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Anthracycline oligosaccharides: facile stereoselective synthesis of 2,6-dideoxy-α-L-*lyxo*-hexopyranosides

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ABSTRACT

Glycosylation of benzyl 2,3,6-trideoxy-3-trifluoroacetamido-α-L-*lyxo*-hexopyranoside (**6**) with 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-L-*lyxo*-hex-1-enitol (**1**) or 4-*O*-acetyl-1,5-anhydro-3-*O*-benzyl-2,6-dideoxy-L-*lyxo*-hex-1-enitol (**2**) in the presence of trimethylsilyl triflate/triethylamine gave α-(1→4)-linked disaccharide derivatives **7** and **8**, respectively. In the presence of trimethylsilyl triflate only, 3,4-di-*O*-acetyl-1-*O*-*tert*-butyldimethylsilyl-2,6-dideoxy-β-L-*lyxo*-hexopyranose (**3**) and **6** gave mainly **7**. Condensation of **1** or **2** with **9**, obtained by *O*-deacylation of **8**, afforded benzyl [*O*-(3,4-di-*O*-acetyl-2,6-dideoxy-α-L-*lyxo*-hexopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-2,6-dideoxy-α-L-*lyxo*-hexopyranosyl)-(1→4)-(2,3,6-trideoxy-3-trifluoroacetamido-α-L-*lyxo*-hexopyranoside)] (**11**) and its 3″-*O*-benzyl analogue **12**, respectively.

INTRODUCTION

β-Rhodomycins and other anthracyclines of the aclacinomycin type possess one or two oligosaccharide chains, usually a trisaccharide, composed of α-(1→4)-linked deoxy sugars[1,2], and 2,6-dideoxy-α-L-*lyxo*-hexopyranosyl-(1→4)-2,3,6-trideoxy-3-dimethylamino-L-*lyxo*-hexopyranose is the most common unit.

The main problem in the synthesis of such disaccharides is considered to be the condensation step, where the unreactive axial HO-4 of the daunosamine acceptor is to be glycosylated with the "2-deoxy-L-fucose" donor[3–5].

Glycosylation procedures, *e.g.*, the Koenigs–Knorr and the *N*-iodosuccinimide methods, yielded only 40% of the disaccharide or failed[6,7]. The synthesis of the "2-deoxy-α-L-fucosyl" disaccharides based[8] on the use of $(Bu_3Sn)_2O$–*N*-iodosuccinimide and 3,4-di-*O*-acetyl-L-fucal (**1**) represents a considerable improvement, but an additional reduction step is needed in order to obtain 2-deoxyglycosides.

We now describe a new, highly efficient glycosylation procedure for the synthesis of 2,6-dideoxy-α-L-*lyxo*-hexopyranosides ("2-deoxy-α-L-fucopyranosides") and the preparation of di- and tri-saccharide units of anthracyclines.

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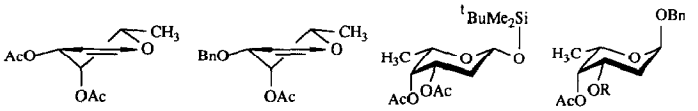
RESULTS AND DISCUSSION

In order to gain access to oligosaccharide units for the preparation of semi-synthetic rhodomycins, the glycosylation of the daunosamine acceptor benzyl 2,3,6-trideoxy-3-trifluoroacetamido-α-L-*lyxo*-hexopyranoside[4,6] (**6**) with 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-L-*lyxo*-hex-1-enitol (**1**), 4-*O*-acetyl-1,5-anhydro-3-*O*-benzyl-2,6-dideoxy-L-*lyxo*-hex-1-enitol (**2**), and 3,4-di-*O*-acetyl-1-*O*-*tert*-butyldimethylsilyl-2,6-dideoxy-β-L-*lyxo*-hexopyranose (**3**) was developed. The glycals **1** (ref. 9), **2** (ref. 10), and **3** (ref. 11, 12) are known compounds.

