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# A CONVENIENT SYNTHESIS OF *p*-NITROPHENYL 2-DEOXY-2-(THIOACETAMIDO)-β-D-GLUCOPYRANOSIDE, -GALACTOPYRANOSIDE, AND THEIR 1-THIO ANALOGS AS INHIBITORS OF 2-ACETAMIDO-2-DEOXY-β-D-GLUCOSIDASE

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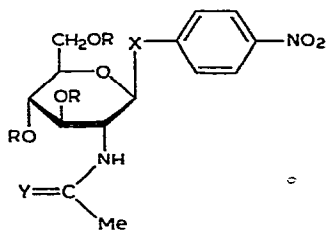
## ABSTRACT

The acetamido group of *p*-nitrophenyl 2-acetamido-2-deoxy-β-D-glucopyranoside, -β-D-galactopyranoside, and their 1-thio analogs was modified by replacement of the amide-carbonyl oxygen atom with sulfur by treatment of their fully acetylated derivatives with phosphorus pentasulfide in pyridine. The resulting *p*-nitrophenyl 2-deoxy-2-thioacetamido-β-D-hexopyranoside triacetates were *O*-deacetylated with catalytic amounts of sodium methoxide in methanol to obtain *p*-nitrophenyl 2-deoxy-2-thioacetamido-β-D-glucopyranoside, -β-D-galactopyranoside, and their 1-thio analogs. These derivatives inhibited 2-acetamido-2-deoxy-β-D-glucosidase from *Turbatrix aceti* to various extents. Also obtained in significant yields in the aforementioned reaction with phosphorus pentasulfide in pyridine were the two hitherto unreported thiazolines, namely, 2-methyl(2-acetamido-3,4,6-tri-*O*-acetyl-α-D-glucopyrano)[2′,1′:4,5]-2-thiazoline and 2-methyl(2-acetamido-3,4,6-tri-*O*-acetyl-α-D-galactopyrano)[2′,1′:4,5]-2-thiazoline.

## INTRODUCTION

Recently, several reports have appeared in the literature concerning the synthesis of, and enzymic studies with, various analogs of *p*-nitrophenyl 2-acetamido-2-deoxy-β-D-glucopyranoside (**1B**), which is commonly employed as a substrate in the assay of 2-acetamido-2-deoxy-β-D-glucosidase[1–6]. In these derivatives, the acetamido methyl group of **1B** was replaced by hydrogen[1,3], or various alkyl[1,3], haloalkyl[2], or aryl[4,5] groups. Many of these derivatives were hydrolyzed by 2-acetamido-2-deoxy-β-D-glucosidase (EC 3.2.1.30) from different sources at a rate considerably lower than that[1–4] for **1B**. However, in these studies, no data were gathered to evaluate the effect of these analogs on the rate of hydrolysis of **1B** by 2-acetamido-2-deoxy-β-D-glucosidase. We considered it of interest to examine the effect on glycosidase activity of the replacement of the amide-carbonyl oxygen atom of **1B** by another hetero atom, namely sulfur. Consequently we have synthesized *p*-nitrophenyl 2-deoxy-2-thio-



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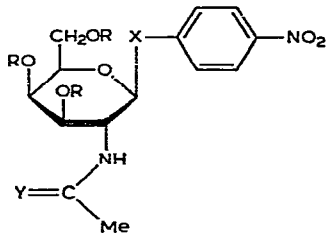

5 X = O, Y = O
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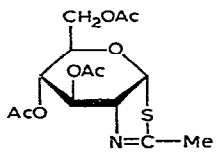
Series A, R = Ac ; Series B, R = H



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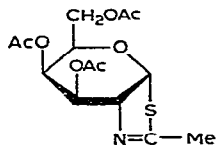

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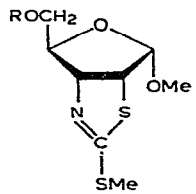

11 R = H
12 R = Ac

acetamido-β-D-glucopyranoside (**2B**), and -galactopyranoside (**6B**), and their 1-thio analogs **4B** and **8B**, respectively. Also reported herein are data on the inhibition of the nematode (*Turbatrix aceti*) 2-acetamido-2-deoxy-β-D-hexosidase[7] by the *p*-nitrophenyl 2-deoxy-2-thioacetamido-β-D-glycosides **2B**, **4B**, **6B**, and **8B**.

