*Carbohydrate Research*, 84 (1980) 53–60
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

# SYNTHESIS OF *O*-α-L-FUCOPYRANOSYL-(1→3)-*O*-β-D-GALACTOPYRANOSYL-(1→4)-D-GLUCOSE (3′-*O*-α-L-FUCOPYRANOSYLLACTOSE), AND AN IMPROVED ROUTE TO ITS β-(1″→3′)-LINKED ISOMER

HANS H. BAER AND SAEED A. ABBAS
*Department of Chemistry, University of Ottawa, Ottawa K1N 9B4 (Canada)*
(Received October 10th, 1979; accepted for publication, November 30th, 1979)

ABSTRACT

Isopropylidenation of lactose with 2,2-dimethoxypropane in *N*,*N*-dimethylformamide at 80–85° gave a 1:2 mixture of the kinetically favored 4′,6′-acetal **1** and the thermodynamically more-stable 3′,4′-acetal **2**, which were separated by chromatography. The 1,2,3,6,2′,6′-hexaacetate (**3**) and the 1,2,3,6,2′,6′-hexabenzoate (**4**) of **2**, as well as the corresponding, deacetonated esters **5** and **6**, were prepared by standard procedures. Condensation of 1,2,3,6,2′,6′-hexa-*O*-acetyl-α,β-lactose (**5**) with 2,3,4-tri-*O*-benzyl-L-fucopyranosyl bromide by the method of bromide-ion catalysis gave the α-(1″→3′)-linked, protected trisaccharide **8**. Deacetylation followed by hydrogenolytic removal of the benzyl groups afforded the title trisaccharide **10**. The hexaacetate **5** was also condensed with 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide, under Koenigs–Knorr conditions, which provided an improved route to the corresponding, β-(1″→3′)-linked trisaccharide.

## RESULTS

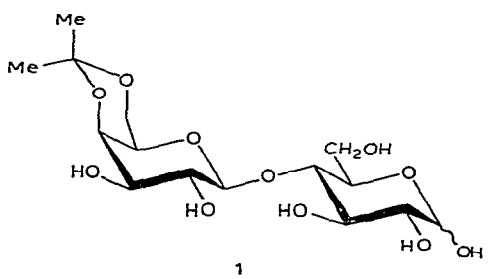
Previous papers in this series described the synthesis of 3′-*O*-β-L-fucopyranosyllactose[1] and 6′-*O*-α-L-fucopyranosyllactose[2]. In continuation of this work, we have now prepared a new isomer, namely, 3′-*O*-α-L-fucopyranosyllactose (**10**). These synthetic trisaccharides should be of interest to biochemists because of the occurrence of closely related fucosyl-oligosaccharides in human milk which contains[3], *inter alia*, the 2′-*O*- and 3-*O*-α-L-fucopyranosyl derivatives of lactose. The synthetic products should be potentially useful, for example, in blood-group research where they might serve as probes in immunochemical studies of combining-sites on antibodies and lectins that show specificity for L-fucose[4].

In an earlier article[1], we recorded the reaction of lactose with 2,2-dimethoxypropane in *N*,*N*-dimethylformamide containing 0.1% (w/v) of *p*-toluenesulfonic acid, performed under mild conditions (3 h at ~25°). The procedure was essentially that of acetonation as previously applied to numerous monosaccharides by Evans *et al.*[5] and Hasegawa *et al.*[6–8], who found it to be kinetically controlled in many cases. The product, obtained in 76% yield, consisted mostly of 4′,6′-*O*-isopropylidene-

