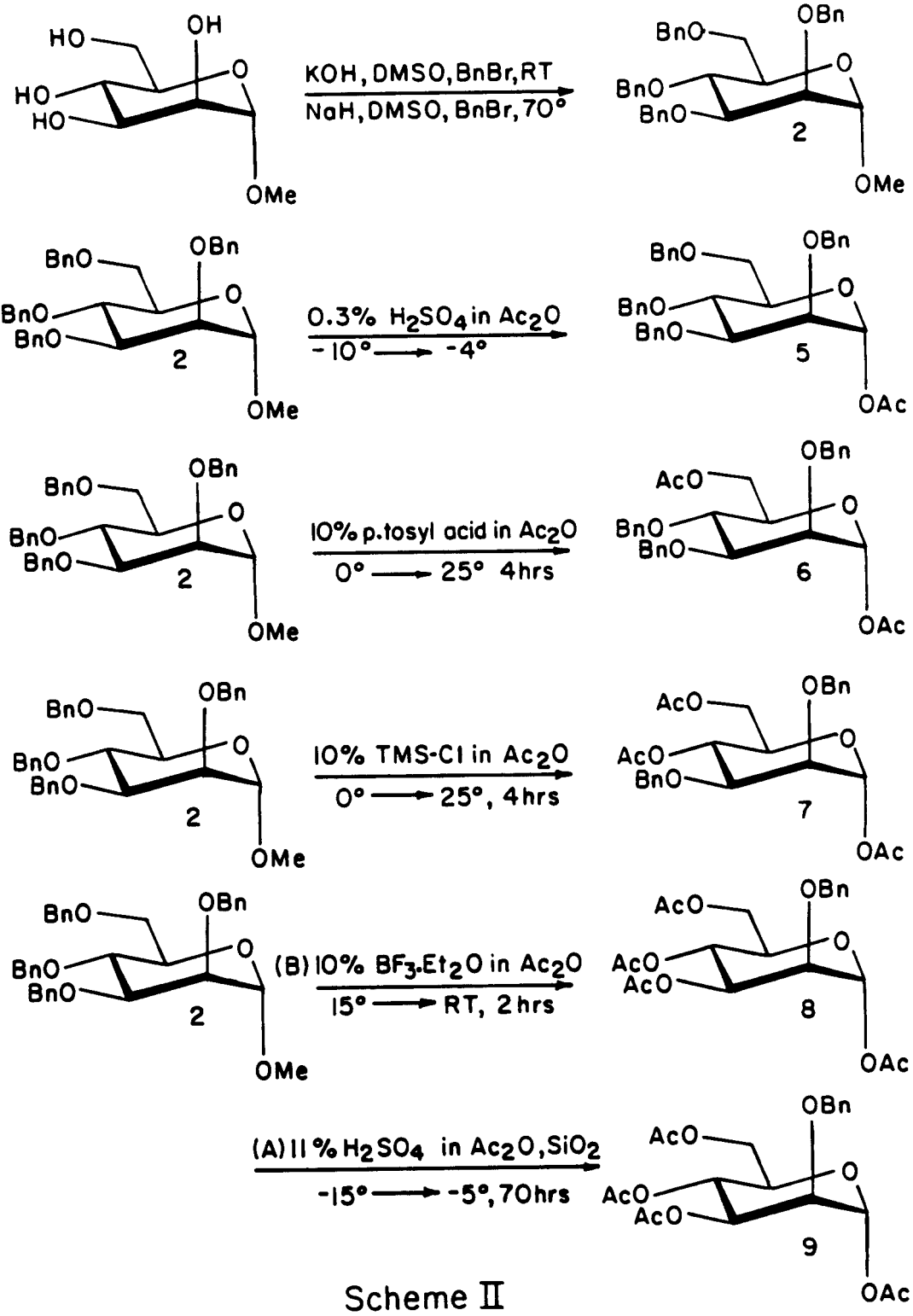
As the starting material for preparations of glycosylating synthons without participating group, the perbenzylated methyl α-D-mannopyranoside (**2**) was chosen since it can be conveniently made from inexpensive commercially available methyl α-D-mannopyranoside by a variation of the described procedure.[6,14,15] Similarly, perbenzylated orthoester **3** is easily accessible by a modification of existing methods.[9] Acetolysis was mainly carried out by acetic anhydride–sulfuric acid, but acetolytic conditions generally varied as to the acid in acetic anhydride (H_2SO_4, $CH_3C_6H_4SO_3H$, $BF_3.Et_2O$, $[CH_3]_3SiCl$, SiO_2), concentration of the acid, and careful temperature control. The sequential product formation starting from **2** is summarized in Scheme I, and the conditions required for the selective formation of a particular product starting from **2** are described in the experimental part (cf. also Scheme II). The relative reactivity of differently located groups follow approximately the order: 1-OMe≥6-OBn> 4-OBn> 3-OBn≈2-OBn, as it was, in part, observed before.[7,9-12]

The products were usually of sufficient purity (90–95%). This was not, however, true in the case of **8** and **9**, and preparative HPLC has been used to separate them and obtain either **8** or **9** in pure state. Using two PrepPak 500 cartridges in series containing about 0.8 kg of silica gel, ten grams of mixtures of **8** and **9** could be handled easily. It should also be noted that under certain conditions 6-OBn is slightly more susceptible to acetolysis than 1-OMe; the difference in reactivity is so small though that it is difficult to take advantage of it preparatively (eg. for the synthesis of **12**).