## RESULTS AND DISCUSSION

The reaction of 2-acetamido-2-deoxy-β-D-hexopyranosides **1A**, **3A**, **5A**, and **7A** with phosphorus pentasulfide for 2–3 h in boiling pyridine under reflux afforded the corresponding 2-deoxy-2-thioacetamido-β-D-hexopyranosides **2A**, **4A**, **6A**, and **8A** in 50–60% yields. Of the four thioacetamido glycosides, only *p*-nitrophenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-thioacetamido-β-D-galactopyranoside (**6A**) failed to crystallize. The reaction with phosphorus pentasulfide in pyridine has been employed in the carbohydrate field to convert acetamido sugars into thioacetamido analogs, from which the free amino group is then generated by treatment with methanolic ammonia under pressure[8,9]. However, to the best of our knowledge, selective *O*-deacetylation of thioacetamido sugars does not appear to have been attempted. The four acetylated thioacetamido glycosides **2A**, **4A**, **6A**, and **8A** were readily characterized from their i.r. spectra which showed, as expected[10], conspicuous absence of the amide type I band (C=O) near 1660 $cm^{-1}$ that is present in the parent *p*-nitrophenyl 2-acetamido-2-deoxy-β-D-glycosides **1A**, **3A**, **5A**, and **7A**.

The thioacetamido derivatives **2A**, **4A**, **6A**, and **8A** were *O*-deacetylated with catalytic amounts of sodium methoxide in methanol[11], and the crystalline *p*-nitrophenyl 2-deoxy-2-thioacetamido-β-D-glycosides **2B**, **4B**, **6B**, and **8B** were isolated in 84–90% yields. The chromatographic mobility of each thioacetamido glycoside was higher than that of the corresponding parent acetamido derivative in the solvent system employed. The i.r. spectra of each acetamido/thioacetamido pair of compounds were strikingly similar, except as indicated earlier.

In the reaction of the acetylated *p*-nitrophenyl 2-acetamido-2-deoxy-β-D-glycopyranosides **1A**, **5A**, and **7A** with phosphorus pentasulfide in pyridine, significant amounts of a byproduct were formed, which was separated from the thioacetamido glycosides **2A**, **6A**, and **8A** by chromatography on silica gel. The byproduct from the 2-acetamido-2-deoxy-β-D-glycoside **1A**, and -D-galactosides **5A** and **7A**, was characterized from the i.r. spectra as the heretofore unreported thiazoline analogs **9** and **10** of 2-methyl(2-acetamido-3,4,6-tri-*O*-acetyl-α-D-glucopyrano)-[2′,1′:4,5]-2-oxazoline and 2-methyl(2-acetamido-3,4,6-tri-*O*-acetyl-α-D-galactopyrano)[2′,1′:4,5]-2-oxazoline, respectively. In the i.r. spectra of **9** and **10**, there was a band present at 1630 $cm^{-1}$ (C=N), in addition to the ester-carbonyl absorption at 1750 $cm^{-1}$; there was no aromatic or NH absorption. The C=N absorption of the 2-thiazolines would be expected at a frequency lower than that of the 2-oxazolines, for which the absorption is observed[12,13] at 1670 $cm^{-1}$. This would be in keeping with the absorption of ester-carbonyl groups at a frequency higher than that of the analogous thioester carbonyl (-S-C=O) absorption[14]. Goodman has reported[15] that the thiazolines **11** and **12**, which have the C=N group flanked by two sulfur atoms, the C=N absorption occurs at a frequency (1570 $cm^{-1}$) lower than that for **9** and **10**. The *p*-nitrophenyl 2-acetamido-2-deoxy-β-D-hexopyranosides **1A** and **5A** appeared to be more inclined to form the thiazolines **9** and **10**, respectively, than their

TABLE I

INHIBITION OF *Turbatrix aceti* 2-ACETAMIDO-2-DEOXY-β-D-GLUCOSIDASE BY *p*-NITROPHENYL 2-DEOXY-2-THIOACETAMIDO-β-D-GLUCOPYRANOSIDES AND -GALACTOPYRANOSIDES[a]

| *Compound* | *Inhibition (%)* | | |
|---|---|---|---|
| *Inhibitor concentration* | 0.563 mM | 1.125 mM | 2.250 mM |
| **2B** | 44.5 | 53.6 | 68.2 |
| **4B** | 0 | 0.9 | 12.5 |
| **6B** | 55.3 | 68.0 | 82.6 |
| **8B** | 7.4 | 11.8 | 21.9 |

[a]Assays were performed in 0.05M sodium phosphate buffer, pH 4.8 at a substrate (**1B**) concentration of 2.25 mM and 0.031 μg of protein in a total volume of 225 μl. The assay mixtures were incubated for 10 min at 37°. One ml of 0.2 M sodium carbonate was added to terminate the assays, and the amount of *p*-nitrophenol released was determined from the absorbance at 400 nm. Appropriate blanks were set up simultaneously.

