Carbohydrate Research, 132 (1984) 119–126
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYNTHESIS OF 2-ACETAMIDO-2-DEOXY-4-*O*-β-D-GALACTOPYRANOSYL-3-*O*-METHYL-D-GLUCOPYRANOSE (*N*-ACETYL-3-*O*-METHYLLACTOSAMINE) AND ITS BENZYL α-GLYCOSIDE*

KHUSHI L. MATTA, RASHMI VIG, AND SAEED A. ABBAS

Department of Gynecologic Oncology, Roswell Park Memorial Institute, New York State Department of Health, 666 Elm Street, Buffalo, New York 14263 (U.S.A.)

(Received February 21st, 1984; accepted for publication, March 17th, 1984)

ABSTRACT

Benzyl 2-acetamido-2-deoxy-3-*O*-methyl-α-D-glucopyranoside (**3**) was obtained by deacetalation of its 4,6-*O*-benzylidene derivative (**2**). Compound **2** was prepared by methylation of benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside with methyl iodide–silver oxide in *N,N*-dimethylformamide. Diol **3** was selectively benzoylated and *p*-toluenesulfonylated, to give the 6-benzoic and 6-*p*-toluenesulfonic esters (**4** and **5**, respectively). Displacement of the sulfonyl group of **5** with sodium benzoxide in benzyl alcohol afforded the 6-*O*-benzyl derivative (**6**). Glycosylation of **4** with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**7**) in dichloromethane, in the presence of 1,1,3,3-tetramethylurea, furnished the disaccharide derivative **8**. Similar glycosylation of compound **6** with bromide **7** gave the disaccharide derivative **10**. *O*-Deacetylation of **8** and **10** afforded disaccharides **9** and **11**. The structure of compound **9** was established by ^{13}C-n.m.r. spectroscopy. Hydrogenolysis of the benzyl groups of **11** furnished the disaccharide 2-acetamido-2-deoxy-4-*O*-β-D-galactopyranosyl-3-*O*-methyl-D-glucopyranose (*N*-acetyl-3-*O*-methyllactosamine).

INTRODUCTION

L-Fucosyltransferases constitute a family of enzymes that are responsible for catalyzing transfer of the L-fucosyl group from GDP-L-fucose to appropriate carbohydrate acceptors. Much of the interest in the study of this class of enzymes has been due to the participation of L-fucose in the antigenic determinants of several human blood-groups[2]. More recently, this interest was enhanced because the possibility that these enzymes are involved in the process of premalignant transformations has been suggested[3].

*Synthetic Studies in Carbohydrates, Part XL. For Part XXXIX, see ref. 1.

0008-6215/84/$ 03.00

Based upon the "one enzyme–one linkage" concept[4], as many as eleven different L-fucosyltransferases are probably required for the synthesis of the various α-L-fucosylic linkages that are widely distributed in mammalian glycoproteins, glycolipids, and oligosaccharides[2].

Of these L-fucosyltransferases, the enzyme β-galactosyl-α-(1→2)-L-fucosyltransferase catalyzes the reaction

$$\text{GDP-Fuc} + \beta\text{-Gal-R} \rightarrow \alpha\text{-Fuc-}(1\rightarrow2)\text{-}\beta\text{-Gal-R} + \text{GDP},$$

where R represents the rest of the blood-group-active molecule. In this context, this enzyme is considered to be responsible for formation of the product having H blood-group activity.

α-L-Fucosyltransferase from various mammalian sources has been studied, and it has also been purified to homogeneity[2]. From those studies, it appears that the acceptor-specificity of this enzyme is largely dependent on its source. For example, of the different saccharides employed for specificity studies on the α-(1→2)-L-fucosyltransferase of porcine submaxillary-gland, the disaccharides β-Gal-(1→3)-GalNAc and β-Gal-(1→3)-GlcNAc were found[2] to be better acceptors for this enzyme than those compounds having the sequence β-Gal-(1→4)-GlcNAc or β-Gal-(1→4)-Glc. By contrast, the last two disaccharides, as well as glycolipids containing these two disaccharide units, were found to be the acceptors of preference for α-(1→2)-L-fucosyltransferase from such other sources as human serum[5] and bovine spleen[6].