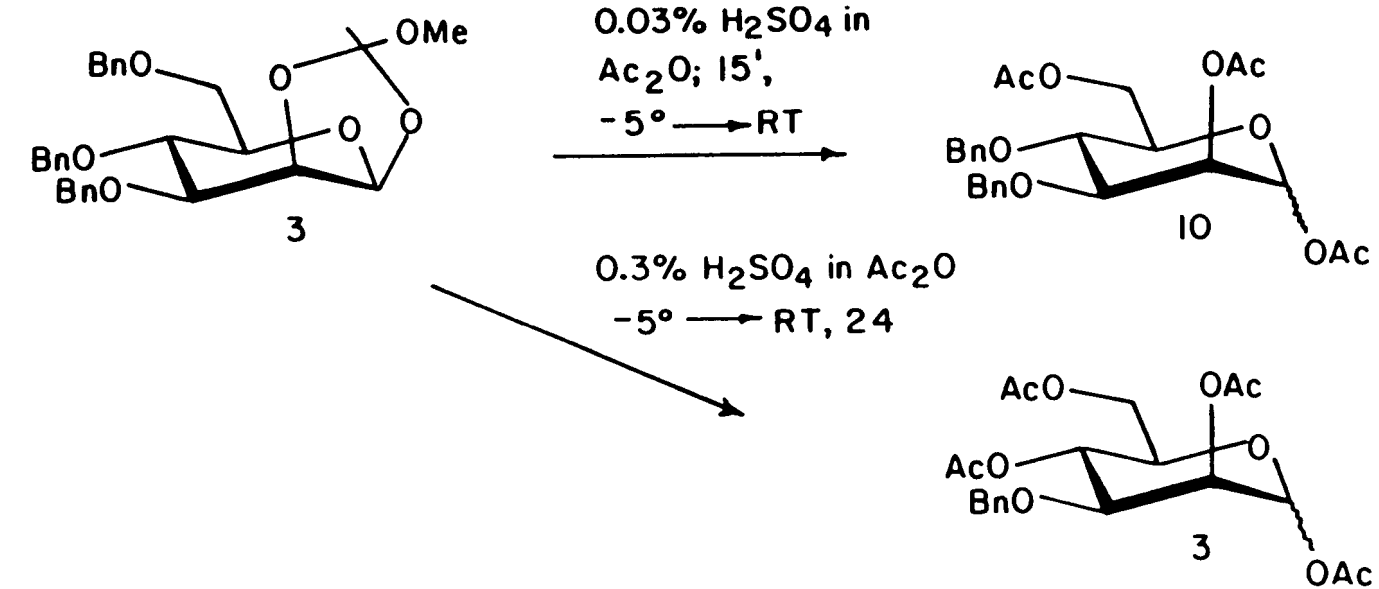
Compounds **7** and **8** or **9** were also obtained by acetolysis of **4** (cf. Scheme III). The overall yield of the synthetic sequence leading to **4** starting from methyl 4,6-O-benzylidene-α-D-mannopyranoside (**14**) is not very high. This is true also for an alternate route of regioselective alkylation[16,25,26] of **14** which after acetolysis leads to **8**. Consequently, the acetolysis of **2** clearly represents a simpler procedure.