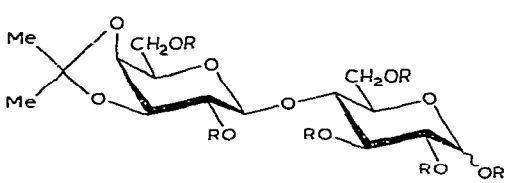
0008-6215/80/0000–0000/$ 02.25, 

α,β-lactose (**1**) together with a minor proportion of an unidentified by-product that could be removed by column chromatography. In the present study, the by-product was isolated crystalline and, by permethylation and subsequent hydrolysis producing 2,6-di-*O*-methyl-D-galactose, shown to be the isomeric 3,4-acetal (**2**). Acetonation of lactose, performed with the same reagent but at[7] 80–85° for 45 min, gave a similar yield of an acetal mixture in which **2** was now the major, and **1** the minor, component. Column-chromatographic separation then furnished the pure isomers in yields of 45 and 21%, respectively. Crystalline **2** apparently was a mixture of anomers (as was[1] **1**); the n.m.r. spectrum showed a 3.5-Hz doublet for the α anomer, but with an intensity considerably less than that expected for 1 proton, and although the signal for H-1β could not be discerned because of crowding in the adjoining, upfield region, a small upward mutarotation of **2** in water solution suggested the initial presence of the β anomer in excess of its equilibrium proportion.

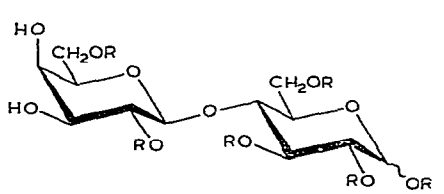
The result just described tends to indicate that, at least with lactose, elevated temperature causes thermodynamic control to prevail in this method of acetonation.




1

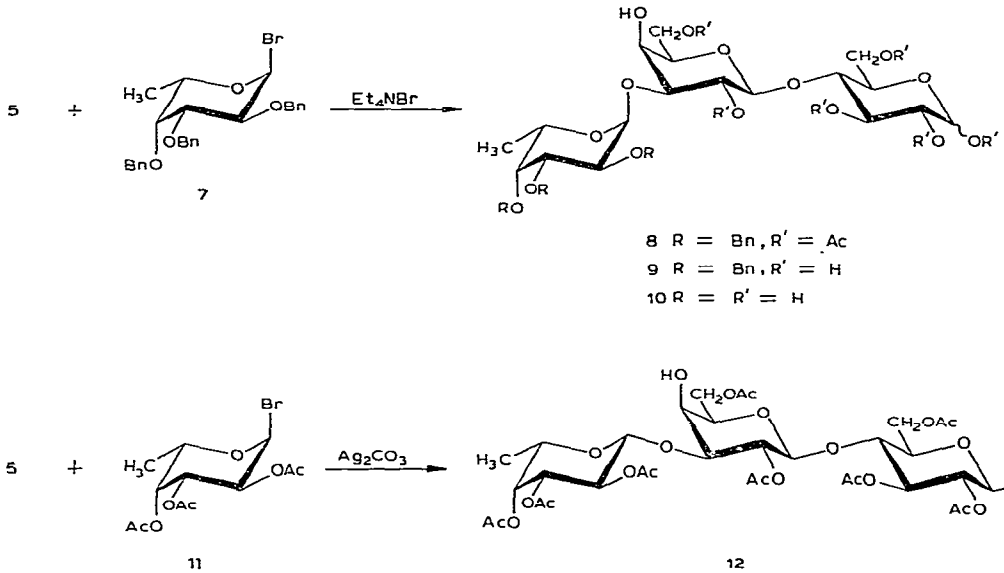



2 R = H (α,β anomers)
3 R = Ac (mainly β anomer)
4 R = Bz (mainly α anomer)




5 R = Ac
6 R = Bz

This fact does not seem surprising; but it is noteworthy that Kiso and Hasegawa[8], having examined the behavior of D-glucose in the same reaction, attributed to kinetic control not only the pyranose 4,6-acetal that they obtained at ~20°, but also the various furanoid and open-chain acetals formed at 95°. It is also interesting to contrast the formation of **1** and **2** with other, recent observations. When the kinetic acetonation of sugars with alkyl isopropenyl ethers, elaborated by Gelas and Horton[9], was applied[10a] to lactose, the 4′,6′:2′,6-diacetal was produced. Acetonation with *neat* 2,2-dimethoxypropane at reflux temperature gave[10b] a tetra-acetal.