It is noteworthy that glycoconjugates containing such carbohydrate units as β-Gal-(1→4)-GlcNAc or β-Gal-(1→4)-Glc are capable of accepting the L-fucosyl group from GDP-L-fucose at two different positions; thus, an L-fucosyl group can be incorporated at either O-2 of the terminal D-galactosyl group, under catalysis by α-(1→2)-L-fucosyltransferase, or O-3 of the 2-acetamido-2-deoxy-D-glucose or the D-glucose residue, under catalysis by a related enzyme, α-(1→3)-L-fucosyltransferase. The two enzyme activities are invariably found together in the same source; for example, human serum[5]. Thus, unless these two activities are free from each other, the identification and isolation of the enzymic product becomes laborious and cumbersome, when such acceptors are employed in the assay procedure.

It therefore seems needless to stress that the availability of some compounds capable of acting as acceptors for a single enzyme, even in the presence of other, related enzymes, would be of particular importance in such studies. For this reason, we initiated a program for the synthesis of a variety of compounds, not only for ascertaining the specificity of L-fucosyltransferases, but also for that of other glycosyltransferases[7]. In furtherance of these efforts, we now describe the synthesis of the title saccharide. It seems reasonable to anticipate that such a compound would act as a specific acceptor for α-(1→2)-L-fucosyltransferase by virtue of its lacking a free hydroxyl group at C-3 of the 2-acetamido-2-deoxy-D-glucose moiety.

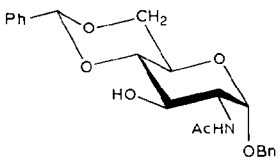
RESULTS AND DISCUSSION

Methylation of benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**1**) with methyl iodide–silver oxide in *N*,*N*-dimethylformamide for 6 h at room temperature, followed by purification by column chromatography, afforded benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-α-D-glucopyranoside (**2**). The structure of **2** was supported by its infrared (i.r.) spectrum, which showed the absence of an absorption for a hydroxyl group, and was further confirmed by its ^{1}H-n.m.r. spectrum, which revealed that a methoxyl group (a three-proton singlet at δ 3.48) had been introduced.

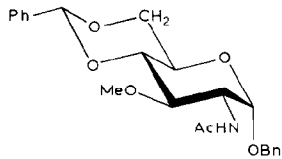
Cleavage of the benzylidene group of **2** with hot, 60% aqueous acetic acid afforded diol **3**, the ^{1}H-n.m.r. spectrum of which, as would be expected, was devoid of any signals attributable to the benzylidene group protons. On treatment of **3** with 1.1 molar equivalents of benzoyl chloride in dichloromethane–triethylamine solution for 3.5 h at about −40° (bath), and processing in the usual manner[8], examination of the crude product by thin-layer-chromatography (t.l.c.) revealed the presence of a major product, faster-migrating than **3**; a faster-migrating contaminant, presumably the 4,6-diester, was also revealed. Purification of the crude mixture in a column of silica by using 30:1 (v/v) chloroform–acetone as the eluant, gave, in 71% yield, the monobenzoate **4**.

Selective *p*-toluenesulfonylation of **3** with *p*-toluenesulfonyl chloride in pyridine furnished the 6-*O*-tosyl derivative (**5**), the sulfonic group of which was readily displaced with sodium benzoxide in benzyl alcohol, to afford benzyl 2-acetamido-6-*O*-benzyl-2-deoxy-3-*O*-methyl-α-D-glucopyranoside (**6**).

Glycosylation of **4** with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**7**) in dichloromethane, in the presence of 1,1,3,3-tetramethylurea, and processing