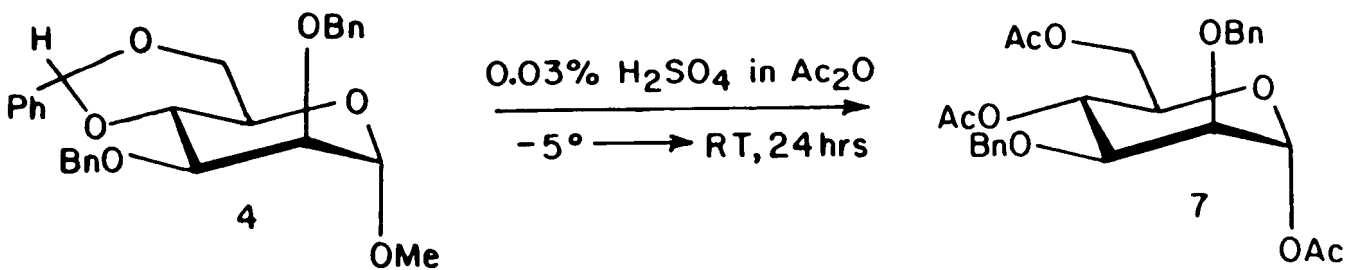


Scheme I



Scheme II





Scheme III

Many naturally occurring oligosaccharides (cf **1**) contain other monosaccharides on C-2 of the D-mannose units, which are bound in the larger oligosaccharide by an α-linkage. 2-O-Acetyl derivatives of a protected mannose would provide both the participating group and the temporary protection required for their synthesis. Consequently acetolysis of **3** can provide 3,4,6,-tri-O-benzyl (**11**),[9] 6-O-acetyl-3,4-di-O-benzyl (**10**),[7,9,10] and 4,6-di-O-acetyl-3-O-benzyl (**9**)[9] derivatives of 1,2-di-O-acetyl-D-mannopyranoside. The tribenzyl derivative **11** showed a pronounced tendency to lose the primary benzyl group (cf. Fig. 3).

We have studied carefully the time-course of various acetolytic conditions in order to ascertain the optimal conditions for the formation of the desired product and its protection against further acetolysis. The tetrabenzyl derivative **2**, for instance, gave **6** within 30 minutes in better than 90% yield and 95% purity, and further acetolysis to **7** proceeded quite slowly (cf. Fig. 1). On the other hand, much more drastic conditions and reaction times were required to obtain **9** from **10** (cf. Fig. 2). The acetolysis of the orthoester **3** to **11** had to be done carefully because of the sensitivity of 6-O-benzyl group (cf. Fig 3), contrary to intuitively expected large difference in acid sensitivity of the orthoester and primary benzyl groups. The stability of **7** under acetolytic conditions of the benzylidene derivative **4** is remarkable and it confirms that 2-O- and 3-O- benzyl groups are the most difficult to remove by acetolysis (cf. Fig. 4).

It seems that compounds having more than one benzyl exhibit a more pronounced sensitivity of these benzyls toward acetolysis (eg. **8** and **9** vs. **7**, as if one benzyl group would render the other one more vulnerable to the attack by the acetoxonium ion. This phenomenon, however, helps to control reactions of polybenzylated compounds more effectively.

In summary, from **2** it can be prepared **5**,[6] **6**, **8**, and **9**; while **9**, **10**, and **11** are easily available from **3**,[7,9] and **7** from **4**.[25] We believe that these procedures simplify syntheses of more complicated oligosaccharides, and we have used them extensively in our laboratory (cf.[27]).

EXPERIMENTAL

General Procedures. Optical rotations were measured with a Perkin-Elmer polarimeter (Model 140) at 26±1 °C. Microanalyses were

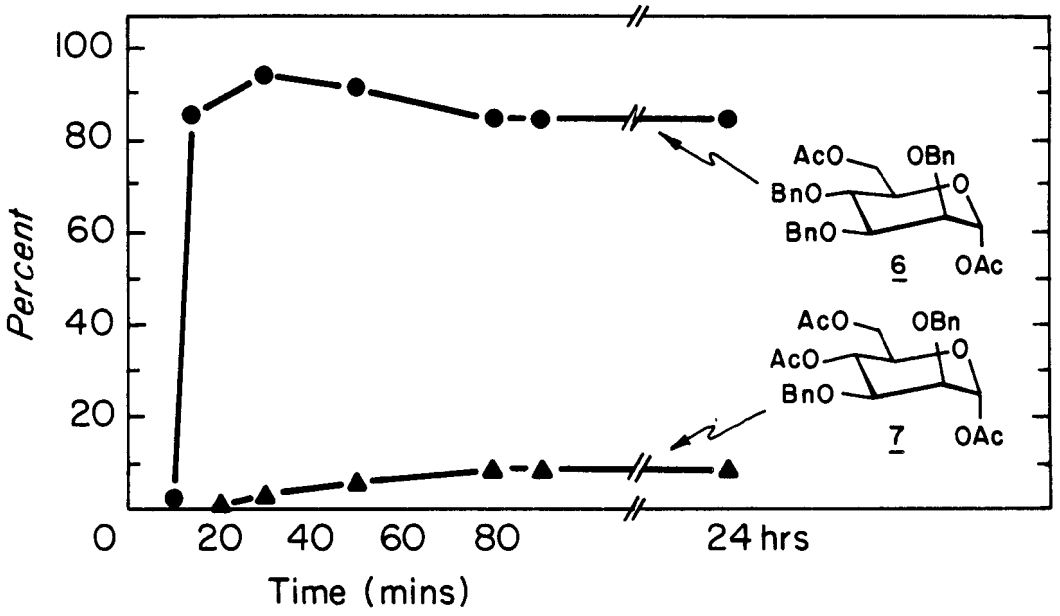


Figure 1. The time course of acetolysis of **2** to **6** and **7**.