1-thio counterparts. This aspect of the work was not pursued further, as the main objective was the synthesis of *p*-nitrophenyl 2-deoxy-2-thioacetamido-β-D-hexopyranosides **2B**, **4B**, **6B**, and **8B**.

The data on the inhibition of *T. aceti* 2-acetamido-2-deoxy-β-D-glucosidase[7] by **2B**, **4B**, **6B**, and **8B** at three different concentrations are given in Table I. Neither the *p*-nitrophenyl 2-deoxy-2-thioacetamido-β-D-glucopyranoside (**2B**) nor the -galactoside (**6B**) was hydrolyzed by the enzyme. It may be seen from data in Table I that the *p*-nitrophenyl 1-thioglycosides **4B** and **8B** are less inhibitory than the 1-oxy analogs **2B** and **6B**, and the D-galactosides **6B** and **8B** are more effective inhibitors than the analogous D-glucosides **2B** and **4B**, respectively. Kanfer and Spielvogel have observed that 2-acetamido-2-deoxy-D-galactono-1,5-lactone was a more effective inhibitor of 2-acetamido-2-deoxy-β-D-glucosidase from bovine serum albumin than was 2-acetamido-2-deoxy-D-glucono-1,5-lactone[16].

## EXPERIMENTAL

*General methods.* — Melting points were determined on a Fisher–Johns apparatus and are uncorrected. Optical rotations were measured at room temperature in a 1-dm cell with a Perkin–Elmer Model 241 automatic polarimeter. I.r. spectra were recorded with a Perkin–Elmer Model 257 spectrophotometer. T.l.c. was performed on plates coated with a 0.25-mm layer of silica gel G (Sigma Chemical Co., St. Louis, Missouri). Visualization was effected both with iodine vapor, and by charring with sulfuric acid. Solvent systems employed for t.l.c. were 25:1 chloroform–methanol for acetylated derivatives and 30:10:1 ethyl acetate–acetic acid–water for deacetylated compounds. Column chromatography was performed on Hi-Flosil (Applied Science Laboratories, State College, Pennsylvania). Evaporations were performed under diminished pressure at <40°. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

p-*Nitrophenyl 3,4,6-tri*-O-*acetyl-2-deoxy-2-thioacetamido-β-D-glucopyranoside* (**2A**). — A solution of *p*-nitrophenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside[17] (**1A**, 0.608 g) and phosphorus pentasulfide (0.290 g) in dry pyridine (12 ml) was boiled for 2 h under reflux with stirring. After the reaction, pyridine was removed by evaporation of toluene from the mixture, chloroform being added as necessary to dissolve the insoluble material. The residual syrup was dissolved in chloroform (25 ml), and the solution was washed successively with water (3 × 10 ml), saturated aqueous sodium hydrogencarbonate (3 × 20 ml), and water (4 × 20 ml). The dried (magnesium sulfate) chloroform solution was evaporated to a syrup (0.536 g) that was chromatographed on a column (2.5 × 27 cm) of silica gel, with chloroform as solvent. Fractions were monitored by t.l.c. and those containing a product ($R_F$ 0.92) migrating faster than **2A** were pooled and processed separately (see later under **9**). Evaporation of the pooled fractions containing **2A** left a crystalline residue, which was triturated with heptane and filtered to yield 0.329 g (52.3%) of light-yellow crystals. Recrystallization from 2-propanol afforded analytically pure **2A**

as a 2-propanol solvate with 93% recovery; m.p. 107–110°, $[\alpha]_D$ −12.8° (*c* 0.23, chloroform); $R_F$ 0.67; $\nu_{max}^{KBr}$ 3280–3210 (NH), 1760 and 1735 (C=O), 1613, 1592, and 1498 (aromatic), 1580 (shoulder, thioamide type II band), 1522 and 1343 ($NO_2$), 1220 (acetate C-O-C), 868, 860, 755, and 742 $cm^{-1}$.