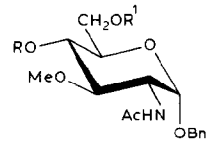


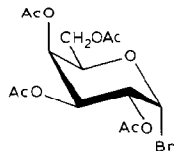
1



2

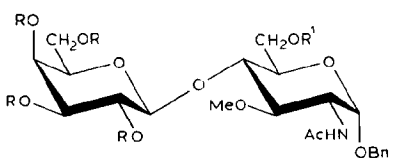
Bn = $PhCH_2$



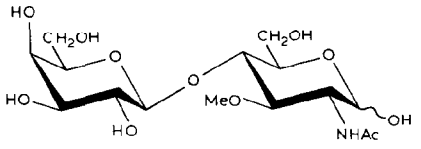


3 R = R^1 = H
4 R = H, R^1 = Bz
5 R = H, R^1 = $SO_2C_6H_4Me$-*p*
6 R = H, R^1 = Bn

7



8 R = Ac, R^1 = Bz
9 R = R^1 = H
10 R = Ac, R^1 = Bn
11 R = H R^1 = Bn



12

in the usual way, gave the crude disaccharide derivative **8**, which, without purification, was subjected to Zemplén transesterification, and the product mixture so obtained stirred for 2 h in a mixture of methanol (8 mL) and chloroform (75 mL). The solid residue was removed by filtration, and the filtrate concentrated, and purified in a column of silica by elution, first, with solvent *D* (to remove a little **3**, resulting from unreacted **4**), and then with 13:6:1 (v/v/v) chloroform–methanol–water, to give (in 50% yield, based on **4**) amorphous disaccharide **9**.

Glycosylation of compound **6** with bromide **7**, followed by processing, and then *O*-deacetylation of the intermediate **10** as described for **4** (to give **8** and **9**), gave a solid residue, which was subjected to column chromatography on silica gel. Elution with solvent *C* removed unreacted **6**. On elution with solvent *D*, evaporation of the fractions corresponding to the desired product, and crystallization of the residue from methanol–ether, afforded, in 56% yield from **6**, disaccharide **11**, the ^{1}H- and ^{13}C-n.m.r. spectra of which (see Experimental section) were in accord with its overall structure.

Hydrogenolysis of the benzyl groups of **11** in the presence of 10% palladium-on-carbon furnished 2-acetamido-2-deoxy-4-*O*-β-D-galactopyranosyl-3-*O*-methyl-D-glucopyranose (*N*-acetyl-3-*O*-methyllactosamine, **12**) as the dihydrate.

EXPERIMENTAL

General methods. — These were the same as those already described[1], except that the following solvent systems (v/v) were used for chromatography: *A*, 15:1 chloroform–acetone; *B*, 20:1 chloroform–acetone; *C*, 5:1 chloroform–acetone; and *D*, 5:1 chloroform–methanol.

Benzyl 2-acetamido-4,6-O-benzylidene-2-deoxy-3-O-methyl-α-D-glucopyranoside (**2**). — A solution of benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**1**, 6 g) and methyl iodide (7 mL) in *N*,*N*-dimethylformamide (80 mL) was stirred for 6 h at room temperature in the presence of freshly prepared silver oxide (12 g). The solid material was then filtered off, using a bed of Celite, and thoroughly washed with *N*,*N*-dimethylformamide, and the filtrate and washings were combined and evaporated to dryness. The residue was suspended in chloroform, the solid material filtered off, the filtrate successively washed with

water, aqueous sodium thiosulfate, and water, dried, and concentrated to a small volume, and the concentrate applied to a column of silica gel. On elution with solvent *A*, and evaporation of the fractions containing the product, crystallization of the residue from chloroform–hexane afforded **2** (3.2 g, 52%); m.p. 252–254°, $[\alpha]_D$ +94.7° (*c* 1.0, chloroform); ν_{max}, no absorption near 3400 cm^{-1} (OH); ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.86 (s, 3 H, NAc), 3.48 (s, 3 H, OMe), 4.84 (d, 1 H, *J* 3.5 Hz, H-1), 5.40 (s, 1 H, PhCH), 7.40 (m, 10 H, aromatic), and 8.40 (d, 1 H, *J* 9 Hz, NH).

Anal. Calc. for $C_{23}H_{27}NO_6$: C, 66.80; H, 6.58; N, 3.38. Found: C, 66.69; H, 6.47; N, 3.15.

*Benzyl 2-acetamido-2-deoxy-3-*O*-methyl-α-*D*-glucopyranoside* (**3**). — A solution of **2** (3 g) in 60% aqueous acetic acid was heated for 1 h at ~100°. The acetic acid was evaporated under diminished pressure, the last traces being removed by co-evaporation with several added portions of toluene. The residue was purified in a column of silica gel by using 8:1 (v/v) chloroform–methanol as the eluant, to give, after recrystallization from methanol–ether, diol **3** (2.8 g, 90%); m.p. 174–175°, $[\alpha]_D$ +182° (*c* 1.0, methanol); ν_{max}^{KBr} 3400–3350 (OH), 1600, 740, and 700 cm^{-1} (aromatic).