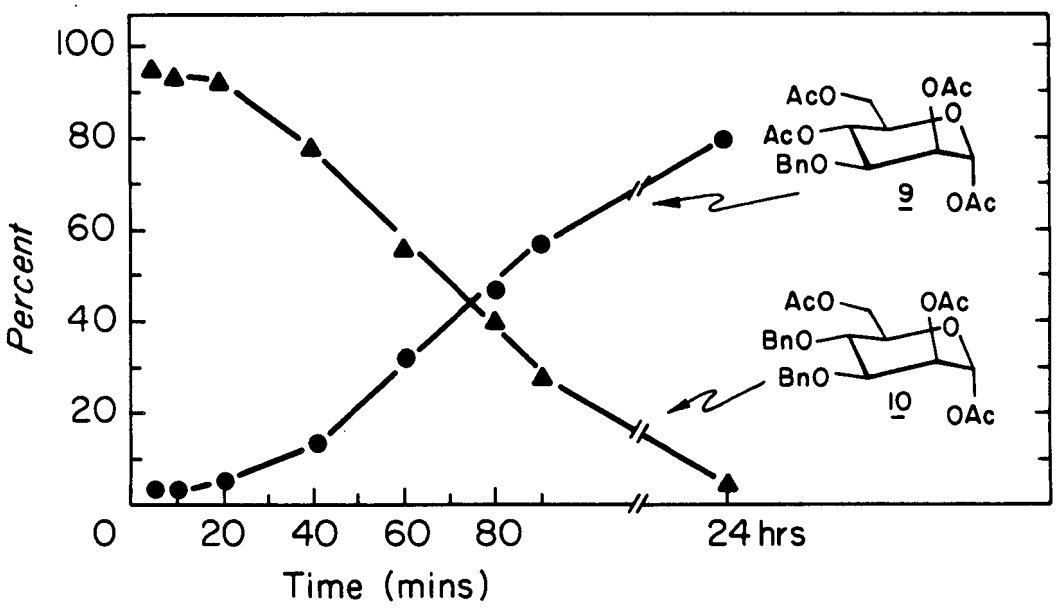


Figure 2. The time course of acetolysis of **10** to **9**.

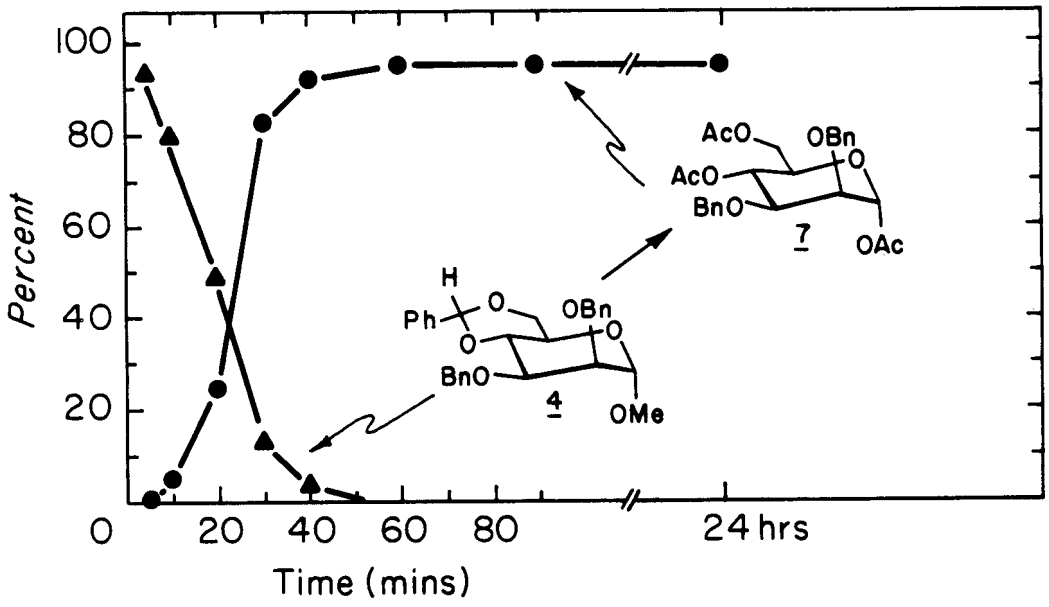


Figure 3. The time course of acetolysis of **3**.

