Syntheses of derivatives of lacto-*N*-biose. I. 4,6-Di-*O*-acetyl-3-*O*-(tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-α,β-D-glucopyranosyl chloride

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Procedures are reported for the synthesis of 4,6-di-*O*-acetyl-3-*O*-(tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-α,β-D-glucopyranosyl chloride, a reagent useful for the reliable introduction of β-D-Gal*p*-(1→3)-β-D-GlcNAc*p* units (lacto-*N*-biose I units) into oligosaccharide structures. A benzyl glycoside intermediate is hydrogenolyzed to the alcohol which is subsequently converted to the glycosyl chlorides by use of the Vilsmeier reagent in the presence of *sym*-collidine. A comparison is made of the oxazoline method for the preparation of β-glycosides from 2-amino-2-deoxysugars and the phthalimido procedure developed in this laboratory.

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On rapporte des méthodes de synthèse du chlorure de di-*O*-acétyl-4,6-*O*-(tétra-*O*-acétyl-β-D-galactopyrannosyl)-3-déoxy-2-phtalimido-2-α,β-D-glucopyrannosyle, un réactif pratique pour l'introduction d'unités β-D-Galp-(1→3)-β-D-GlcNAc*p* (unités de lacto-*N*-biose I) dans la structure d'oligosaccharides. On hydrogénolyse le glycoside de benzyle intermédiaire en alcool, que l'on transforme ensuite en chlorure de glycosyle en utilisant un réactif de Vilsmeier en présence de *sym*-collidine. On établit une comparaison entre la méthode aux oxazolines pour la préparation des β-glycosides à partir des sucres amino-2-déoxy-2 et la méthode du phtalimide mise au point dans ce laboratoire.

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Lacto-*N*-biose I (βDGal(1→3)DGlcNAc) was first isolated by partial acid hydrolysis of "lacto-*N*-tetraose" (1) which has this disaccharide β-linked to the 3′-position of lactose. The disaccharide βDGal(1→3)DGlc does not appear to have received a trivial name.

Lacto-*N*-biose I, like *N*-acetyllactosamine, is a building unit of the core chains of human blood group determinants. When present in the terminal tetra- or pentasaccharide of a human ABH antigenic determinant, the resulting structure is said to have the Type 1 chain (2). This is in contrast to the Type 2 chain (2) wherein *N*-acetyllactosamine forms the core structure unit of the ABH determinant. The Lewis family of human blood group determinants are Type 1 structures (3–5). The purpose of this communication is to report the preparation of a reagent **9** which we expect can play an important role in efforts designed to achieve the incorporation of Type 1 (lacto-*N*-biose I) units as β-glycosides.

We consider the use of 2-deoxy-2-phthalimido-glycosyl halides (6) as reagents for the synthesis of a β-linkage between an alcohol and an aminosugar which has the amino group in equatorial orientation to be particularly attractive, both for reasons of reliability and yield. In our experience, the method can be used in the presence of a wide range of both acid- and alkali-labile protecting groups. The yields are generally good to excellent and, to date, the formation of the α-glycoside as a byproduct has not been detected. When the reaction conditions are carefully controlled so as to minimize side reactions (highly pure reagents and solvents, low temperature, and strictly anhydrous conditions), excellent yields are normally achieved using equimolar amounts of the reactants (6).

Since we first announced our interest in the synthesis of the core structural units for the human blood group determinants,[3] a number of contributions to the same end have appeared from other laboratories. These investigations have generally employed the classical oxazoline method (7) for the establishment of a β-linkage between *N*-acetyl-D-glucosamine and another sugar. As a result, there now exists a substantial experimental basis for comparing the oxazoline and phthalimido methods. To do so appears timely since recently condensations using the oxazoline method which led to derivatives of chitobiose were reported (8) and the opinion was stated that the improved oxazoline method which employs 1,2-dichloroethane as solvent (9) provides yields that are as satisfactory as

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those by the phthalimido route. We do not believe that the facts support this statement and take this occasion to explain why we hold this opinion.