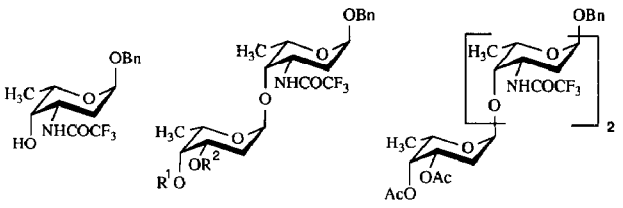


1 **2** **3** **4** R = Ac, **5** R = Bn

The use of glycals for the glycosylation of alcohols in the presence of Lewis acids, *e.g.*, BF_3, gives mainly 2,3-unsaturated α-glycosides[13,14], and, in the presence of *N*-iodosuccinimide, gives the 2-deoxy-2-iodo-α-glycosides[7,8]. Starting from the glycals **1** and **2**, an approach that favours the formation of 2-deoxy-α-glycosides[15] involves a modified trimethylsilyl trifluoromethanesulfonate (trimsyl triflate) procedure[16,17]. In order to examine the coupling ability of **1** and **2**, the benzyl glycosides **4** and **5** were prepared. The reaction of **1** and **2** with benzyl alcohol in the presence of trimsyl triflate–triethylamine (5:1) and molecular sieves 4 Å in dichloromethane at −65° gave >90% of **4** or **5**, respectively, and no pseudoglycals or β-glycosides were formed. Under similar conditions, glycosylation of **6** with **1** afforded the α-(1→4)-linked disaccharide derivative **7** in excellent yield. Likewise, condensation of **2** with **6** gave 86% of **8**. Glycosylation of **6** with 4-*O*-acetyl-3-*O*-benzyl-2,6-dideoxy-α-L-*lyxo*-hexopyranosyl bromide under Koenigs–Knorr conditions gave ~40% of **8**, as reported[6]. In the absence of triethylamine, glycosylation (0.3 equiv. of trimsyl triflate, molecular sieves 4 Å, dichloromethane, −50°) of **6** with **3** afforded 76% of **7** and considerable quantities of by-products were detected (t.l.c.). When **3** and **6** were reacted with 0.6 equiv. of trimsyl triflate, transglycosylation was promoted and the by-products were identified as the benzyl glycoside **4** and the trisaccharide derivative **10**. $^1H,^1H$-COSY and long-range $^1H,^1H$-COSY experiments were used to assign the resonances of the sugar protons in the ^1H-n.m.r. spectra of **7** and **10**.

O-Deacetylation (0.5M NaOH) of **8** gave the glycoside **9**, which is an acceptor for the synthesis of trisaccharides *via* the *N*-iodosuccinimide route, as shown by Monneret *et al.*[6]. In contrast, the trimsyl triflate–triethylamine method could be used to obtain the trisaccharides in a one-step process. Thus, coupling of **1** with **9** at −65° gave 78% of **11**. Similarly, but at −75°, condensation of **9** with **2**, which was more reactive than **1**, afforded 76% of **12**. Although each reaction afforded mainly the trisaccharide derivative, by-products, formed by transglycosylation, were obtained in considerable quantities.

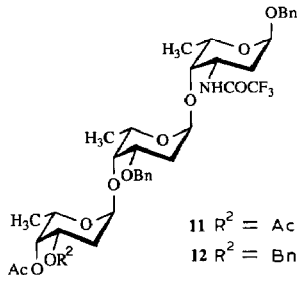
The glycosylation procedures reported above have potential for "2-deoxy-L-fucosylation".



6 7 $R^1 = R^2 = Ac$ 10

8 $R^1 = Ac, R^2 = Bn$

9 $R^1 = H, R^2 = Bn$



11 $R^2 = Ac$

12 $R^2 = Bn$

EXPERIMENTAL

General. — Reactions were carried out at ambient temperature unless otherwise stated. Solutions were concentrated under reduced pressure at $<40°$ (bath). Organic solutions were washed with 0.1M potassium dihydrogen phosphate or 0.1M sodium citrate adjusted to the appropriate pH using 0.1M NaOH or 0.1M HCl. Melting points, determined on a Büchi apparatus, are uncorrected. ^{1}H-N.m.r. spectra were recorded with a Bruker AC-200 or Jeol GX-400 spectrometer, for solutions in $CDCl_3$ (internal Me_4Si) unless stated otherwise. The ^{1}H resonances were assigned by ^{1}H,^{1}H-COSY experiments, using the standard pulse sequences of the Jeol software. $[\alpha]_D$ values were determined with a Perkin–Elmer 241 polarimeter equipped with 10-cm cuvettes, for solutions in $CHCl_3$ at 24°, unless noted otherwise. Reactions were monitored by t.l.c. on Silica Gel 60 F_{254} (Merck) with detection by u.v. light or by charring with sulfuric acid. Preparative chromatography was performed on Kieselgel 60 (Merck, 0.015–0.040 mm). The glycosylations were performed under argon or nitrogen.