Treatment of **2** with boiling acetic anhydride in the presence of sodium acetate gave 90% of a crystalline 1,2,3,6,2′,6′-hexaacetate (**3**) which, on the basis of its relatively low dextrorotation ($[\alpha]_D$ +22.8°) and a prominent, 8-Hz doublet for H-1 in the n.m.r. spectrum, was judged to be composed mainly of the β anomer. However, some of the α anomer was also present, as evidenced by a less-intense, 3.7-Hz doublet occurring at lower field. Benzoylation of **2** with benzoyl chloride in pyridine gave in 91% yield the corresponding hexabenzoate (**4**), evidently as the α anomer ($[\alpha]_D$ +58.1°, $J_{1,2}$ ~4 Hz). Deacetonation[11] of **3** and **4** with 90% trifluoroacetic acid readily furnished crystalline 1,2,3,6,2′,6′-hexa-*O*-acetyl-α,β-lactose (**5**) and the corresponding hexabenzoate (**6**), respectively.

The hexa-*O*-acetyllactose **5** was condensed with 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide[12,13] (**7**) by the method of bromide-ion catalysis according to Lemieux and co-workers[13]. The major reaction-product (**8**), isolated crystalline in 42.5% yield after column chromatography, contained a trace of a second component that could readily be removed by recrystallization. Zemplén deacetylation of **8**, followed by hydrogenolytic debenzylation of the resulting, crystalline tri-*O*-benzyl trisaccharide (**9**), furnished in high yield the title compound (**10**) as an amorphous

powder that was pure according to t.l.c. and microanalysis. The constitution of **10** was verified by permethylation as described for the isomers obtained earlier[1,2]; the 2,4,6-tri-*O*-methyl-D-galactose thereby produced proved indistinguishable from an authentic sample.

As the hexaacetate **5** had become conveniently accessible, we decided to condense it also with 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide[14] (**11**) in a Koenigs–Knorr reaction. Under the conditions employed (see Experimental), 50% of **5** remained unchanged and was recovered by means of chromatography; the part that did react gave, in 82% yield, the crystalline nonaacetate (**12**) of 3′-*O*-β-L-fucopyranosyllactose. It was identical with the condensation product that had arisen[1], through an accompanying acetyl migration, from condensation of **11** with the 1,2,3,6,2′,3′-*O*-acetyl isomer of **5**. The present approach to **12** (and hence, to the free trisaccharide[1]) is no doubt superior.

## EXPERIMENTAL

*General methods.* — These were the same as those previously employed[1]. Optical rotations were measured at ~25°. Unless otherwise indicated, n.m.r. spectra were taken from solutions in chloroform-*d* containing tetramethylsilane as the internal standard. The following solvent combinations (v/v) were used for t.l.c. and column chromatography, unless stated otherwise: (*A*) 8:1 chloroform–methanol, (*B*) the same, 7:1, (*C*) the same, 4:1, (*D*) the same, 3:1, (*E*) the same, 2:1, (*F*) 3:2:1 ethyl acetate–2-propanol–water, (*G*) 1:2 petroleum ether (b.p. 30–60°)–ether, (*H*) the same, 1:5, (*I*) 1:1 toluene–methanol, and (*J*) the same, 10:1.

*4-O-(3,4-O-Isopropylidene-β-D-galactopyranosyl)-α,β-D-glucopyranose* (**2**). — Anhydrous lactose (25 g) was stirred at 80–85° in *N*,*N*-dimethylformamide (250 mL). *p*-Toluenesulfonic acid monohydrate (250 mg) was added, followed by 2,2-dimethoxypropane (18 g) in three portions at 5-min intervals. The lactose gradually dissolved within ~30 min, and the solution was kept at 80–85° for an additional 15 min. It was then cooled, and triethylamine (5 mL) was added. Evaporation of the solvent, with coevaporation of added toluene (bath temperature, 50°), gave a residue showing, in t.l.c. (solvent *E*), a strong spot of *O*-isopropylidenelactoses ($R_F$ 0.3) together with weak spots of unchanged lactose ($R_F$ ~0.1) and of unidentified components ($R_F$ 0.6 and 0.9). The product was chromatographed on a column of silica gel (250 g) by means of solvent *A*. The effluent containing the main products gave, on evaporation, an amorphous material (21 g, ~75%) which was shown by t.l.c. (solvent *F*) to be a mixture of the 3′,4′-acetal **2** (major product, $R_F$ ~0.5) and 4′,6′-acetal **1** (minor product, $R_F$ ~0.3). Rechromatography on a similar column using solvent *F* as the eluent accomplished separation to give **2** (12.6 g, 45%), a mixed fraction (0.6 g, 2%), and **1** (5.9 g, 21%). Compound **2** was recrystallized from 2-propanol–ethyl acetate; m.p. 85–87°, $[\alpha]_D$ +60.3 (15 min)→+65° (19 h, final; *c* 1.8, water); n.m.r. (100 MHz in $CD_3OD$): δ 5.10 (d, ~0.5 H, $J_{1,2}$ 3.5 Hz, H-1α), 1.47 and 1.32 (2 s, 3 H