Anal. Calc. for $C_{16}H_{23}NO_6$: C, 59.06; H, 7.12; N, 4.30. Found: C, 59.14; H, 7.25; N, 4.36.

*Benzyl 2-acetamido-6-*O*-benzoyl-2-deoxy-3-*O*-methyl-α-*D*-glucopyranoside* (**4**). — To a cold (−40°), stirred solution of **3** (2.2 g, 7 mmol) in dichloromethane (30 mL) containing triethylamine (15 mL) was added a solution of benzoyl chloride (1.13 g, 8 mmol) in dichloromethane (20 mL), dropwise, during 0.5 h. After being stirred for 3 h at −40°, the mixture was allowed to warm to room temperature (0.5 h). It was then successively washed with ice-cold water, ice-cold 1% hydrochloric acid, cold saturated sodium hydrogencarbonate solution, and water, dried, and evaporated under diminished pressure, to yield a syrup which, in t.l.c. (solvent *B*) showed one major, slower-migrating product, together with a faster-migrating, minor product, presumably the 4,6-dibenzoate. The crude product was subjected to column chromatography on silica gel. Elution with 30:1 (v/v) chloroform–acetone removed the faster-migrating product. On elution with solvent *B*, evaporation of the fraction corresponding to the major product afforded, after recrystallization from ethyl acetate–hexane, monobenzoate **4** (1.9 g, 71%); m.p. 163–164°, $[\alpha]_D$ +96.5° (*c* 1.0, chloroform); ν_{max}^{KBr} 3450 (OH), 1720 (ester), 1645 (amide), and 708 cm^{-1} (aromatic); ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.88 (s, 3 H, NAc), 3.50 (s, 3 H, OMe), 7.38–8.15 (m, 10 H, aromatic), and 8.40 (d, 1 H, *J* 8 Hz, NH).

Anal. Calc. for $C_{23}H_{27}NO_7$: C, 64.32; H, 6.35; N, 3.29. Found: C, 64.25; H, 6.53; N, 3.08.

*Benzyl 2-acetamido-2-deoxy-3-*O*-methyl-6-*O*-p-tolylsulfonyl-α-*D*-glucopyranoside* (**5**). — To a cold (0°, bath), stirred solution of **3** (2 g, 4 mmol) in dry pyridine (15 mL) was added *p*-toluenesulfonyl chloride (1.75 g, 6 mmol), and stirring was continued for 8 h at ~0°. A little ice was then added, and the mixture was

stirred for 1 h, and evaporated to dryness, and the residue was dissolved in chloroform; the chloroform solution was successively washed with aqueous sodium hydrogencarbonate and water, dried, and concentrated, and the concentrate was applied to a column of silica gel. On elution with solvent *C*, evaporation of the fractions corresponding to the product afforded compound **5** (2.2 g, 76%); amorphous $[\alpha]_D$ +123.5° (*c* 1, methanol); ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.84 (s, 3 H, NAc), 2.42 (s, 3 H, CH_3), 3.42 (s, 3 H, OMe), 4.66 (d, 1 H, *J* 3 Hz, H-1), 5.50 (d, 1 H, *J* 6 Hz, exhangeable in D_2O, OH), 7.35–7.88 (m, 9 H, aromatic), and 8.20 (d, 1 H, *J* 9 Hz, exchangeable in D_2O, NH).

Anal. Calc. for $C_{23}H_{29}NO_8S$: C, 57.61; H, 6.09; N, 2.92; S, 6.67. Found: C, 57.36; H, 6.18; N, 2.78; S, 6.57.