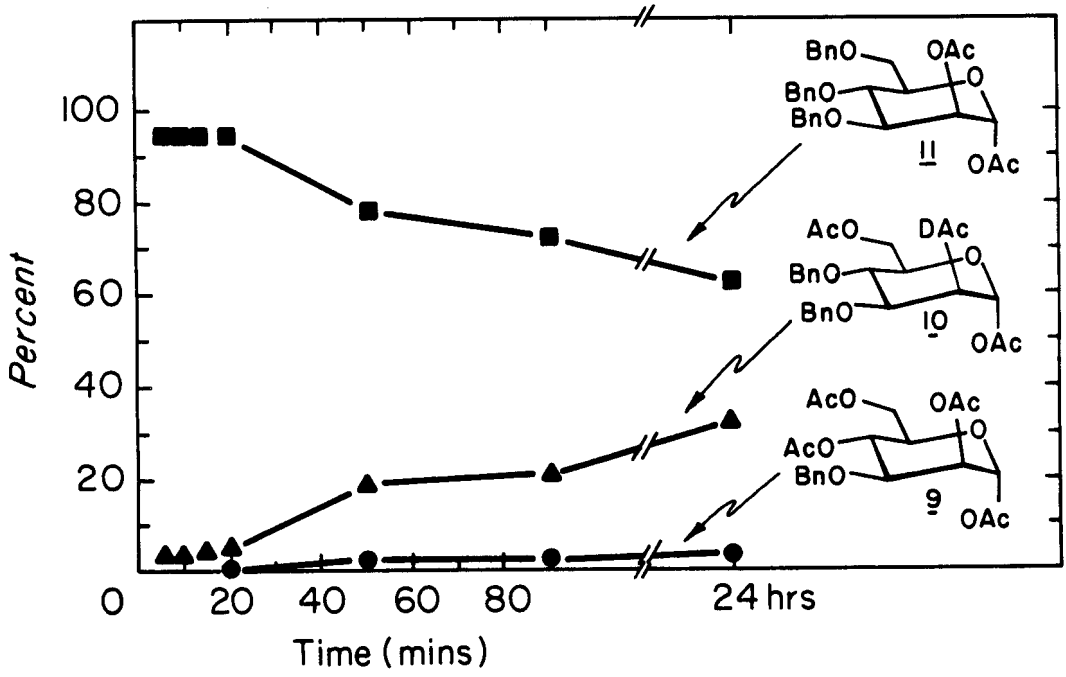


Figure 4. The time course of acetolysis of **4** to **7**.

performed by the Microanalytical Laboratory Ltd., Markham, Ontario. ^1H NMR spectra were recorded at 360 MHz with a Nicolet spectrometer at the NMR Laboratory of the Centre for Determination of Carbohydrate Structures, University of Toronto (Director: Dr. A. A. Grey). They were obtained at 23±2 °C in $CDCl_3$ containing 1%TMS as the internal standard. Infrared spectra were recorded with a Perkin-Elmer (Model 1430) Infrared Spectrometer, and calibrated at 1601 cm^{-1} of polystyrene film using thin films on NaCl plates.

Thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} (Merck) plastic plates and visualized by quenching of ultraviolet fluorescence and/or spraying with 50% aqueous sulfuric acid and heating at 100 °C. Silica gel 60 (230-400 mesh; Merck) was used for flash column chromatography. Analytical HPLC was performed on a μ-Porasil column (30 cm x 3.9 mm i.d., Waters) using either DuPont series 8800 or Beckman Model 324 instruments with a mass detector Model 750/14 (Applied Chromatography Systems, Ltd.). Preparative HPLC used a Magnum 40 column (58 cm x 48 mm i.d., dry packed with silica gel 53μm Partisil Prep 40, Whatman) or two PrepPak 500 Si cartridges in series, with PrepLC/System 500A (Waters). The solvent mixture used in HPLC separations was hexane:ethyl acetate: dichloromethane (7:2:1).

Dimethyl sulfoxide (Fisher) was dried by storing it over 4A molecular sieves and BaO and used without further purification. Dimethyl formamide (Aldrich) was distilled from CaH_2 and stored over 4A molecular sieves prior to use. All other solvents were glass distilled in the laboratory. Solvents from all work-ups were removed at reduced pressure using a rotary evaporator at temperatures not exceeding 40 °C.

All compounds were extensively characterized, but the values are cited only in the case of the compound previously unreported.