each, $CMe_2$). By comparison, **1** showed the same H-1 signal, but the $CMe_2$ singlets were at δ 1.47 and 1.40.

*Anal.* Calc. for $C_{15}H_{26}O_{11}$ (382.4): C, 47.12; H, 6.85. Found: C, 46.94; H, 6.77.

A sample of **2** was permethylated and subsequently hydrolyzed as previously described[1] for **1**. 2,6-Di-*O*-methyl-D-galactose was identified by direct comparison with authentic samples of the 2,6- and 2,3-dimethyl ethers, which are clearly differentiated by t.l.c. with solvent *B*.

In the earlier report[1] on the preparation of **1**, a by-product that migrated marginally faster than the main product was mentioned. In a repetition of that work using 30 g of lactose, the by-product (3 g) has now been isolated by means of the aforedescribed, chromatographic technique. It proved identical with **2** by t.l.c. and n.m.r.

*1,2,3,6-Tetra-*O*-acetyl-4-*O*-(2,6-di-*O*-acetyl-3,4-*O*-isopropylidene-β-*D*-galacto-pyranosyl)-α,β-*D*-glucopyranose* (**3**). — A mixture of acetic anhydride (60 mL) and anhydrous sodium acetate (6.0 g) was heated to boiling, removed temporarily from the heat source, and the acetal **2** (5.0 g) was added portionwise at such a rate as to maintain even refluxing. At the end, the mixture was briefly brought to boiling again, and then cooled and poured onto crushed ice. Processing by chloroform extraction in the usual manner gave crude **3** (7.5 g, 90%) as a solid. Recrystallized from ethyl acetate–hexanes, it showed m.p. 172–174°, $[\alpha]_D$ +22.8° (*c* 0.6, chloroform); n.m.r. (100 MHz): δ 5.66 (d, $J_{1,2}$ 8 Hz, H-1β, major anomer), 6.26 (d, $J_{1,2}$ 3.7 Hz, H-1α, minor anomer), 2.1 (center of a cluster of OAc singlets integrating to 18 H), 1.54 and 1.33 (2 s, 3 H each, $CMe_2$).

*Anal.* Calc. for $C_{27}H_{38}O_{17}$ (634.6): C, 51.10; H, 6.04. Found: C, 51.48; H, 6.20.

*1,2,3,6-Tetra-*O*-benzoyl-4-*O*-(2,6-di-*O*-benzoyl-3,4-*O*-isopropylidene-β-*D*-galac-topyranosyl)-α-*D*-glucopyranose* (**4**). — Benzoyl chloride (15 mL) was added dropwise to a cooled (0°) solution of the acetal **2** (5.0 g) in dry pyridine (75 mL). The mixture was then allowed to attain room temperature, stored for 1 h, and finally warmed (60–65°) for 4 h. The excess of reagent was decomposed by the addition of a little water to the cooled mixture, which was then diluted with chloroform (150 mL) and washed successively with water, ice-cold 1.5M sulfuric acid, water, saturated sodium hydrogencarbonate solution, and water. After drying (magnesium sulfate), the organic phase was evaporated to give a syrup from which added portions of toluene were evaporated. The hexabenzoate **4** was then crystallized from a small amount of warm dichloromethane by careful addition of ethanol. The product (12.0 g, 86%) was homogeneous in t.l.c. (solvent *J*); m.p. 154–157°, $[\alpha]_D$ +58.1° (*c* 1, chloroform); n.m.r. (100 MHz): δ 8.1–7.2 (30 H, OBz), 6.74 (d, 1 H, *J* ~4 Hz, H-1), 1.53 and 1.27 (2 s, 3 H each, $CMe_2$).