General procedure. — To a stirred mixture of glycosyl donor (2.33 mmol), glycosyl acceptor (2.10 mmol), and powdered molecular sieves 4 Å (2.50 g) in dichloromethane (120 mL) were added triethylamine (25 μL, 0.18 mmol) and trimsyl triflate (125 μL, 0.69 mmol) at −65°. The mixture was stirred for 2 h, dichloromethane (250 mL) and triethylamine (0.4 mL) were added, and the mixture was filtered, washed with 0.1M

citrate buffer (pH 5, 250 mL × 2), 0.1M phosphate buffer (pH 7.5, 150 mL), and water (250 mL × 2), dried (Na_2SO_4), and concentrated *in vacuo*. Column chromatography of the residue on silica gel (180 g) gave the α-glycoside.

*Benzyl 3,4-di-*O*-acetyl-2,6-dideoxy-*α*-*L*-lyxo-hexopyranoside* (**4**). — Condensation of **1** (274 mg, 1.28 mmol) and benzyl alcohol (140 mg, 1.28 mmol) at −65° gave **4** (371 mg, 90%), isolated as a syrup, $[\alpha]_D$ −123° (*c* 1). ^{1}H-N.m.r. data (200 MHz): δ 7.30–7.21 (m, 5 H, Ph), 5.24 (ddd, 1 H, $J_{2a,3}$ 12.2, $J_{2e,3}$ 5.2, $J_{3,4}$ 3.0 Hz, H-3), 5.11 (bs, 1 H, H-1), 4.98 (d, 1 H, H-4), 4.58 (d, 1 H, $J_{A,B}$ 12.1 Hz, PhC*H*A), 4.42 (d, 1 H, PhC*H*B), 4.01 (q, 1 H, $J_{5,6}$ 6.5 Hz, H-5), 2.07 (s, 3 H, Ac), 1.99 (ddd, 1 H, $J_{1,2a}$ 3.6, $J_{2a,2e}$ 12.6 Hz, H-2*a*), 1.88 (s, 3 H, Ac), 1.81 (dd, 1 H, H-2*e*), 1.14 (d, 3 H, H-6).

Anal. Calc. for $C_{17}H_{22}O_6$ (322.36): C, 63.34; H, 6.88. Found: C, 63.37; H, 6.87.

*Benzyl 4-*O*-acetyl-3-*O*-benzyl-2,6-dideoxy-*α*-*L*-lyxo-hexopyranoside* (**5**). — Condensation of **2** (335 mg, 1.28 mmol) and benzyl alcohol (140 mg, 1.28 mmol) at −65° gave **5** (441 mg, 93%), isolated as a syrup, $[\alpha]_D$ −172° (*c* 1). ^{1}H-N.m.r. data (200 MHz): δ 7.32–7.22 (m, 10 H, 2 Ph), 5.36 (d, 1 H, $J_{3,4}$ 3.0 Hz, H-4), 5.06 (bs, 1 H, H-1), 4.69 (d, 1 H, $J_{A,B}$ 12.2 Hz, PhC*H*A), 4.67 (d, 1 H, $J_{A',B'}$ 12.0 Hz, PhC*H*A′), 4.48 (d, 1 H, PhC*H*B′), 4.42 (d, 1 H, PhC*H*B), 4.02 (q, 1 H, $J_{5,6}$ 6.5 Hz, H-5), 3.97 (ddd, 1 H, $J_{2a,3}$ 12.5, $J_{2e,3}$ 5.2 Hz, H-3), 2.17 (s, 3 H, Ac), 2.04 (ddd, 1 H, $J_{1,2a}$ 3.3, $J_{2a,2e}$ 12.8 Hz, H-2*a*), 1.95 (dddd, 1 H, $J_{1,2e}$ 1.2, $J_{2e,4}$ 1.0 Hz, H-2*e*), 1.17 (d, 3 H, H-6).