First of all, we consider that it would have been more appropriate for Kiso *et al.* (8) to compare the 30–36% yields obtained in their synthesis of derivatives of chitobiose by the oxazoline method with the 68% yield that was reported for the synthesis of a chitobiose derivative by the phthalimido method (6). It is particularly important in this regard that the latter work employed an alcohol (2,2,2-trichloroethyl 3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside) which is of a type notorious for its resistance to glycosylation (10). After finding the oxazoline method unattractive for the synthesis of paragloboside (βDGal(1→4)βDGlcNAc(1→3)βDGal(1→4)βDGlc) analogs,[4] Ponpipom *et al.* turned to the phthalimido method (11). It was reported that the synthesis was then accomplished in high yield and with excellent stereoselectivity.

Similarly, Bundle and Josephson (12) have reported that whereas 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride and the 1,2-oxazoline derivative obtained from it were not effective in the glycosylation of the 2-position of a 3,4-di-*O*-benzyl-α-L-rhamnopyranoside, the phthalimido method provided the desired compound in good yield (70%). These experiences match our own. For example, with a large excess of 2,2,2-trichloroethanol, the oxazoline method after substantial examination provided 2,2,2-trichloroethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside in 46% yield along with the α-anomer in 6.1% yield (13). On the other hand, when suitable precautions were taken to exclude water, the phthalimido method provided 2,2,2-trichoroethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside in 89% yield (6) and no α-anomer was detected.

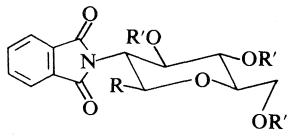
Augé and Veyrières (14) achieved a synthesis of lacto-*N*-triose I (βDGal(1→3)βDGlcNAc(1→3)-DGal) using the oxazoline derived from lacto-*N*-biose I. An 84% yield was reported. However, the yield was based on the alcohol (6-*O*-allyl-1,2,4-tri-*O*-benzyl-α-D-galactose) and a one molar excess of the oxazoline was used in the condensation. Thus, the yield may have been reported as 42%. This is to be contrasted with the condensation of acetylated phthalimido-chloride derived from lactosamine (24) with an equimolar amount of 2,2,2-trichloroethyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside which proceeded in 80% yield (15).

The condensation of the oxazoline derived from D-glucosamine with 1,2;3,4-di-*O*-isopropylidene-α-D-galactose has provided perhaps the most favorable yield (81%) ever reported (16) using this method. Recently, 6-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-1,2;-3,4-di-*O*-isopropylidene-α-D-galactose was synthesized in 86% yield (17). The condensation of **9** with an equimolar amount of 1,2;3,4-di-*O*-isopropylidene-α-D-galactose gave the desired β-glycoside in 75% yield after one recrystallization (15). It is to be noted, however, that the yields were not acceptable when the alcohol was 1,2;5,6-di-*O*-isopropylidene-α-D-galactofuranose (15). In this case, electrophilic attack to open an isopropylidene group appeared to be an important competing reaction.

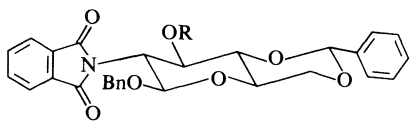
In contrast to the results obtained by the phthalimido method, virtually all of the yields which have been reported for the establishment of an intersugar glycosidic bond using the oxazoline method are less than 50% when the amount of the oxazoline is used to calculate the yield (18–23). This is of importance since the aminosugar component, especially in the form of higher saccharides, is often the more difficultly available starting material. It is these considerations that prompt us to publish the preparation of the title compound **9**. An accompanying paper (24) describes the preparation of the related structure derived from lactosamine.

The transformations used to achieve **9** are outlined using the formulas **1** to **9** and these are described in detail in the Experimental portion of this paper. The reaction sequence is modelled on the procedure used by Lemieux and Driguez (13) to build the lacto-*N*-biose I portion of the Lewis-a determinant. A point of interest is that the condensation of **4** with acetobromogalactose proceeded in 74% yield under Helferich conditions but using a 133% excess of the bromide. Over one-third of the bromide was converted to tetra-*O*-acetyl-β-D-galactopyranosyl cyanide. This result is to be contrasted with the previously reported (13) condensation of acetobromogalactose with 2,2,2-trichloroethyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside under similar conditions. Using only a 50% excess of the bromide, the β-linked disaccharide was obtained in 91% yield. It is apparent, therefore, that the phthalimido group has an important shielding influence on the reactivity of the 3-hydroxyl of **4** and this property may have an important influence on the success of synthetic strategies which follow similar lines.