*Anal.* Calc. for $C_{57}H_{50}O_{17}$ (1007.0): C, 67.98; H, 5.01. Found: C, 67.77; H, 5.00.

*1,2,3,6-Tetra-*O*-acetyl-4-*O*-(2,6-di-*O*-acetyl-β-*D*-galactopyranosyl)-α,β-*D*-gluco-pyranose* (**5**). — The isopropylidene derivative **3** (4.0 g) was treated, with swirling at room temperature, with a mixture of trifluoroacetic acid (9 mL) and water (1 mL). When **3** had all dissolved, the mixture was immediately diluted with ether (100 mL),

which caused precipitation of crystalline **5** (3.6 g). The precipitate was isolated by filtration, washed well with ether, and recrystallized from ethyl acetate–ether to give pure **5** (3.0 g, 80%), m.p. 190–192°, $[\alpha]_D$ +4.5° (*c* 2.4, chloroform); n.m.r. (100 MHz): $\delta$ 6.24 (d, $J_{1,2}$ 3.7 Hz, H-1$\alpha$, minor anomer), 5.68 (d, $J_{1,2}$ 7.7 Hz, H-1$\beta$), major anomer), 2.1-region (cluster of OAc signals).

*Anal.* Calc. for $C_{24}H_{34}O_{17}$ (594.5): C, 48.48; H, 5.76. Found: C, 48.84; H, 6.02.

*1,2,3,6-Tetra-*O*-benzoyl-4-*O*-(2,6-di-*O*-benzoyl-β-*D*-galactopyranosyl)-α-*D*-glucopyranose* (**6**). — The isopropylidene derivative **4** (4.0 g) was deacetonated as just described for **3**, except that the crude product (3.2 g) was precipitated from the solution by addition of aqueous methanol. Recrystallized from acetone–ethanol, **6** (2.85 g, 73%) melted at 231–233° with sintering from 220°; $[\alpha]_D$ +74° (*c* 2.7, chloroform).

*Anal.* Calc. for $C_{54}H_{46}O_{17}$ (966.9): C, 67.07; H, 4.80. Found: C, 66.91; H, 4.68.

O-(*2,3,4-Tri-*O*-benzyl-α-*L*-fucopyranosyl)-(1→3)-*O*-(2,6-di-*O*-acetyl-β-*D*-galactopyranosyl)-(1→4)-1,2,3,6-tetra-*O*-acetyl-β-*D*-glucopyranose* (**8**). — 2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl bromide (**7**) was freshly prepared as reported[2], and used immediately. A solution of **7** (~3.2 g, obtained from 4.0 g of the 1-*p*-nitrobenzoate) and tetraethylammonium bromide (2.5 g) in dichloromethane (25 mL) was stirred for 30 min with molecular sieve type 4A (5 g), under protection from light and moisture. Then a solution of the hexaacetate **5** (1.8 g) in dichloromethane (25 mL) was added, followed by ethyldiisopropylamine (1 g). The mixture was stirred for 3 days at room temperature. After this time, t.l.c. (ether) indicated the presence of a major product ($R_F$ 0.6) accompanied by a trace of a marginally slower-moving product. There were also traces of faster-moving spots (that were due to decomposition of **7**), an unidentified spot at $R_F$ 0.3, and a minor spot of starting compound **5** ($R_F$ 0.15–0.2). The mixture was filtered with the aid of Celite, the filter residue washed well with dichloromethane, and the filtrate washed with water, dried (magnesium sulfate), and concentrated to a small volume. The solution was applied to a column of silica gel (120 g) which was eluted with solvent *H*. The fractions containing the major product together with the slightly slower-migrating by-product were evaporated to give 1.3 g (42.5%) of crystalline trisaccharide. Recrystallized from ethyl acetate–petroleum ether, **8** (1.0 g) was chromatographically pure; it migrated at a slightly faster rate than the analogous 6′-α-L-fucosyl isomer[2] (t.l.c. in ether or solvent *H*). It melted at 156–158° with prior softening at 125–130°, $[\alpha]_D$ −20.5° (*c* 0.7, chloroform); n.m.r. (100 MHz): $\delta$ 7.30 (narrow m, 15 H, Ph), 5.64 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 2.11, 2.09, 2.08, 2.04, 2.015, and 1.78 (6 s, 3 H each, OAc), and 1.07 (d, 3 H, *J* 6 Hz, *C*-Me). Unresolved ring-proton signals in the region of $\delta$ 4.0–5.2, and *Ph*-$CH_2$ signals centered at $\delta$ 3.75, integrated for a total of 24 protons.

