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SYNTHESIS OF METHYL 3-*O*- AND 2-*O*-(2-ACETAMIDO-2-DEOXY-β-D-GLUCOPYRANOSYL)-α-D-GALACTOPYRANOSIDE*

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ABSTRACT

Condensation of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside with 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide (**1**) in dichloromethane, in the presence of silver trifluoromethanesulfonate, 2,4,6-trimethylpyridine, and molecular sieves, afforded methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-α-D-galactopyranoside (**4**). Deacetalation of **4** in hot, 80% aqueous acetic acid gave methyl 2-*O*-benzoyl-3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-α-D-galactopyranoside (**5**), which, on deacylation, followed by peracetylation, furnished the peracetylated disaccharide derivative (**6**). The structures of **5** and **6** were established by ^{1}H-n.m.r. spectroscopy. *O*-Deacetylation of **6** afforded the title β-(1→3)-linked disaccharide **7**. For the synthesis of the β-(1→2)-linked isomer, methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside was similarly condensed with bromide **1** to give the fully protected disaccharide derivative (**8**). Cleavage of the benzylidene group of **8** gave methyl 3-*O*-benzoyl-2-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-α-D-galactopyranoside (**9**). Deacetylation of **9**, followed by peracetylation, afforded the peracetate (**10**). *O*-Deacetylation of **10** gave the β-(1→2)-linked disaccharide (**11**). The structures of the disaccharides **7** and **11** were confirmed by ^{13}C-n.m.r. spectroscopy.

INTRODUCTION

The disaccharide 3-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-D-galactopyranose ("lacto-*N*-biose II") was first isolated[2] by partial hydrolysis of the human-milk oligosaccharide "lacto-*N*-tetraose" with acid. It was later obtained[3] in crystalline form from a blood-group A glycoprotein, prepared from hog gastric-mucus. Subsequently, it was demonstrated[4] that it occurs as part of the structure of all four human blood-group A, B, H, and Le^a substances, and it was postulated[5]

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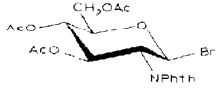
that it forms part of the core structure, and also occurs in the side chain, attached to 2-acetamido-2-deoxy-D-galactose that is further *O*-glycosylically linked to protein.

In a continuing program for the synthesis of oligosaccharides that occur as part of glycoconjugates, we recently described the synthesis of two 2-acetamido-2-deoxy-D-glucose-containing disaccharides[6], and also that of a related trisaccharide[7]. Such oligosaccharides can play an important role in specificity studies of glycosidases[8] and glycosyltransferases[9]. As a further contribution to this program, we now describe the synthesis of the methyl α-glycoside of lacto-*N*-biose II and of its (1→2)-linked isomer.

RESULTS AND DISCUSSIONS

3-*O*-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-D-galactopyranose has previously been obtained[10] (after customary deblocking) by the condensation of 2-methyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-*d*]-2-oxazoline with either a sugar alcohol, the preparation of which required "a rather tedious route", or with a diol that was prone to diglycosylation to give both a disaccharide and a trisaccharide[10]. In another attempted synthesis of this disaccharide, the alkali-labile[11] (1→3)-glycosidic linkage was completely ruptured during the final deacyla-



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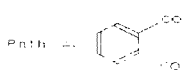
2 R = Bz, R' = H
3 R = H, R' = Bz



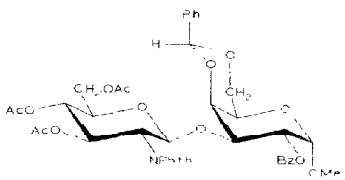


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TABLE I

PROPOSED ^{13}C-N M R CHEMICAL SHIFTS[a]

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-1'*	*C-2'*	*C-3'*	*C-4'*	*C-5'*	*C-6'*	*OCH_3*	*NAc*
[b]	99.80	68.29	69.49	68.70	70.89	60.52	—	—	—	—	—	—	54.27	—
[c]	101.56	55.41	74.21	70.44	76.74	60.88	—	—	—	—	—	—	55.02	22.96
7	99.40	67.23	78.97	67.67	70.76	60.74	101.89	56.27	74.51	70.24	76.49	60.36	54.19	22.90
11	98.86	77.67	68.21[d]	68.56[d]	70.54	61.03[e]	102.45	56.02	74.61	70.54	76.73	60.34[e]	54.13	22.92

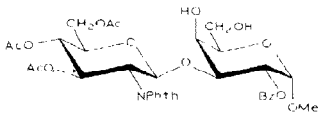
[a]In Me_2SO-d_6, with Me_4Si as the internal standard. [b]Methyl α-D-galactopyranoside. [c]Methyl 2-acetamido-2-deoxy-β-D-glucopyranoside. [d,e]Assignments having the same superscript may have to be interchanged.

tion step[12]. More recently, an alternative route to this disaccharide was described by Anderson and co-workers[13].