Methyl 2,3,4,6-tetra-O-benzyl-α-D- mannopyranoside (2).

a. In a round bottom flask, equipped with a magnetic stirrer, an addition funnel, and an argon inlet, containing dimethyl sulfoxide (250 mL), were placed methyl α-D-mannopyranoside (Aldrich, 10.1 g; 55 mmol) and powdered KOH (35.0 g; 640 mmol). Benzyl chloride (47 mL; 404 mmol) was added slowly at room temperature, and resulting reaction mixture was

stirred overnight (15 h), diluted with ether (200 mL), and washed with water (4x100 mL). After further extraction with hexane (4x50mL), the organic solvent was washed with sat. aq. NaCl solution (50 mL), which was washed with ether (2x50 mL); the organic extracts were dried over $MgSO_4$ and concentrated to dryness to give an oil. Preparative HPLC (hexane: ethyl acetate 9:1) gave 2 (24.3 g, 43.8 mmol, 80%). Other batches gave yields between 66-87%). Physical data agree with those previously published.[6]

b. Using procedure a, methyl α-D-mannopyranoside (10.2 g, 55 mmol), powdered KOH (35.7 g, 640 mmol), and benzyl bromide (48 mL, 400 mmol) in dimethyl sulfoxide (250 mL) gave **2** (25.7 g, 86%) after purification by flash chromatography on a silica gel column. Yields of other batches were between 71-94%.

c. A solution of methyl α-D-mannopyranoside (1.0 g, 5.1 mmol) and NaH (1.7 g, 42 mmol, 60% mineral oil dispersion) in dimethyl formamide (20 mL) was stirred at room temperature for 1 h; the temperature was allowed to reach 70-75 °C and benzyl bromide (5.7 mL, 48 mmol) in dimethyl formamide (5 mL) was added slowly, and the mixture was stirred overnight at the same temperature. After cooling, water was added (50 mL), the resulting solution was extracted with hexane (3x50 mL), the hexane solution was washed with sat. aq. saline solution (25 mL), which was washed with hexane (2x25 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated to dryness. The resulting oil was diluted with ethyl acetate (5 mL), 5% aq. ammonia (15 mL) was added, and the solution was stirred at room temperature for 2 h. The solution was extracted with chloroform (3x25 mL), the chloroform extracts were washed with sat. aq. saline solution (15 mL), which was washed with chloroform (2x12 mL). The combined chloroform extracts were dried over $MgSO_4$, concentrated to dryness, and the residue subjected to chromatography on silica gel yielding **2** (2.9 g, 97%).

General Procedure for Acetolyses. The carbohydrate derivative (15-25 g) was dissolved in acetic anhydride (100-120 mL) and brought to the desired temperature. A solution of an acid (generally sulfuric) in acetic anhydride (150-200 mL) brought to the same temperature was added quickly but not at once under vigorous stirring. The reaction course was followed by TLC on silica gel GF_{258} and in some cases confirmed later by HPLC using

μ-porasil column (aliquots of reaction mixtures were taken at appropriate intervals and after a separate work-up were subjected to HPL chromatography). The reaction was quenched by pouring the reaction mixture onto ice-water, and after neutralization with $NaHCO_3$ the products were exhaustively extracted with $CHCl_3$, and subjected to chromatography on a short column of silica gel.

Acetolysis of methyl 2,3,4,6-tetra-O-benzyl-α-D-mannopyranoside (2) to:

a, 1,6-Di-O-acetyl-2,3,4-tri-O-benzyl-α-D-mannopyranose (6). A solution of **2** (7 g) in acetic anhydride (60 mL) at -4 °C was treated with H_2SO_4 (0.25 mL) in acetic anhydride (30 mL) for 40 min and worked up as described above. The yield of pure **6** was 5.3 g (77%), and it showed in its ^{1}NMR spectrum a signal for H-1 at δ=6.21 ppm (d, $J_{1,2}$=1.9 Hz, 1H).

b, 1,4,6-Tri-O-acetyl-2,3-di-O-benzyl-α-D-mannopyranose (7). To a solution of **2** (0.24 g) in acetic anhydride (1.7 mL) was added trimethylsilyl chloride (neat, 0.22 mL) at 0-5 °C, and the reaction mixture was stirred at room temperature and monitored by TLC. After 48 h it was poured onto ice-water (100 mL), the solution was neutralized with aq. $NaHCO_3$, extracted exhaustively with ether which was subsequently washed with saturated saline, dried over Na_2SO_4, concentrated to dryness, and subjected to chromatography on a silica gel column (hexane-ethyl acetate, 2:1) to give **7** (0.096 g; 45%). The ^{1}H NMR spectrum of **7** gave a signal for H-1 at δ=6.18 ppm (d, $J_{1,2}$=1.9 Hz, 1H).

c, Methyl 6-O-acetyl-2,3,4-tri-O-benzyl-α-D-mannopyranoside (12) accompanied with **6** and **7**. To a solution of **2** (0.38 g) in acetic anhydride (3 mL) containing molecular sieves (3A; 1.33 g) at -20 °C was slowly added a solution of p-toluenesulfonic acid monohydrate (10-20 mg) in acetic anhydride (2 mL), and the reaction mixture was stirred at room temperature and monitored by TLC. After 1-4 h and the work-up as in b, **12** (74 mg; 22%) was obtained together with **7** (46 mg; 13%), and **6** (139 mg; 38%). The ^{1}HNMR spectrum of **12** had a signal for H-1 at δ=4.74 ppm (d, $J_{1,2}$<1 Hz, 1H).