*Anal.* Calc. for $C_{20}H_{24}N_2O_{10}S \cdot 0.75C_3H_8O$: C, 50.46; H, 5.71; S, 6.06. Found: C, 50.61; H, 6.06; S, 6.52.

p-*Nitrophenyl 3,4,6-tri*-O-*acetyl-2-deoxy-1-thio-2-thioacetamido-β*-D-*glucopyranoside* (**4A**). — A solution of **3A** (ref. 18, 0.600 g) and phosphorus pentasulfide (0.277 g) in dry pyridine (12 ml) was boiled for 2 h under reflux, and processed as already described for **2A**. After recrystallization from 2-propanol, pale-yellow crystals (0.372 g, 60%) of **4A** were obtained as a 2-propanol solvate; m.p. 166–167°, $[\alpha]_D$ −9.4° (*c* 0.33, chloroform); $R_F$ 0.75; $\nu_{max}^{KBr}$ 3280 and 3200 (NH), 1750 and 1732 (C=O), 1598 and 1575 (aromatic), 1515 and 1335 ($NO_2$), 1240 (shoulder) and 1220 (acetate C-O-C), 853, 843, 832, and 728 $cm^{-1}$.

*Anal.* Calc. for $C_{20}H_{24}N_2O_9S_2 \cdot C_3H_8O$: C, 49.27; H, 5.75; S, 11.44. Found: C, 49.25; H, 6.01; S, 11.48.

p-*Nitrophenyl 3,4,6-tri*-O-*acetyl-2-deoxy-2-thioacetamido-β*-D-*galactopyranoside* (**6A**). — A mixture of **5A** (ref. 19, 0.560 g, prepared in 48% yield by fusion of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-*β*-D-galactose and *p*-nitrophenol) and phosphorus pentasulfide (0.270 g) in dry pyridine (10 ml) was boiled for 3 h under reflux and processed as described for **2A**. The yield of syrupy **6A**, which could not be crystallized, was 0.278 g (48%). An analytical sample of **6A** was obtained as an amorphous powder from another run; $[\alpha]_D$ +12.0° (*c* 0.35, chloroform); $R_F$ 0.59; $\nu_{max}^{film}$ 3310 and 3220 (NH), 1740 (C=O), 1612, 1590, and 1495 (aromatic), 1550 (amide, type II band), 1620 and 1346 ($NO_2$), 1235 (acetate C-O-C), 868, 853, 765, and 758 $cm^{-1}$.

*Anal.* Calc. for $C_{20}H_{24}N_2O_{10}S$: C, 49.58; H, 4.99; S, 6.62. Found: C, 49.59; H, 5.21; S, 5.98.

Fractions containing a faster-moving component ($R_F$ 0.92) that preceded **6A** from the column of silica gel were pooled and treated separately (see under **10**).

p-*Nitrophenyl 3,4,6-tri*-O-*acetyl-2-deoxy-1-thio-2-thioacetamido-β*-D-*galactopyranoside* (**8A**). — The crystalline glycoside **8A** was obtained as a 2-propanol solvate in 51.8% yield from **7A** (ref. 18, 0.600 g) after the reaction and isolation as just described for **2A**; m.p. 135–137°, $[\alpha]_D$ +20.1° (*c* 0.29, chloroform); $R_F$ 0.68; $\nu_{max}^{KBr}$ 3285 (NH), 1750 and 1738 (C=O), 1595 and 1580 (aromatic), 1538 (amide, type II band), 1515 and 1340 ($NO_2$), 1250 and 1225 (acetate C-O-C), 855, 840, 762, and 745 $cm^{-1}$.

*Anal.* Calc. for $C_{20}H_{24}N_2O_9S \cdot 0.25C_3H_8O$: C, 48.39; H, 5.08; S, 12.44. Found: C, 47.92; H, 4.91; S, 11.83.

Fractions containing a component ($R_F$ 0.92) that eluted from the silica-gel column before **8A** were saved, and treated as described later under **10**.