In our present synthesis, the precursor (*i.e.*, the peracetylated derivative) to the free disaccharide would be similar to that described by Shapiro *et al.*[12], and hence, the β-(1→3) linkage would be likely to be ruptured during any attempted deacetylation in an alkaline medium. However, as our aim was primarily to utilize this disaccharide (as its peracetylated glycosyl halide) for further oligosaccharide syntheses[14], this problem does not present any practical difficulties.

Glycosylation of the readily accessible methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside[15] **2** with 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide (**1**) in dichloromethane for 3 h at room temperature in the presence of silver trifluoromethanesulfonate, 2,4,6-trimethylpyridine, and molecular sieves, and purification of the crude product by column chromatography, afforded, in 80% yield, the fully protected disaccharide **4**. The ^{1}H-n.m.r. spectrum of **4** was in agreement with the structure expected; H-1′ was observed as a doublet at δ 5.70, with a spacing of 8 Hz, whereas H-1 resonated as a doublet at δ 5.03 (*J* 4 Hz), in accord with a β and an α configuration, respectively, of the two glycosidic linkages.

Brief treatment of **4** with hot, 80% aqueous acetic acid cleaved the 4,6-benzylidene group to give **5**, which was purified in a column of silica gel. Deacylation of **5** at 70° in 85% hydrazine hydrate in ethanol, as previously described[6,7], and



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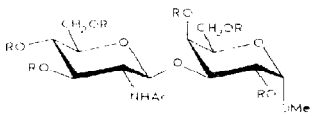


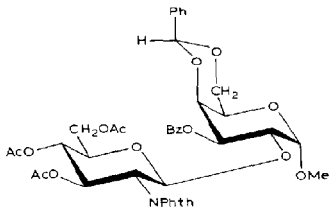
6 R = Ac
7 R = H

peracetylation of the resulting intermediate gave, after column-chromatographic purification, crystalline peracetate **6**, the ^{1}H-n.m.r. spectrum of which contained signals in support of its overall structure (see Experimental section). *O*-Deacetylation of **6** in methanolic sodium methoxide afforded the title disaccharide **7** as the monohydrate. The ^{13}C-n.m.r. spectrum of **7** was consistent with the structure proposed (see Table I).

For the synthesis of the β-(1→2)-linked isomer, methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside[15] **3** was condensed with bromide **1** to give, in 86% yield, crystalline disaccharide **8**. The structure of **8** was evidenced by its ^{1}H-n.m.r. spectrum; H-1′ and H-1 were observed as doublets at δ 5.56 (*J* 8 Hz) and 5.14 (*J* 4 Hz), in agreement with a β and an α configuration, respectively, of the two glycosidic linkages.

Cleavage of the benzylidene group of **8** in hot, 80% aqueous acetic acid gave,

in ~89% yield, the diol **9** as the hemihydrate. Deacylation of **9**, and peracetylation of the resulting intermediate as described for **5** (to give **6**), afforded the peracetylated, crystalline disaccharide derivative **10**. *O*-Deacetylation of **10** with methanolic sodium methoxide gave the title disaccharide **11**, also as the monohydrate. The ^{1}H-n.m.r. spectra of **9** and **10**, and the ^{13}C-n.m.r. spectrum of **11**, were all in accord with the structures proposed (see Experimental section and Table I).



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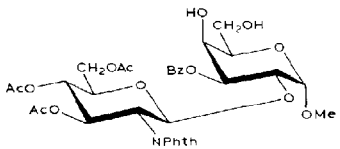

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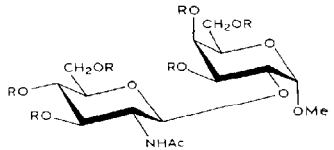

10 R = Ac
11 R = H

EXPERIMENTAL

General methods. — These were the same as those already described[6,7], except that the following solvent systems (v/v) were used for chromatography: *A*, 4:1 benzene–ether; *B*, 20:1 chloroform–acetone; *C*, 40:5:1 dichloromethane–ethyl acetate–acetone; *D*, 10:1 benzene–ether; *E*, 30:1 chloroform–acetone; *F*, 5:1 chloroform–acetone; *G*, 2:1 ethyl acetate–hexane; and *H*, 4:1 ethyl acetate–hexane.