[4]M. M. Ponpipom, R. L. Bugianesi, and T. Y. Shen. 2nd Joint Conference CIC/ACS, Montreal, May 30 – June 2, 1977. Abstracts of Papers, CARB 26.

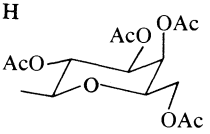


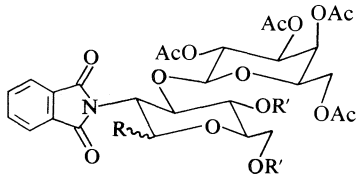
1 R = Br, R′ = Ac
2 R = OBn, R′ = Ac
3 R = OBn, R′ = H



4 R = H

5 R =





6 R = OBn(β), R′ = H
7 R = OBn(β), R′ = Ac
8 R = OH(α,β), R′ = Ac
9 R = Cl(α,β), R′ = Ac

The replacement of the anomeric hydroxyls of appropriately blocked structures by chlorine is conveniently accomplished (28)[3] using the Vilsmeier reagent (25–27). We conduct the reaction in the presence of *sym*-collidine to neutralize the liberated hydrogen chloride. Since the Vilsmeier reagent is also available in the bromide form (29, 30), the more reactive glycosyl bromides are also available in this way. We would also like to note that the reaction can be applied to such acid-labile compounds as 2,3,4,6-di-*O*-isopropylidene-D-mannopyranose.[5] In the phthalimido method, under the conditions for glycosylation which utilize an equimolar mixture of silver triflate and *sym*-collidine as promotor (6), the more stable chlorides are adequately reactive. No effort was made to separate the α and β-anomers of the glycosyl halides since the mixture was found to provide as good yields in the glycosylation reactions as did the pure β-form.

Experimental

All solvent extracts were dried over anhydrous sodium sulfate prior to solvent removal using a rotary evaporator under the vacuum of a water aspirator. The ^{1}H nmr spectra were measured at 100 MHz (Varian HA-100). Unless otherwise stated, deuteriochloroform was used as a solvent and internal TMS as a standard. Thin layer chromatograms (tlc) were developed on a Silica Gel G (E. Merck A.B., Darmstadt) and visualized with 5% sulfuric acid in ethanol after heating at 100°C. Column chromatography was performed on silica gel (CAMAG). Nitromethane, benzene, acetonitrile, dichloromethane, and 2,4,6-trimethylpyridine (*sym*-collidine) were dried and freshly distilled prior to use. All solid reactants for glycosylation were dried, prior to use, overnight over phosphorus pentoxide under high vacuum. *N,N*-Dimethylchloroforminium chloride (Vilsmeier reagent) was prepared by the method of Bosshard *et al.* (27).

*Benzyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (2)*

A solution of 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide (6) (**1**), mp 122–123°C, $[\alpha]_D^{24}$ +57.3° (*c* 1.0, $CHCl_3$), (14.95 g, 30 mmol) in dry nitromethane (20 mL) was added to a cooled (−30°C) solution of benzyl alcohol (3.24 g, 30 mmol), silver trifluoromethanesulfonate (8.0 g, 31 mmol), and 2,4,6-trimethylpyridine (3.75 g, 31 mmol) in dry nitromethane (30 mL) under nitrogen. The mixture was stirred at −30°C for 2 h and then diluted with chloroform (100 mL). The solid was removed by filtration and the filtrate was evaporated *in vacuo*. The foamy residue was dissolved in chloroform (100 mL), and washed sequentially with ice-water, 5% aqueous hydrogen chloride, and with aqueous sodium bicarbonate solution. Solvent removal after drying left a foam which was crystallized from diethyl ether (13.88 g, 88%), mp 106–108°C. Recrystallization from ethanol raised the melting point to 108–109°C, $[\alpha]_D^{22}$ −12.6° (*c* 0.5, $CHCl_3$); ^{1}H nmr δ: 7.86–7.60 (m, 4H, phthalimido), 7.07 (s, 5H, C_6H_5), 5.78 (dd, 9 and 11 Hz, H-3), 5.37 (d, 8 Hz, H-1), 5.17 (t, 9 Hz, H-4), 4.95–3.75 (m, 6H), 2.12, 2.0, 1.84 (s, 3 OAc). *Anal.* calcd. for $C_{27}H_{27}NO_{10}$: C 61.71, H 5.18, N 2.67; found: C 61.66, H 5.11, N 2.48.