*Anal.* Calc. for $C_{51}H_{62}O_{21}$ (1011.0): C, 60.58; H, 6.18. Found: C, 60.30; H, 6.43.

O-(*2,3,4-Tri-*O*-benzyl-α-*L*-fucopyranosyl)-(1→3)-*O*-β-*D*-galactopyranosyl-(1→4)-*D*-glucopyranose* (**9**). — Compound **8** (500 mg) was dissolved in methanol (50 mL) containing a catalytic amount of sodium methoxide. After 8 h at room temperature, the methanolysis was complete as indicated by t.l.c. (solvent *C*); the deacetylated

product **9** migrated slightly faster than the corresponding 6′-α-L-fucosyl isomer[2]. Deionization with a cation-exchange resin, filtration through Celite, and evaporation of the solvent gave crystalline **9** (370 mg, 98%), which was recrystallized from methanol–ether; m.p. 155–157°, $[\alpha]_D$ −13.9° (*c* 1.3, 3:1 chloroform–methanol). The air-dried product analyzed as a dihydrate, virtually unchanged after drying *in vacuo* at 110°.

*Anal.* Calc. for $C_{39}H_{50}O_{15} \cdot 2\,H_2O$ (794.8): C, 58.93; H, 6.85. Found: C, 58.98; H, 6.39; free from ash.

O-α-L-*Fucopyranosyl*-(*1→3*)-O-β-D-*galactopyranosyl*-(*1→4*)-D-*glucose* (**10**). — A solution of **9** (400 mg) in 95% ethanol (25 mL) plus methanol (15 mL) was shaken under hydrogen (60 lb.in.$^{-2}$) for 3–4 days at room temperature, in the presence of 10% palladium-on-carbon (400 mg). Processing then gave **10** as a white solid (230 mg, 89.5%) which contained a trace of faster-migrating contaminants, presumably due to incompletely hydrogenolyzed material (t.l.c. with solvent *F*). The product was purified by passage through a small column of silica gel (20 g). Elution with solvent *D* removed the impurities, and **10** was subsequently eluted with methanol and was obtained as a dry, white powder, $[\alpha]_D$ −39 (3 min)→−42.6° (2 h, final; *c* 1, water).

*Anal.* Calc. for $C_{18}H_{32}O_{15}$ (488.4): C, 44.26; H, 6.60. Found: C, 43.99; H, 6.89.

Borohydride reduction of **10** followed by permethylation and hydrolysis, and identification of the resulting 2,4,6-tri-*O*-methyl-D-galactose by t.l.c. in three different solvent systems, were performed exactly as described[1,2] for previously synthesized fucopyranosyllactoses.

O-(*2,3,4-Tri*-O-*acetyl*-β-L-*fucopyranosyl*)-(*1→3*)-O-(*2,6-di*-O-*acetyl*-β-D-*galactopyranosyl*)-(*1→4*)-*1,2,3,6-tetra*-O-*acetyl*-β-D-*glucopyranose* (**12**). — A solution of the hexaacetate **5** (1.0 g) in dry dichloromethane (25 mL) was stirred for 1 h with freshly prepared silver carbonate (1 g) and Drierite (5 g), under exclusion of light and moisture. A solution of freshly prepared 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide[14] (~2.8 g) in dry dichloromethane (25 mL) was then added dropwise with stirring which was continued for a total of 5 h, after which time the bromide had all been consumed (t.l.c. with solvent *I*). Examination by t.l.c. (double irrigation with ether) also revealed that a substantial proportion of **5** was still present besides the slightly faster-moving, main product **12**. The solution was filtered through Celite, washed with water, dried (magnesium sulfate), and evaporated to give a yellowish syrup. This was chromatographed on a column of silica gel (60 g). First, elution with solvent *G* removed the less-polar products of decomposition of the fucosyl bromide. Subsequent elution with ether yielded the trisaccharide **12** (0.60 g) followed by a small amount of unidentified material and, finally, unchanged **5** (0.50 g). The trisaccharide nonaacetate **12** was crystallized from ethyl acetate–ether–petroleum ether; m.p. 222–224°, undepressed on admixture with a sample from previous work[1].