Methyl 2-O-benzoyl- (**2**) *and -3-O-benzoyl-* (**3**) *-4,6-O-benzylidene-α-D-galactopyranoside.* — Prepared essentially as described by Szeja[15], except that dichloromethane was used as the solvent instead of benzene, compound **2** was obtained in 63% yield, and had m.p. 204–206°, $[\alpha]_D$ +152.9° (*c* 1.2, chloroform); lit.[15] m.p. 206–207°, $[\alpha]_D$ +153.1° (*c* 1, chloroform). Compound **3** was obtained as

a minor component in the preparation of **2**, and had m.p. 141–143°, $[\alpha]_D$ +239° (*c* 1.0, chloroform); lit.[15] m.p. 142–143°, $[\alpha]_D$ +241.5° (*c* 1, chloroform).

Methyl 2-O-benzoyl-4,6-O-benzylidene-3-O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-α-D-galactopyranoside (**4**). — A mixture of **2** (3.12 g), silver trifluoromethanesulfonate (2.93 g), 2,4,6-trimethylpyridine (1.3 g), and molecular sieves type 4A (6 g) in dichloromethane (70 mL), protected from light and moisture, was stirred for 0.5 h at room temperature in an atmosphere of nitrogen. A solution of 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide (**1**; 5.4 g) in dichloromethane (30 mL) was added dropwise, with stirring, during 0.5 h, and stirring was continued for a further 1 h. T.l.c. (solvent *A*, *B*, or *C*) then revealed the presence of a major product, slower-migrating than **2**; a small proportion of **2** was also revealed by t.l.c. (solvent *C*). More portions of the silver trifluoromethanesulfonate (0.73 g), and 2,4,6-tri-methylpyridine (0.32 g) were added, followed by the dropwise addition of a solution of bromide **1** (1.35 g) in dichloromethane (10 mL), and the stirring was continued for an additional 1.5 h. After the customary processing[6,7], t.l.c. (solvent *A*, *B*, or *C*) showed, in addition to the major product, some faster- and some slower-migrating contaminants (presumably due to the decomposition of **1**). Additionally, t.l.c. (solvent *C*) revealed the presence of a trace of **2**. The mixture was subjected to column chromatography on silica. Elution with solvent *D* removed the faster-migrating contaminants (including **2**). Elution with solvent *E*, and evaporation of the fraction corresponding to the major product, yielded a foam, which, on crystallization from acetone–ether–hexane, afforded **4** (5.2 g, 80%); m.p. 195–197°, $[\alpha]_D$ +115.1° (*c* 0.52, chloroform); ^{1}H-n.m.r. data ($CDCl_3$): δ 7.90–7.20 (complex, 14 H, aromatic), 5.79 (dd, 1 H, *J* 10 and 8 Hz, H-2′), 5.70 (d, 1 H, *J* 8 Hz, H-1′), 5.64 (s, 1 H, PhCH), 5.45 (dd, 1 H, *J* 10 and 4 Hz, H-2), 5.22 (t, 1 H, *J* 10 Hz, H-3′), 5.03 (d, 1 H, *J* 4 Hz, H-1), 3.36 (s, 3 H, OCH_3), 2.15, 2.05, and 1.85 (s, 9 H, 3 OAc), and 4.60-3.60 (unresolved signals, 9 H).

Anal. Calc. for $C_{41}H_{41}NO_{16}$: C, 61.26; H, 5.15; N, 1.74. Found: C, 60.96; H, 5.24; N, 1.59.

Methyl 2-O-benzoyl-3-O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-α-D-galactopyranoside (**5**). — Crystalline **4** (4.5 g) was taken up in 80% aqueous acetic acid (45 mL) and heated for 0.5 h at ~100°. T.l.c. (solvent *F*) then indicated the disappearance of **4** and the presence of a slower-migrating product. 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 with solvent *F* as the eluant, to give **5** (3.2 g, 79.8%), amorphous; $[\alpha]_D$ +125° (*c* 0.84, chloroform); ^{1}H-n.m.r. data ($CDCl_3$): δ 7.80–7.10 (complex, 9 H, aromatic), 5.79 (dd, 1 H, *J* 10 and 8 Hz, H-2′), 5.62 (d, 1 H, *J* 8 Hz, H-1′), 5.35 (dd, 1 H, *J* 10 and 4 Hz, H-2), 5.14 (t, 1 H, *J* 10 Hz, H-3′), 4.92 (d, 1 H, *J* 4 Hz, H-1), 3.34 (s, 3 H, OCH_3), 3.00–2.40 (m, 2 H, exchangeable in D_2O, 2 OH), 2.15, 2.04 and 1.80 (s, 9 H, 3 OAc), and 3.70–3.34 (unresolved signals, 9 H).