*2-Methyl*(*2-acetamido-3,4,6-tri*-O-*acetyl*-α-D-*glucopyrano*)[*2',1':4,5*]-*2-thiazoline* (**9**). — Fractions containing the product migrating faster than **2A** (see foregoing

under 2A) were pooled and evaporated to afford the thiazoline **9** as a pale-yellow syrup; yield 0.122 g (28.2%); $R_F$ 0.92 (preponderant), 0.67 (trace, corresponds to 2A). The analytical sample, prepared by rechromatography as described before, had $[\alpha]_D$ −30.8° (*c* 0.27, chloroform). $\nu_{max}^{film}$ 1755 and 1740 (C=O), 1630 (C=N), 1373 (C-$CH_3$), 1250–1220 $cm^{-1}$ (acetate C-O-C), no NH or aromatic absorption.

*Anal.* Calc. for $C_{14}H_{19}NO_7S$: C, 48.69; H, 5.55; S, 9.27. Found: C, 48.42; H, 5.66; S, 9.16.

*2-Methyl-(2-acetamido-3,4,6-tri-*O*-acetyl-α-*D*-galactopyrano)[2′,1′:4,5]-2-thiazoline* (**10**). — The component (**10**) eluted from the column before **6A** (see foregoing preparation of **6A**) was isolated as a pale-yellow syrup by evaporation of appropriate fractions; yield, 0.078 g (19.5%); $[\alpha]_D$ +110.2° (*c* 0.63, chloroform); $R_F$ 0.92; $\nu_{max}^{film}$ 1650 (C=O), 1630 and 1618 (C=N), 1373 (C-$CH_3$), 1250 (shoulder) and 1230 $cm^{-1}$ (acetate C-O-C), no NH or aromatic absorption.

*Anal.* Calc. for $C_{14}H_{19}NO_7S$: C, 48.69; H, 5.55; S, 9.27. Found: C, 48.21; H, 5.30; S, 8.40.

Similarly, the thiazoline **10** was obtained in 9.6% yield from **7A** (see foregoing preparation of **8A**); t.l.c. of this product showed a major spot corresponding to **10**, a minor spot for **8A**, and traces of two additional, slower-migrating ($R_F$ 0.33 and 0.44) components; the i.r. spectrum was essentially identical with that of analytical **10** obtained from **5A**, except for additional absorptions at 1680 (medium), 1550 (shoulder), and 1520 $cm^{-1}$ (weak) in the preparation from **7A**.

p-*Nitrophenyl 2-deoxy-2-thioacetamido-β-*D*-glucopyranoside* (**2B**). — To a solution of **2A** (0.250 g) in dry methanol (2 ml) was added 25 μl of 0.5M sodium methoxide in methanol. After 5 h, the solution was made neutral with methanol-washed Dowex-50 ($H^+$) resin, filtered, and evaporated to dryness. The crystalline residue was triturated with anhydrous ether and filtered to yield **2B** as colorless crystals; yield, 0.158 g (85.4%); m.p. 143–145°, $[\alpha]_D$ +58.9° (*c* 0.29, methanol); $R_F$ 0.62; $\nu_{max}^{KBr}$ 3440–3240 (OH, NH), 1650 ($H_2O$), 1610, 1592, and 1490 (aromatic), 1510 and 1340 ($NO_2$), 1172 (thioamide, type I band[10]), 865, 850, 752, and 735 $cm^{-1}$.

*Anal.* Calc. for $C_{14}H_{18}N_2O_7S \cdot 0.75H_2O$: C, 45.22; H, 5.29; S, 8.62. Found: C, 45.28; H, 5.52; S, 8.78.

p-*Nitrophenyl 2-deoxy-1-thio-2-thioacetamido-β-*D*-glucopyranoside* (**4B**). — Deacetylation of **4A** (0.210 g) as described for **2A** afforded 0.132 g (84.2%) of light-yellow crystals of **4B**; m.p. 160–162°, $[\alpha]_D$ +85.5° (*c* 0.25, methanol); $R_F$ 0.67; $\nu_{max}^{KBr}$ 3480–3220 (OH, NH), 1650 ($H_2O$), 1595 and 1578 (aromatic), 1512 and 1340 ($NO_2$), 1178 (thioamide, type I band[10]), 888, 858, 840, 836, 742, and 735 $cm^{-1}$ (shoulder).