Anal. Calc. for $C_{22}H_{26}O_5$ (370.45): C, 71.33; H, 7.07. Found: C, 71.37; H, 7.09.

*Benzyl 2,3,6-trideoxy-4-*O*-(3,4-di-*O*-acetyl-2,6-dideoxy-*α*-*L*-lyxo-hexopyranosyl)-3-trifluoroacetamido-*α*-*L*-lyxo-hexopyranoside* (**7**). — (*a*) Condensation of **1** (0.50 g, 2.33 mmol) and **6** (0.70 g, 2.10 mmol) in the presence of triethylamine (25 μL, 0.18 mmol), trimsyl triflate (125 μL, 0.69 mmol), and powdered molecular sieves 4 Å (2.50 g) in dichloromethane (120 mL) at −60° gave **7** (0.95 g, 83%).

(*b*) To a stirred solution of **6** (0.87 g, 2.61 mmol), **3** (0.90 g, 2.56 mmol), and powdered molecular sieves 4 Å (3.60 g) in dichloromethane (120 mL) at −50° was added trimsyl triflate (94 μL × 2, 1.04 mmol) in two portions 2 h apart. The mixture was stirred for 6 h at −50°, then worked-up. Column chromatography (8:5:1 light petroleum–dichloromethane–acetone) of the residue on silica gel (180 g) gave **7** (1.06 g, 76%). The preparation of **7** has been reported without any experimental details[4].

Compound **7** had m.p. 85–88°, $[\alpha]_D$ −179° (*c* 1); lit.[4] $[\alpha]_D$ −209°. ^{1}H-N.m.r. data (400 MHz): δ 8.01 (d, 1 H, $J_{3,NH}$ 8.5 Hz, NH-3), 7.29–7.20 (m, 5 H, Ph), 5.36 (ddd, 1 H, $J_{2'a,3'}$ 12.3, $J_{2'e,3'}$ 4.7, $J_{3',4'}$ 2.8 Hz, H-3′), 5.18 (bs, 1 H, H-4′), 4.94 (d, 1 H, $J_{1',2'a}$ 3.5 Hz, H-1′), 4.91 (d, 1 H, $J_{1,2a}$ 3.5 Hz, H-1), 4.60 (d, 1 H, $J_{A,B}$ 11.3 Hz, PhC*H*A), 4.50 (m, 1 H, H-3′), 4.46 (d, 1 H, PhC*H*B), 4.21 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 3.96 (q, 1 H, $J_{5,6}$ 6.5 Hz, H-5), 3.46 (s, 1 H, H-4), 2.10 (s, 3 H, Ac), 2.09 (ddd, 1 H, $J_{2'a,2'e}$ 13.0 Hz, H-2′*a*), 1.94 (s, 3 H, Ac), 1.91 (dd, 1 H, H-2′*e*), 1.84 (dd, 1 H, $J_{2e,3}$ 4.4, $J_{2a,2e}$ 12.8 Hz, H-2*e*), 1.74 (ddd, 1 H, $J_{2a,3}$ 12.7 Hz, H-2*a*), 1.13 (d, 3 H, H-6′), 1.09 (d, 3 H, H-6).

Anal. Calc. for $C_{25}H_{32}F_3NO_9$ (547.53): C, 54.84; H, 5.89; N, 2.56. Found: C, 54.87; H, 5.89; N, 2.53.

*Benzyl 4-*O*-(4-*O*-acetyl-3-*O*-benzyl-2,6-dideoxy-*α*-*L*-lyxo-hexopyranosyl)-2,3,6-trideoxy-3-trifluoroacetamido-*α*-*L*-lyxo-hexopyranoside* (**8**). — Condensation of **2** (0.61

g, 2.33 mmol) and **6** (0.70 g, 2.10 mmol) in the presence of triethylamine (25 μL, 0.18 mmol), trimsyl triflate (125 μL, 0.69 mmol), and powdered molecular sieves 4 Å (2.50 g) in dichloromethane (120 mL) at −60° gave **8** (1.07 g, 86%), m.p. 127°, $[\alpha]_D$ −242° (*c* 1); lit.[6] m.p. 127–128°, $[\alpha]_D$ −167°.