ACKNOWLEDGMENT

This work was financially supported by the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

1 H. H. BAER AND S. A. ABBAS, *Carbohydr. Res.*, 77 (1979) 117–129.
2 H. H. BAER AND S. A. ABBAS, *Carbohydr. Res.*, 83 (1980) 146–151.
3 J. MONTREUIL, *C. R. Acad. Sci.*, 239 (1954) 510–511; 242 (1956) 192–193; *Bull. Soc. Chim. Biol.*, 39 (1957) 395–411; R. KUHN, H. H. BAER, AND A. GAUHE, *Chem. Ber.*, 88 (1955) 1135–1146; 89 (1956) 2513; R. KUHN AND A. GAUHE, *Justus Liebigs Ann. Chem.*, 611 (1958) 249–253.
4 E. A. KABAT, *Structural Concepts in Immunology and Immunochemistry*, 2nd edn., Holt, Rinehart and Winston, New York, 1976.
5 M. E. EVANS, F. W. PARRISH, AND L. LONG, JR., *Carbohydr. Res.*, 3 (1967) 453–462; M. E. EVANS AND F. W. PARRISH, *ibid.*, 28 (1973) 358–364; 54 (1977) 105–114.
6 A. HASEGAWA, N. KURIHARA, D. NISHIMURA, AND M. NAKAJIMA, *Agric. Biol. Chem.*, 32 (1968) 1123–1129; A. HASEGAWA AND H. G. FLETCHER, JR., *Carbohydr. Res.*, 29 (1973) 209–222; M. KISO AND A. HASEGAWA, *ibid.*, 52 (1976) 95–101.
7 A. HASEGAWA AND H. G. FLETCHER, JR., *Carbohydr. Res.*, 29 (1973) 223–237; A. HASEGAWA, T. SAKURAI, AND N. HASEGAWA, *ibid.*, 45 (1975) 19–27.
8 M. KISO AND A. HASEGAWA, *Carbohydr. Res.*, 52 (1976) 87–94.
9 J. GELAS AND D. HORTON, *Carbohydr. Res.*, 71 (1979) 103–121; 67 (1978) 371–387; 45 (1975) 181–195; M. L. WOLFROM, A. B. DIWADKAR, J. GELAS, AND D. HORTON, *ibid.*, 35 (1974) 87–96.
10 (*a*) E. FANTON, J. GELAS, AND D. HORTON, *Abstr. Pap. Am. Chem. Soc./Chem. Soc. Jpn. Chem. Congr.*, (1979) CARB-63; *Chem. Commun.*, (1980) 21–22; (*b*) L. HOUGH, A. C. RICHARDSON, AND L. A. W. THELWALL, *Carbohydr. Res.*, 75 (1979) c11–c12.
11 J. E. CHRISTENSEN AND L. GOODMAN, *Carbohydr. Res.*, 7 (1968) 510–512.
12 M. DEJTER-JUSZYNSKI AND H. M. FLOWERS, *Carbohydr. Res.*, 18 (1971) 219–226.
13 R. U. LEMIEUX AND H. DRIGUEZ, *J. Am. Chem. Soc.*, 97 (1975) 4069–4075; R. U. LEMIEUX, D. R. BUNDLE, AND D. A. BAKER, *ibid.*, 97 (1975) 4076–4083.
14 H. M. FLOWERS, A. LEVY, AND N. SHARON, *Carbohydr. Res.*, 4 (1967) 189–195.