Anal. Calc. for $C_{34}H_{37}NO_{16} \cdot 0.5\,H_2O$: C, 56.34; H, 5.30; N, 1.93. Found: C, 56.05; H, 5.44; N, 1.99.

Methyl 3-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-2,4,6-tri-O-acetyl-α-D-galactopyranoside (**6**). — Compound **5** (3 g) was heated for 15 min at 70° in a mixture of ethanol (60 mL) and 85% hydrazine hydrate (30 mL). The mixture was evaporated, and several portions of ethanol were added to, and evaporated from, the residue, which was then mixed with 1:2 (v/v) acetic anhydride–pyridine (100 mL), and heated for 20 min at 90°. The acetic anhydride and pyridine were removed under diminished pressure, and the residue was suspended in chloroform, the solid material filtered off, the filtrate concentrated, and the concentrate applied to a column of silica gel. Elution with solvent *G*, followed by solvent *H*, and evaporation of the fractions containing the product, yielded a solid, which was recrystallized from ethyl acetate–hexane to furnish **6** (2.22 g, 81.6%); m.p. 197–199°, $[\alpha]_D$ +95° (*c* 1.1, chloroform); ^{1}H-n.m.r. data ($CDCl_3$): δ 3.41 (s, 3 H, OCH_3) and 2.20–1.80 (cluster of singlets, 21 H, 6 OAc and NAc).

Anal. Calc. for $C_{27}H_{39}NO_{17}$: C, 49.91; H, 6.06; N, 2.16. Found: C, 49.97; H, 6.30; N, 2.28.

Methyl 3-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-α-D-galactopyranoside (**7**). — Compound **6** (0.35 g) was taken up in 0.1M sodium methoxide in methanol (15 mL) and kept for 1 h at room temperature. A few drops of glacial acetic acid were then added, the solution was evaporated to dryness, and the residue was redissolved in methanol, and de-ionized with Amberlite IR-120 (H^+) cation-exchange resin. The resin was filtered off, the methanol evaporated, and several portions of ethanol were added to, and evaporated from, the residue, to give **7** (0.2 g, 95%), amorphous; $[\alpha]_D$ +87.8° (*c* 0.65, water); for ^{13}C-n.m.r. data, see Table I.

Anal. Calc. for $C_{15}H_{27}NO_{11} \cdot H_2O$: C, 43.36; H, 7.05; N, 3.37. Found: C, 43.70; H, 7.12; N, 3.27.

Methyl 3-O-benzoyl-4,6-O-benzylidene-2-O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-α-D-galactopyranoside (**8**). — A mixture of compound **3** (1.56 g), silver trifluoromethanesulfonate (1.47 g), 2,4,6-trimethylpyridine (0.65 g), and molecular sieves type 4A (4 g) in dichloromethane (30 mL), protected from light and moisture, was stirred for 0.5 h in an atmosphere of nitrogen. A solution of **1** (2.7 g) in dichloromethane (15 mL) was added dropwise, with stirring, during 20 min, and the stirring was continued for an additional 40 min, whereupon more silver trifluoromethanesulfonate (0.73 g) and 2,4,6-trimethylpyridine (0.33 g) were added, followed by the dropwise addition of **1** (1.35 g) in dichloromethane (10 mL). After stirring for 1 h, t.l.c. (solvent *C*) revealed the presence of a major product, slower-migrating than **3**, and a trace of **3**; and some faster- and some slower-migrating contaminants were also revealed.

After processing, and column-chromatographic purification as described for the (1→3)-linked isomer **4**, the residue gave, on recrystallization from acetone–ether–hexane, compound **8** (2.8 g, 86.4%); m.p. 220–222°, $[\alpha]_D$ +212.7° (*c* 1.4,

chloroform); ^{1}H-n.m.r. data ($CDCl_3$): δ 7.90–7.20 (complex, 14 H, aromatic), 5.77 (dd, 1 H, *J* 10 and 8 Hz, H-2'), 5.56 (d, 1 H, *J* 8 Hz, H-1'), 5.45 (s, 1 H, PhCH), 5.40 (dd, partially superimposed by PhCH, 1 H, *J* 10 and 4 Hz, H-3), 5.16 (t, partially superimposed by H-1, 1 H, *J* 10 Hz, H-3'), 5.14 (d, 1 H, *J* 4 Hz, H-1), 3.47 (s, 3 H, OCH_3), 2.11, 2.02, and 1.78 (s, 9 H, 3 OAc), and 4.50–3.70 (unresolved signals, 9 H).