Benzyl 2-deoxy-2-phthalimido-β-D-glucopyranoside (3)

A solution of the acetate **2** (12.60 g, 24 mmol) in a mixture of acetone (200 mL), water (100 mL), and concentrated hydrochloric acid (40 mL) was kept at 70°C for 6 h. Evaporation of acetone left a suspension which was collected by filtration, washed with cold water, and dried when a solid was obtained (9.20 g, 97% yield), mp 173–175°C. Recrystallization from ethyl acetate raised the melting point to 176–177°C, $[\alpha]_D^{25}$ −34.2° (*c* 0.76, Me_2CO). The ^{1}H nmr spectrum was consistent with expectations. *Anal.* calcd. for $C_{21}H_{21}NO_7$: C 63.14, H 5.30, N 3.51; found: C 63.09, H 5.27, N 3.43.

*Benzyl 4,6-*O*-benzylidine-2-deoxy-2-phthalimido-β-D-glucopyranoside (4)*

A solution of glycoside **3** (8.0 g, 20 mmol), α,α-dimethoxytoluene (6.08 g, 40 mmol), and *p*-toluenesulfonic acid (200 mg) in freshly distilled acetonitrile (200 mL) was stirred at room temperature for 16 h. Neutralization with triethylamine (2 mL) and solvent

[5]R. U. Lemieux and S. Z. Abbas, unpublished work.

removal left a sticky solid which was triturated several times with Skellysolve "B" and finally collected by filtration. Recrystallization from ethanol yielded colorless needles (8.96 g, 92% yield), mp 183–184°C; $[\alpha]_D^{25}$ −75.4° (*c* 1.2, $CHCl_3$). The ^1H nmr spectrum was consistent with expectations. *Anal.* calcd. for $C_{28}H_{25}NO_7$: C 68.98, H 5.17, N 2.88; found: C 68.85, H 5.06, N 2.70.

Benzyl 3-O-(tetra-O-acetyl-β-D-galactopyranosyl)-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (5)

A solution of the alcohol **4** (7.31 g, 15 mmol) in a 1:1 mixture of nitromethane and benzene (600 mL) was distilled until 100 mL of distillate was collected. The temperature was adjusted to 60°C, mercuric cyanide (5.05 g, 20 mmol) and acetobromogalactose (8.22 g, 20 mmol) were added. After the mixture was stirred at 60°C for 24 h, additional amounts of mercuric cyanide (3.74 g) and the bromide (6.17 g, 15 mmol) were added and the mixture was stirred for 28 h at 60°C. The cooled solution was washed with 30% aqueous potassium iodide solution (2 × 250 mL), with aqueous sodium bicarbonate (2 × 250 mL), and with brine (500 mL). Each washing was back-extracted with chloroform (2 × 200 mL). The combined organic layers were evaporated to a foam which was dissolved in 90% aqueous acetic acid (50 mL) and the solution was stirred at room temperature for 30 min in case orthoesters had formed. The solution was diluted with chloroform (200 mL) and washed with ice-water (3 × 200 mL) and sodium bicarbonate solution (2 × 250 mL). Solvent removal left a foam which was passed through a short alumina (Woelm, neutral) column using ethyl acetate – diethyl ether (1:1). Solvent removal yielded a colorless foam (21 g). Addition of diethyl ether caused the crystallization of tetra-*O*-acetyl-β-D-galactopyranosyl cyanide (4.7 g), mp 168–170°C; $[\alpha]_D^{24}$ +36.2° (*c* 2.15, $CHCl_3$) (lit. (31) mp 168–169°C; $[\alpha]_D^{20}$ +37.2° (*c* 7.95, $CHCl_3$)).