Benzyl 2-acetamido-6-O-benzyl-2-deoxy-3-O-methyl-α-D-glucopyranoside (**6**)*. — A solution of **5** (2 g) in *N*,*N*-dimethylformamide (18 mL) containing M sodium benzoxide (8 mL) in benzyl alcohol was kept for 1 h at 90°; it was then cooled, concentrated, and diluted with chloroform (200 mL), and the chloroform solution successively washed with aqueous sodium hydrogencarbonate, saturated aqueous sodium chloride, and water, dried, and evaporated to dryness. The residue was then dissolved in 4:1 (v/v) ethanol–water, and the solution treated with charcoal, the suspension filtered, the filtrate concentrated, and the concentrate applied to a column of silica gel. Elution with solvent *C*, and evaporation of the fractions corresponding to the product gave, after recrystallization from ethyl acetate–hexane, compound **6** (1.32 g, 76%); m.p. 145–146°, $[\alpha]_D$ +137.2° (*c* 1, methanol); ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.86 (s, 3 H, NAc), 3.46 (s, OMe), 4.64 (d, 1 H, *J* 3.5 Hz, H-1), 5.36 (d, 1 H, *J* 5.5 Hz, exchangeable in D_2O, OH), 7.35–7.46 (m, 10 H, aromatic), and 8.06 (d, 1 H, *J* 9 Hz, exchangeable in D_2O, NH).

Anal. Calc. for $C_{23}H_{29}NO_6$: C, 66.48; H, 7.04; N, 3.37. Found: C, 66.65; H, 7.12; N, 3.28.

Benzyl 2-acetamido-2-deoxy-4-O-β-D-galactopyranosyl-3-O-methyl-α-D-glucopyranoside (**9**). — To a stirred solution of **4** (1.8 g, 4.2 mmol) and bromide **7** (3.4 g, 8.4 mmol) in dichloromethane (50 mL) was added a solution of 1,1,3,3-tetramethylurea (1.5 mL) in dichloromethane (40 mL). The mixture was then protected from light, and treated with silver trifluoromethanesulfonate (1.6 g), and stirring was continued for 48 h at room temperature. The solids were then filtered off and thoroughly washed with dichloromethane, and the filtrate and washings were combined, successively washed with saturated aqueous sodium hydrogencarbonate and water, dried, and evaporated to dryness, to afford crude disaccharide derivative **8** as a syrup which was utilized in the next step without purification or characterization.

A solution of crude **8** (5.4 g) in absolute methanol (60 mL) was treated with M sodium methoxide (5.5 mL), and the solution was stirred overnight at room tem-

*Subsequently, compound **6** was obtained in 50% yield by reductive ring-opening of the benzylidene group of **2** following a recent procedure of Garegg *et al.*[9].

perature. The base was neutralized with a few drops of glacial acetic acid, the solvent removed under diminished pressure, and small portions of toluene were added to, and evaporated from, the residue, to give a solid, which was stirred for 2 h at room temperature in a mixture of methanol (8 mL), and chloroform (75 mL). The suspended material was then filtered off, and the filtrate evaporated, to give a solid which was purified in a column of silica gel by elution, first, with solvent *D* (to remove compound **3**, resulting from unchanged **4**), and then with 13:6:1 (v/v/v) chloroform–methanol–water, to afford amorphous disaccharide **9** (1.02 g; 50% yield, based on **4**); $[\alpha]_D$ +101.5° (*c* 1, methanol); ν_{max}^{KBr} 3400 (OH), 3300, 1650 (amide), 730, and 700 cm^{-1} (aromatic); ^{1}H-n.m.r. data (CD_3OD): δ 1.96 (s, 3 H, NAc), 3.56 (s, 3 H, OMe), 4.98 (d, 1 H, *J* 3.5 Hz, H-1), and 7.20–7.50 (m, 5 H, aromatic); ^{13}C-n.m.r. data (Me_2SO-d_6): δ 22.37 (NAc), 51.69 (C-2), 57.69 (OMe), 59.53, 59.82 (C-6,6′), 67.56 (C-4′), 67.87 (CH_2Ph), 71.23 (C-2′), 71.45 (C-3′), 73.26, 74.85 (C-5,5′), 76.04 (C-4), 78.32 (C-3), 95.84 (C-1), 103.48 (C-1′), and 168.90 (C=O).

Anal. Calc. for $C_{22}H_{33}NO_{11} \cdot 1.5\,H_2O$: C, 51.35; H, 7.05; N, 2.72. Found: C, 51.33; H, 6.82; N, 2.68.

*Benzyl 2-acetamido-6-*O*-benzyl-2-deoxy-4-*O*-β-*D*-galactopyranosyl-3-*O*-methyl-α-*D*-glucopyranoside* (**11**). — Glycosylation of compound **6** (1.2 g), as described for **4** (to give **8**), furnished crude disaccharide derivative **10** (1.8 g), which was utilized without purification in the next step.