Anal. Calc. for $C_{41}H_{41}NO_{16}$: C, 61.26; H, 5.15; N, 1.74. Found: C, 61.30; H, 5.26; N, 1.72.

*Methyl 3-O-benzoyl-2-O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-α-*D*-galactopyranoside* (**9**). — The 4,6-benzylidene derivative **8** (2.4 g) was deacetalated in hot, 80% aqueous acetic acid, and the product purified as described for **5** (to give **6**). The residue so obtained was dissolved in chloroform, and precipitated by the addition of ether–hexane, to furnish **9** (1.9 g, 88.8%), amorphous; $[\alpha]_D$ +119.4° (*c* 1.26, chloroform); ^{1}H-n.m.r. data ($CDCl_3$): δ 7.90–7.10 (complex, 9 H, aromatic), 5.75 (dd, 1 H, *J* 10 and 8 Hz, H-2), 5.54 (d, 1 H, *J* 8 Hz, H-1'), 5.31 (dd, 1 H, *J* 10 and 4 Hz, H-3), 5.12 (t, partially superimposed by H-3 and H-1, 1 H, *J* 10 Hz, H-3'), 5.07 (d, 1 H, partially superimposed on H-3', *J* 4 Hz, H-1), 3.44 (s, 3 H, OCH_3), 3.00–2.30 (m, 2 H, 2 OH), 2.13, 2.03, and 1.78 (s, 9 H, 3 OAc), and 4.50–3.70 (unresolved signals, 9 H).

Anal. Calc. for $C_{34}H_{37}NO_{16} \cdot 0.5\ H_2O$: C, 56.34; H, 5.30; N, 1.93. Found: C, 56.12; H, 5.29; N, 1.90.

*Methyl 2-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranosyl)-3,4,6-tri-O-acetyl-α-*D*-galactopyranoside* (**10**). — Compound **9** (1.8 g) was heated for 15 min at 70° in a mixture of ethanol (40 mL) and 85% hydrazine hydrate (20 mL). The mixture was evaporated, and several portions of ethanol were added to, and evaporated from, the residue, which was then taken up in pyridine (50 mL), cooled to 0–5°, treated with acetic anhydride (25 mL), and heated for 20 min at 90°. After processing as described for **6**, column-chromatographic purification (solvents *G* and *H*), and recrystallization from ethyl acetate–hexane, afforded **10** (1.35 g, 82.8%); m.p. 225–227°, $[\alpha]_D$ +63° (*c* 0.53, chloroform); ^{1}H-n.m.r. data ($CDCl_3$): δ 5.72 and 5.70 (dd, 1 H, *J* 10 and 8 Hz, superimposed by d, 1 H, *J* 8 Hz; H-2' and H-1', respectively), 5.03 and 4.95 (t, 1 H, *J* 10 Hz, superimposed by d, 1 H, *J* 4 Hz; H-2 and H-1, respectively), 3.44 (s, 3 H, OCH_3), and 2.20–1.80 (cluster of singlets, 21 H, 6 OAc and NAc).

Anal. Calc. for $C_{27}H_{36}NO_{17}$: C, 49.91; H, 6.06; N, 2.16. Found: C, 49.75; H, 5.95; N, 1.98.

*Methyl 2-O-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-α-*D*-galactopyranoside* (**11**). — Compound **10** (1 g) was taken up in 0.1M methanolic sodium methoxide (50 mL), and stirred at room temperature. The suspended **10** rapidly dissolved, and, in 15–20 min, crystallization ensued. The mixture was kept for 2 h at room temperature, refrigerated for 2 h, the base neutralized by the addition of a few drops of glacial acetic acid, and the crystalline material filtered off, and

thoroughly washed with cold methanol, to afford **11** (0.53 g, 86.7%); m.p. 280–282° (dec.), $[\alpha]_D$ +74.4° (*c* 0.94, water); for ^{13}C-n.m.r. data, see Table I.

Anal. Calc. for $C_{15}H_{27}NO_{11} \cdot H_2O$: C, 43.36; H, 7.05; N, 3.37. Found: C, 43.46; H, 7.00; N, 3.24.

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