Evaporation of the mother liquor left a foam which was applied to a silica gel (180 g) column and eluted with ethyl acetate – hexane–benzene (1:1:1). Solvent removal of the second and main fraction left a colorless foam (12.7 g). This crude product crystallized from diethyl ether but contained traces of tetra-*O*-acetyl-β-D-galactopyranosyl cyanide. Recrystallization from ethanol yielded colorless needles (9.02 g, 73% yield based on compound **4**), mp 170–171°C; $[\alpha]_D^{24}$ −46.3° (*c* 0.66, $CHCl_3$); ^1H nmr δ: 7.77 (s, 4H, phthalimido), 7.60–7.32 (m, 5H, phenyl), 7.01 (s, 5H, phenyl), 5.57 (s, 1H, CHC_6H_5), 5.14 (d, 9 Hz, H-1), 2.05, 1.90, 1.82, 1.53 (s, 4 OAc). *Anal.* calcd. for $C_{42}H_{43}NO_{16}$: C 61.68, H 5.30, N 1.72; found: C 61.99, H 5.33, N 1.57.

Benzyl 4,6-di-O-acetyl-3-O-(tetra-O-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranoside (7)

A solution of the benzylidene compound **5** (8.18 g, 10 mmol) in 60% aqueous acetic acid (100 mL) was stirred at 100°C for 30 min and diluted with water (100 mL). Solvent removal left a foam (**6**) which was not characterized but acetylated directly with a 2:1 mixture of pyridine – acetic anhydride (90 mL). Solvent removal left a foam which was dissolved in chloroform (100 mL) and washed with 5% aqueous hydrochloric acid, sodium bicarbonate solution, and then with ice-water. Solvent removal then left a foam which was applied to a silica gel column and eluted with a mixture of ethyl acetate – hexane (1:1). Solvent removal of the second fraction yielded a solid (6.15 g, 75% yield based on compound **5**), mp 89–92°C; $[\alpha]_D^{23}$ −42.3° (*c* 1.3, $CHCl_3$). The ^1H nmr spectrum was consistent with expectations. *Anal.* calcd. for $C_{39}H_{43}NO_{18}$: C 57.56, H 5.33, N 1.72; found: C 57.11, H 5.49, N 1.61.

4,6-Di-O-acetyl-3-O-(tetra-O-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-D-glucopyranose (8)

A mixture of compound **7** (4.88 g, 6 mmol) and 5% palladium on carbon (3.0 g) in a 1:1 mixture of ethanol and ethyl acetate (100 mL) was hydrogenated at 50 psi at room temperature for 16 h. The solid was removed by filtration and the filtrate evaporated. The resulting foam was applied to a silica gel column and eluted with a mixture of ethyl acetate – hexane (2:1). The second and main fraction on evaporation left a solid (4.02 g, 93% yield), mp 123–126°C; $[\alpha]_D^{24}$ +12.2° (*c* 1.0, $CHCl_3$). *Anal.* calcd. for $C_{32}H_{37}NO_{18}\cdot H_2O$: C 51.80, H 5.30, N 1.89; found: C 51.97, H 5.12, N 1.77.

4,6-Di-O-acetyl-3-O-(tetra-O-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-α,β-D-glucopyranosyl chloride (9)

A solution of compound **8** (3.62 g, 5 mmol), *N,N*-dimethylchloroforminium chloride (Vilsmeier reagent) (2.56 g, 20 mmol), and collidine (2.42 g, 20 mmol) in dry dichloromethane (20 mL) was stirred at 0°C for 3 h. Dilution with dichloromethane (50 mL), washing with cold water, drying over sodium sulfate, and solvent removal gave a foam which crystallized on addition of diethyl ether (3.53 g, 95% yield), mp 104–109°C; $[\alpha]_D^{24}$ +18.7 (*c* 0.7, chloroform). The ^1H nmr spectrum of the product showed it to be a 3:7 mixture of α and β-anomers; ^1H nmr δ: 8.0–7.74 (m, 4H, phthalimido), 6.11 (d, 0.3H, 4 Hz, H-1), 5.92 (d, 0.7H, 9 Hz, H-1). *Anal.* calcd. for $C_{32}H_{36}NO_{17}Cl$: C 51.79, H 4.89, N 1.88, Cl 4.77; found: C 51.70, H 4.96, N 1.84, Cl 4.90.

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