O-Deacetylation of crude **10** (1.8 g), as described for **8** (to give **9**), afforded a solid residue which was purified by column chromatography on silica gel by elution, first, with solvent *C* (to remove unchanged **6**), and then with solvent *D* to give disaccharide **11** (0.9 g; 56% yield, based on **6**); m.p. 196–197° (from methanol–ether), $[\alpha]_D$ +88.3° (*c* 1.3, methanol); ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.88 (s, 3 H, NAc), 3.40 (s, 3 H, OMe), 4.76 (d, 1 H, *J* 3 Hz, H-1), 7.20–7.50 (m, 10 H, aromatic), and 8.15 (d, 1 H, *J* 9 Hz, NH); ^{13}C-n.m.r. data (Me_2SO-d_6): δ 22.35 (NAc), 51.58 (C-2), 57.64 (OMe), 59.76 (C-6′), 67.51 (C-6), 68.10 (CH_2Ph + C-4′), 70.27 (C-2′), 70.84 (C-3′), 73.30 (C-5′), 74.83 (C-5), 76.27 (C-4), 78.02 (C-3), 95.87 (C-1), 103.56 (C-1′), and 168.90 (C=O).

Anal. Calc. for $C_{29}H_{39}NO_{11}$: C, 60.30; H, 6.81; N, 2.43. Found: C, 60.25; H, 6.87; N, 2.32.

*2-Acetamido-2-deoxy-4-*O*-β-*D*-galactopyranosyl-3-*O*-methyl-*D*-glucopyranose* (**12**). — A solution of compound **11** (0.20 g) in glacial acetic acid (25 mL) was shaken under hydrogen at 344.5 kPa (50 lb. $in.^{-2}$) for 48 h at room temperature in the presence of 10% palladium-on-carbon (0.15 g). The suspension was filtered (using a bed of Celite), the filtrate evaporated under diminished pressure, and the residue crystallized from methanol–ether, to furnish disaccharide **11** (70 mg, 43%); m.p. 193–194°, $[\alpha]_D$ +19° (*c* 0.5, water); ν_{max}^{KBr} 3350 (OH) and 1630 cm^{-1} (amide); ^{1}H-n.m.r. data (CD_3OD): δ 2.00 (s, 3 H, NAc), 3.58 (s, 3 H, OMe), and 5.08 (d, 1 H, *J* 3.5 Hz, H-1).

ACKNOWLEDGMENTS

We are grateful to Mr. Conrad F. Piskorz for his valuable technical assistance, and to Mrs. Onda D. Simmons for recording the n.m.r. spectra. We also thank Marie Fox for kindly typing the manuscript. The n.m.r. studies were supported by National Cancer Institute Core Grant CA-16056. This investigation was supported by Grant No. ROI-CA 24051, awarded by the National Institutes of Health.

REFERENCES

1 K. L. MATTA, S. S. RANA, AND S. A. ABBAS, *Carbohydr. Res.*, 131 (1984) 265–272.
2 T. H. BEYER, J. E. SADLER, J. J. REARICK, J. C. PAULSON, AND R. L. HILL, *Adv. Enzymol.*, 52 (1981) 23–176.
3 (a) E. H. HOLMES AND S. HAKOMORI, *J. Biol. Chem.*, 257 (1982) 7698–7703; (b) 258 (1983) 3706–3713.
4 A. HAGOPIAN AND E. H. EYLAR, *Arch. Biochem. Biophys.*, 128 (1968) 422–433.
5 (a) T. PACUSZKA AND J. KOSCIELAK, *Eur. J. Biochem.*, 64 (1976) 499–506; (b) H. SCHENKEL-BRUNNER, M. A. CHESTER, AND W. M. WATKINS, *ibid.*, 30 (1972) 269–277.
6 S. BASU, M. BASU, AND J.-L. CHIEN, *J. Biol. Chem.*, 250 (1975) 2956–2962.
7 C. F PISKORZ, S. A. ABBAS, AND K. L. MATTA, *Carbohydr. Res.*, 131 (1984) 257–263.
8 S. A. ABBAS, J. L. BARLOW, AND K. L. MATTA, *Carbohydr. Res.*, 88 (1981) 51–60.
9 P. J. GAREGG, H. HULTBERG, AND S. WALLIN, *Carbohydr. Res.*, 108 (1982) 97–101.