d, 1,3,4,6-Tetra-O-acetyl-2-O-benzyl-α-D-mannopyranose (8) and 1,2,4,6-tetra-O-acetyl-3-O-benzyl-α-D-mannopyranose (9).

d-1, A solution of **2** (0.84 g) in acetic anhydride (0.7 mL) was treated with 10% sulfuric acid in acetic anhydride (0.3 mL) at room temperature for 2 h. Then another portion of 10% sulfuric acid in acetic anhydride (9.7 mL) was added, the resulting mixture was stirred for 24 h, and after work-up and chromatography, **8** (0.31 g; 45%) and **9** (traces) were obtained.

d-2, A solution of **2** (15 g) in acetic anhydride (100 mL) was treated with 2% sulfuric acid in acetic anhydride (160 mL) at room temperature for 48 h giving a mixture (1:1) of **8** and **9** (9.0 g; 66%).

d-3, A solution of **2** (10 g) in acetic anhydride (56 mL) containing SiO_2 (50 g) was treated with 11% sulfuric acid in acetic anhydride (90 mL) at -20 °C to -10 °C, and stirred at room temperature for 1-3 h yielding a mixture of **8** (4.2 g; 63%) and **9** (2.07 g; 31%), separated by HPLC (vide infra).

d-4, A solution of **2** (5 g) in acetic anhydride (68 mL) was treated with $BF_3.Et_2O$ (11 mL) at -30 °C, then warmed to room temperature and stirred for 3 h yielding a mixture of **8** (0.8 g; 24%) and **9** (2.3 g; 68%), separated by HPLC (vide infra).

Preparative HPLC used two cartridges PrepPak 500/Si (30 cm x 5.7 cm i.d.) in series, and as a mobile phase hexane: ethyl acetate: methylene chloride (7:2:1), and a refractive index detector (flow rate:200 mL/min). The monobenzyl tetraacetate **8** had $[\alpha]_D$ +7.8° (c. 1.5, $CHCl_3$); ir (neat) 1748 (CO); ^{1}H NMR δ: 7.30-7.40 (m, 5H, $C_6\underline{H}_5CH_2$), 6.19 (d, 1H, J=1.7 Hz, H-1), 5.48 (t, 1H, J=10 Hz, H-4), 5.19 (dd, 1H, J=10 Hz and 3.5 Hz, H-3), 4.74 (d, 1H, J=12 Hz, $C_6H_5C\underline{H}_2$), 4.60 (d, 1H, J=12 Hz, $C_6H_5C\underline{H}_2$), 4.26 (dd, 1H, J=13 Hz and 5 Hz, H-6'), 4.12 (br d, 1H, J=13 Hz, H-6), 4.02 (m, 1H, H-5), 3.82 (dd, 1H, J=2.4 Hz and 2.6 Hz, H-2), and 2.13, 2.09, 2.04, and 1.99 (4s, 12H, $C\underline{H}_3COO$). Anal. calcd for $C_{21}H_{26}O_{10}$ (438.16): C 57.51, H 5.98; found C 57.62, H 5.81. Compound **9** exhibited[9] in its ^{1}NMR spectrum a signal for H-1 at δ=6.08 ppm (d, $J_{1,2}$=2 Hz, 1H).

3,4,6-Tri-O-benzyl-1,2-O-(1-methoxyethylidene)-β-D-mannopyranose (3). To a solution of powdered KOH (3.70 g) in dimethyl

sulfoxide (12 mL) in a round bottom flask, equipped with a magnetic stirrer, an addition funnel, and an argon inlet, was added 3,4,6-tri-O-acetyl-1,2-O-(1-methoxyethylidene)-β-D-mannopyranose (1. g) and the resulting mixture was stirred at room temperature for 30 min. Benzyl chloride (4.7 mL; 40.4 mmol) was added slowly at room temperature, and the reaction mixture was stirred overnight (17 h). Then water (100 mL) was added, the aq. layer was extracted with ether (3x25 mL) which was subsequently washed with sat. aq. saline solution (25 mL). The latter was extracted with ether (2x25 mL), the combined ethereal extracts were dried over $MgSO_4$ and concentrated to dryness to give a heavy oil, which after chromatography and crystallization from aq. methanol containing a few drops of collidine gave **3**; mp. 75-77 °C, lit.[9] 76-78 °C (1.33 g; 94%). Physico-chemical data agree with those previously published.[9]

Acetolyses of 3,4,6-tri-O-benzyl-1,2-O-(1-methoxy ethylidene) -β-D-mannopyranose (3).

a, A solution of **3** (1 g) in acetic anhydride (20 mL) at -5 °C was treated with a 1% solution of sulfuric acid in acetic anhydride (10 mL) at - 5 °C for 15 min to give **10**; mp. 79-80 °C, lit.[9] 80-81.5 °C (0.6 g; 61%). The ^1H NMR spectrum a signal for H-1 at δ=6.18 ppm (d, $J_{1,2}$=2 Hz, 1H).

b, A solution of **3** (0.5 g) in acetic anhydride (20 mL) cooled to -3 °C was treated with a 2% sulfuric acid in acetic anhydride (10 mL) for 30 min, and then at room temperature for 24 h yielding **9** (0.15 g; 40%).