*Benzyl 4-O-(3-O-benzyl-2,6-dideoxy-α-*L*-lyxo-hexopyranosyl)-2,3,6-trideoxy-3-trifluoroacetamido-α-*L*-lyxo-hexopyranoside* (**9**). — To a solution of **8** (1.0 g, 1.68 mmol) in methanol (150 mL) was added aqueous 0.5M NaOH (3.7 mL). The mixture was stirred for 18 h, neutralised with 0.1M aqueous HCl, and concentrated *in vacuo*. A solution of the residue in 2:1 light petroleum–ethyl acetate (200 mL) was washed with saturated brine (100 mL) and water, dried (Na_2SO_4), and concentrated *in vacuo*. Column chromatography (7:1 dichloromethane–ethyl acetate) of the crude product on silica gel afforded **9** (0.70 g, 76%), $[\alpha]_D$ −140° (*c* 1); lit.[6] syrup, $[\alpha]_D$ −123° (*c* 1.6).

*Benzyl [O-(3,4-di-O-acetyl-2,6-dideoxy-α-*L*-lyxo-hexopyranosyl)-(1→4)-O-(2,3,6-trideoxy-3-trifluoroacetamido-α-*L*-lyxo-hexopyranosyl)-(1→4)-(2,3,6-trideoxy-3-trifluoroacetamido-α-*L*-lyxo-hexopyranoside)]* (**10**). — To a stirred mixture of **3** (1.0 g, 2.88 mmol), **6** (1.0 g, 3.00 mmol), and powdered molecular sieves 4 Å (3.50 g) in dichloromethane (100 mL) at −50° was added trimsyl triflate (104 μL × 4, 2.25 mmol) in 4 portions at intervals of 2 h. The mixture was stirred for 12 h at −50°, then worked-up. Column chromatography (8:5:1 light petroleum–dichloromethane–acetone) of the residue on silica gel (200 g) gave **4** (105 mg, 12%), **7** (898 mg, 57%), and **10** (129 mg, 16%).

Compound **10** had m.p. 108–110°, $[\alpha]_D$ −181° (*c* 0.28). ^{1}H-N.m.r. data (400 MHz): δ 8.11 (d, 1 H, $J_{3',NH'}$ 8.5 Hz, NH-3′), 8.03 (d, 1 H, $J_{3,NH}$ 9.1 Hz, NH-3), 7.28–7.20 (m, 5 H, Ph), 5.29 (ddd, 1 H, $J_{2''a,3''}$ 12.3, $J_{2''e,3''}$ 4.7, $J_{3'',4''}$ 2.8 Hz, H-3″), 5.18 (bs, 1 H, H-4″), 4.96 (bs, 1 H, H-1″), 4.98 (bs, 1 H, H-1′), 4.88 (bs, 1 H, H-1), 4.59 (d, 1 H, $J_{A,B}$ 12.0 Hz, PHC*H*A), 4.54 (m, 1 H, H-3′), 4.50 (m, 1 H, H-3), 4.44 (d, 1 H, PHC*H*B), 4.19 (dq, 1 H, $J_{4'',5''}$ 1.2, $J_{5'',6''}$ 6.6 Hz, H-5″), 4.16 (dq, 1 H, $J_{4',5'}$ 1.0, $J_{5',6'}$ 6.6 Hz, H-5′), 3.96 (dq, 1 H, $J_{4,5}$ 1.0, $J_{5,6}$ 6.6 Hz, H-5), 3.51 (bs, 1 H, H-4′), 3.48 (bs, 1 H, H-4), 2.12 (ddd, 1 H, $J_{2''a,2''e}$ 12.9 Hz, H-2″*a*), 2.11 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 1.98–1.19 (m, 4 H, H-2*e*, H-2′*a*, H-2′*e*, and H-2″*e*), 1.74 (ddd, 1 H, $J_{1,2a}$ 3.5, $J_{2a,3}$ 12.6, $J_{2a,2e}$ 12.7 Hz, H-2*a*), 1.17 (d, 3 H, H-6), 1.16 (d, 3 H, H-6″), 1.09 (d, 3 H, H-6′).