*Anal.* Calc. for $C_{14}H_{18}N_2O_6S_2 \cdot 0.5H_2O$: C, 43.85; H, 4.99; S, 16.72. Found: C, 43.88; H, 5.22; S, 16.43.

p-*Nitrophenyl 2-deoxy-2-thioacetamido-β-*D*-galactopyranoside* (**6B**). — Deacetylation of **6A** (0.278 g) as just described for **2A** yielded pale-yellow crystals of **6B**; yield, 0.174 g (84.5%); m.p. 92–96°, $[\alpha]_D$ +64.0° (*c* 0.25, methanol); $R_F$ 0.55; $\nu_{max}^{KBr}$ 3440–3240 (OH, NH), 1610, 1593, and 1495 (aromatic), 1540 (thioamide, type II

band), 1515 and 1345 ($NO_2$), 1175 (thioamide, type I band[10]), 850, 780 (broad), and 745 $cm^{-1}$.

*Anal.* Calc. for $C_{14}H_{18}N_2O_7S$: C, 46.92; H, 5.06; S, 8.95. Found: C, 46.78; H, 5.16; S, 8.77.

p-*Nitrophenyl 2-deoxy-1-thio-2-thioacetamido-β-*D*-galactopyranoside* (**8B**). — Deacetylation of **8A** (0.200 g) as described for **2A** gave yellow crystals of **8B**; yield, 0.135 g (89.9%); m.p. 111–112°, $[\alpha]_D$ +102.0° (*c* 0.25, methanol); $R_F$ 0.58; $\nu_{max}^{KBr}$ 3460–3240 (OH, NH), 1595 and 1580 (aromatic), 1545 (thioamide, type II band), 1510 and 1340 ($NO_2$), 1175 (thioamide, type I band[10]), 865 (shoulder), 856, 825, 762, and 745 $cm^{-1}$.

*Anal.* Calc. for $C_{14}H_{18}N_2O_6S_2$: C, 44.91; H, 4.85; S, 17.13. Found: C, 44.77; H, 4.91; S, 16.93.

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REFERENCES

1 K. YAMAMOTO, *J. Biochem. (Tokyo)*, 73 (1973) 631–635.
2 K. YAMAMOTO, *J. Biochem. (Tokyo)*, 73 (1973) 749–753.
3 M. VAFINA AND N. V. MOLODTSOV, *Carbohydr. Res.*, 47 (1976) 188–194.
4 M. G. VAFINA, N. V. MOLODTSOV, AND L. I. FEDOREEVA, *Carbohydr. Res.*, 44 (1975) 142–149.
5 M. G. VAFINA AND N. V. MOLODTSOV, *Carbohydr. Res.*, 32 (1974) 161–164.
6 T. MEGA, T. IKENAKA, AND Y. MATSUSHIMA, *J. Biochem. (Tokyo)*, 71 (1972) 107–114.
7 G. S. BEDI, R. H. SHAH AND O. P. BAHL, *Abstr. Joint Meet. Am. Chem. Soc. and Chem. Inst. Can. 2nd*, Montreal, Can., May 29–June 2, 1977, Abstr. CARB-29.
8 K. A. WATANABE, J. BERÁNEK, H. A. FRIEDMAN, AND J. J. FOX, *J. Org. Chem.*, 30 (1965) 2735–2739.
9 M. L. WOLFROM AND M. W. WINKLEY, *J. Org. Chem.*, 33 (1968) 4227–4231.
10 K. NAKANISHI, *Infrared Absorption Spectroscopy*, Holden–Day, Inc., San Francisco, 1962, p. 54.
11 A. THOMPSON, M. L. WOLFROM, AND E. PACSU, *Methods Carbohydr. Chem.*, 2 (1963) 215.
12 C. D. WARREN AND R. W. JEANLOZ, *Carbohydr. Res.*, 53 (1977) 67–84.
13 K. L. MATTA AND J. J. BARLOW, *Carbohydr. Res.*, 53 (1977) 47–56.
14 Ref. 10, pp. 44, 46.
15 L. GOODMAN, *Methods Carbohydr. Chem.*, 6 (1972) 277.
16 J. N. KANFER AND C. H. SPIELVOGEL, *Biochim. Biophys. Acta*, 327 (1973) 405–411.
17 J. FINDLAY, G. A. LEVVY, AND C. A. MARSH, *Biochem. J.*, 69 (1958) 467–476.
18 C. S. JONES, R. H. SHAH, D. J. KOSMAN, AND O. P. BAHL, *Carbohydr. Res.*, 36 (1974) 241–245.
19 J. L. BOSE, R. H. SHAH, AND O. P. BAHL, unpublished results.