Acetolysis of methyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (4). A solution of **4** (0.5 g) in acetic anhydride (20 mL) at -5 °C was treated with 1% sulfuric acid in acetic anhydride (10 mL) at -5 °C for 30 min, and then stirred for 24 h at room temperature yielding **7** (0.18 g; 36%).

ACKNOWLEDGEMENTS

This work was in part supported by a grant from the Medical Research Council of Canada (to JPC). Our thanks are due to Dr W. R. Bruce, Director of the Toronto Branch of the Ludwig Institute for Cancer Research for continuous encouragement and interest in this work. Our thanks are also due to Dr A. A. Grey and Mr A. Lee for recording and discussion of the NMR spectra.

REFERENCES AND FOOTNOTES

1. Presented at 12th International Carbohydrate Symposium, Utrecht, The Netherlands, June 1984.

1. H. H. Lee, D. A. Schwartz, J. F. Harris, J. P. Carver, and J. J. Krepinsky, Can. J. Chem., **64**, 1912 (1986).

2. J. P. Carver, D. A. Cumming, and A. A. Grey, Biology of Carbohydrates (R. Ivatt, Ed.). Plenum Press, New York, NY. 1986.

3. C. M. Closkey, Adv. Carbohydr. Chem., **12**, 137 (1957).

4. R. D. Guthrie and J. F. McCarthy, ibid. **22**, 11 (1967).

5. S. Koto, N. Morishima, Y. Miyata, and S. Zen, Bull. Chem. Soc. Japan, **49**, 2639 (1976).

6. R. Eby, S. J. Sondheimer, and C. Schuerch, Carbohydr. Res., **73**,273 (1979).

7. R. Eby, S. J. Sondheimer, and C. Schuerch, Carbohydr. Res., **73**,273 (1979).

8. E. S. H. El Ashry and C. Schuerch, Bull. Chem. Soc. Japan, **59**, 1581 (1986).

9. M. M. Ponpipom, Carbohydr. Res., **59**, 311 (1977).

10. T. Ogawa and K. Sasajima, Carbohydr. Res., **93**, 67 (1981).

11. H. Paulsen, R. Lebuhn, and O. Lockhoff, Carbohydr. Res., **103** , C7 (1982).

12. H. Paulsen and R. Lebuhn, Liebigs Ann. Chem., 1047 (1983).

13. P. J. Garegg and L. Maron, Acta Chem. Scand., **B33**, 39 (1979).

14. S. Koto, S. Inada, N. Morishima, and S. Zen, Carbohydr. Res., **87**, 294 (1980).

15. E. Decoster, J.-M. Lacombe, J.-L. Strebler, B. Ferrari, and A. A. Pavia, J. Carbohydr. Chem., **2**, 329 (1983).

16. F. M. Winnik, J.-R. Brisson, J. P. Carver, and J. J. Krepinsky, Carbohydr. Res., **103**, 15 (1982).

17. R. Eby, K. T. Webster, and C. Schuerch, Carbohydr. Res., **129**, 111 (1984).

18. R. Eby and C. Schuerch, Carbohydr. Res., **100**, C41 (1984).

19. T. Ogawa and M. Matsui, Carbohydr. Res., **62**, C1 (1978).

20. Y. Kondo, K. Noumi, S. Kitagawa, and S. Hirano, Carbohydr. Res., **123**, 157 (1983).

21. M. A. Nashed, Carbohydr. Res., **60**, 200 (1978).

22. A. Lipták, J. Imre, J. Harangi, P. Nánási, and A. Nészmelyi, Tetrahedron, **38**, 3721 (1982).

23. P. J. Garegg, H. Hultberg, and S. Wallin, Carbohydr. Res., **108**,97 (1982).

24. P. J. Garegg, H. Hultberg, and S. Oscarson, J. Chem. Soc. Perkin Trans. I., 2395 (1982).

25. J. G. Buchanan and J. P. C. Schwartz, J. Chem. Soc., 477 (1962).

26. P. J. Garegg, T. Iversen, and S. Oscarson, Carbohydr. Res., **50**, C12 (1976).

27. R. N. Shah, D. A. Cumming, A. A. Grey, J. P. Carver, and J. J. Krepinsky, Carbohydr. Res., **153**, 155 (1986).