Anal. Calc. for $C_{33}H_{42}F_6N_2O_{12}$ (772.70): C, 51.30; H, 5.48; N, 3.63. Found: C, 51.35; H, 5.51; N, 3.57.

Benzyl O-*(3,4-di-*O*-acetyl-2,6-dideoxy-α-*L*-lyxo-hexopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-2,6-dideoxy-α-*L*-lyxo-hexopyranosyl)-(1→4)-(2,3,6-trideoxy-3-trifluoroacetamido-α-*L*-lyxo-hexopyranoside)* (**11**). — Condensation of **1** (0.29 g, 1.35 mmol) and **9** (0.50 g, 0.90 mmol) in the presence of triethylamine (10 μL, 0.07 mmol), trimsyl triflate (50 μL, 0.27 mmol), and powdered molecular sieves 4 Å (2.0 g) in dichloromethane (120 mL) at −65° gave **11** (0.59 g, 85%) as an amorphous powder, $[\alpha]_D$ −235° (*c* 1.05); lit.[6] $[\alpha]_D$ −159°.

Benzyl O-*(4-*O*-acetyl-3-*O*-benzyl-2,6-dideoxy-α-*L*-lyxo-hexopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-2,6-dideoxy-α-*L*-lyxo-hexopyranosyl)-(1→4)-(2,3,6-trideoxy-3-trifluoroacetamido-α-*L*-lyxo-hexopyranoside)* (**12**). — Condensation of **2** (142 mg, 0.54

mmol) and **9** (200 mg, 0.36 mmol) in the presence of triethylamine (4 μL, 0.028 mmol), trimsyl triflate (20 μL, 0.11 mmol), and powdered molecular sieves 4 Å (800 mg) in dichloromethane (20 mL) at −75° gave **12** (0.23 g, 78%), $[\alpha]_D$ −198° (*c* 1). ^{1}H-N.m.r. data (400 MHz): δ 8.32 (d, 1 H, $J_{3,NH}$ 8.5 Hz, NH-3), 7.36–7.28 (m, 10 H, 2 Ph), 5.27 (bs, 1 H, H-4″), 5.07 (bs, 1 H, H-1″), 4.95 (bs, 2 H, H-1 and H-1′), 4.72 (d, 1 H, $J_{A,B}$ 11 Hz, PhC*H*A), 4.67 (d, 1 H, $J_{A,B}$ 11 Hz, PhC*H*A′), 4.66 (d, 1 H, $J_{A,B}$ 11 Hz, PhC*H*A″), 4.57 (d, 1 H, PhC*H*B), 4.54 (m, 1 H, H-3), 4.52 (d, 1 H, PhC*H*B′), 4.42 (d, 1 H, PhC*H*B″), 4.34 (q, 1 H, $J_{5'',6''}$ 6.5 Hz, H-5″), 4.06 (q, 1 H, $J_{5,6}$ 6.4 Hz, H-5), 4.02 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 3.96 (m, 2 H, H-3 and H-3′), 3.89 (bs, 1 H, H-4), 3.47 (bs, 1 H, H-4′), 2.14 (s, 3 H, Ac), 2.14–1.96 (m, 4 H, H-2′*a*, H-2′*e*, H-2″*a*, and H-2″*e*), 1.90 (dd, 1 H, $J_{2a,2e}$ 12.6, $J_{2e,3}$ 4.6 Hz, H-2*e*), 1.75 (ddd, 1 H, $J_{1,2a}$ 3.6, $J_{2a,3}$ 12.6 Hz, H-2*a*), 1.25 (d, 3 H, H-6′), 1.16 (d, 3 H, H-6), 0.86 (d, 3 H, H-6″).

Anal. Calc. for $C_{43}H_{52}F_3NO_{11}$ (815.89): C, 63.30; H, 6.42; N, 1.72. Found: C, 63.33; H, 6.44; N, 1.68.

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