Carbohydrate Research, 126 (1984) 331–337
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

Synthesis of methyl 3-acetamido-3-deoxy-2-*O*-β-D-glucopyranosyl- and -β-D-galactopyranosyl-α-D-allopyranoside

ANDRZEJ TEMERIUSZ, JANUSZ STĘPIŃSKI, BOGUSŁAWA PIEKARSKA, AND JAN RADOMSKI
Department of Chemistry, University of Warsaw, Warsaw (Poland)
(Received July 15th, 1983; accepted for publication, September 14th, 1983)

Reduction of methyl 4,6-*O*-benzylidene-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-*ribo*-hexopyranosid-3-ulose (**2**) with sodium borohydride followed by debenzylidenation gave[1] 83% of methyl 2-*O*-β-D-glucopyranosyl-α-D-allopyranoside. In a similar manner, methyl 4,6-*O*-benzylidene-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-*ribo*-hexopyranosid-3-ulose (**11**) was converted into methyl 2-*O*-β-D-galactopyranosyl-α-D-allopyranoside. We now report syntheses of methyl 3-acetamido-3-deoxy-2-*O*-β-D-glucopyranosyl-α-D-allopyranoside (**9**) from **2** and methyl 3-acetamido-3-deoxy-2-*O*-β-D-galactopyranosyl-α-D-allopyranoside (**17**) from **11**.

Oximation of **2** gave a mixture of products from which the major product was isolated (85%) crystalline by column chromatography and identified as methyl 4,6-*O*-benzylidene-3-deoxy-3-hydroxyimino-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-*ribo*-hexopyranoside (**3**). ^{13}C-N.m.r. spectroscopy indicated that **3** was an *EZ* mixture, there being two signals at δ 145.8 and 147.2 for C-3 assigned[2] to the *Z* and *E* isomers, respectively. Also, there were doublets for C-1, C-5, PhCH, and the aromatic carbons (see Table I).

Compound **11** also gave an *EZ* mixture of methyl 4,6-*O*-benzylidene-3-deoxy-3-hydroxyimino-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-*ribo*-hexopyranoside (**12**). The ^{13}C-n.m.r. data for **12** in Table II paralleled those for **3** (Table I).

The *Z* and *E* isomerism of the oximes of methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*- and -*threo*-hexopyranosid-3-uloses[3] and of other oximes[2,4] has been discussed in detail. Attempts to isolate the *Z* and *E* isomers of **3** failed. Deacetylation of **3** gave a crystalline *EZ* mixture of methyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-β-D-glucopyranosyl-3-hydroxyimino-α-D-*ribo*-hexopyranoside. Attempts to remove the benzylidene group from **3**, even under mild conditions (acetic acid at room temperature), resulted in deoximation, and **2** was a product. Similar results were obtained with **12**.

When **3** was hydrogenated at high pressure (100 atm.) over Adams' catalyst, a mixture of products was obtained. Column chromatography then gave the major fraction (70%) which was identified as methyl 3-acetamido-4,6-*O*-benzylidene-3-

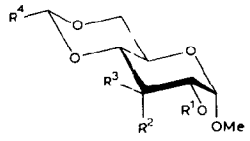
0008-6215/84/$ 03.00

TABLE I

^{13}C CHEMICAL SHIFTS (p.p.m.) FOR COMPOUNDS **1–8**

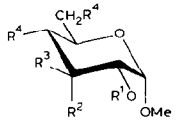
Carbon atoms	*Compound*						
	1[a,d]	**2**[b]	**3**[b]	**5**[b]	**6**[b]	**8**[b]	**7**[c,e]
C-1	100.5	100.1	99.6, 98.7	99.15	99.1	98.6	98.9
C-2	82.2	82.2	74.1	74.2	74.4	73.3	74.8
C-3	69.8	194.6	145.8, 147.2	56.1	56.0	55.9	68.7
C-4	81.8	78.8	73.4	78.8	78.1	63.4	62.5
C-5	62.5	65.3	65.4, 63.9	59.2	59.2	67.9	66.3
C-6	69.4	68.4	68.5	69.2	68.8	62.3	62.3
C-7	102.2	102.0	102.4, 102.1	102.2	105.65		
C-1′	102.2	102.7	99.7	99.6	99.7	99.95	99.2
C-2′	71.9	71.0	71.1	71.1	71.1	70.9	70.7
C-3′	73.0	72.4	72.7	72.6	72.6	72.6	70.7
C-4′	69.0	69.5	69.7	68.4	68.4	68.1	68.1
C-5′	72.4	72.1	71.8	72.2	72.1	72.1	72.2
C-6′	62.4	61.8	61.9	61.9	61.9	61.7	61.6
O-CH_3	55.8	56.0	56.0	58.2	58.4	59.2	55.1
C-CH_3	20.8	20.6, 20.75	20.6, 20.75	19.2, 20.6	19.3, 20.6	19.1, 20.5	20.2, 20.3
						20.7	20.4, 20.6
C_6H_5	126.1, 128.4	126.4, 128.3	126.1, 126.4	126.4, 128.2			
	129.2, 136.6	129.4, 136.4	128.2, 128.3	129.2, 127.3			
			129.2, 129.4				
			136.3, 136.8				
C_6H_{11}					25.8, 26.4		
					27.5, 41.8		
COO	169.4, 169.8	169.4, 169.8	169.4, 169.8	169.4, 170.2	169.4, 170.2	169.5, 170.2	169.0, 169.2
	170.2, 170.3	170.1, 170.5	170.2, 170.7	170.4, 170.7	170.4, 170.7	170.5, 170.7	169.4, 169.6
							170.0, 170.1

[a]In CD_2Cl_2. [b]In $CDCl_3$. [c]In $(CD_3)_2SO$. [d]Ref. 11. [e]Ref. 1.



1 R^1 = A, R^2 = H, R^3 = OH, R^4 = Ph
2 R^1 = A, R^2 = R^3 = O, R^4 = Ph
3 R^1 = A, R^2 = R^3 = NOH, R^4 = Ph
4 R^1 = β-D-Glcp, R^2 = R^3 = NOH, R^4 = Ph
5 R^1 = A, R^2 = NHAc, R^3 = H, R^4 = Ph
6 R^1 = A, R^2 = NHAc, R^3 = H, R^4 = C_6H_{11}
10 R^1 = B, R^2 = H, R^3 = OH, R^4 = Ph
11 R^1 = B, R^2 = R^3 = O, R^4 = Ph
12 R^1 = B, R^2 = R^3 = NOH, R^4 = Ph
13 R^1 = B, R^2 = NHAc, R^3 = H, R^4 = Ph
14 R^1 = B, R^2 = NHAc, R^3 = H, R^4 = C_6H_{11}

A = 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl
B = 2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl



7 R^1 = A, R^2 = R^4 = OAc, R^3 = H
8 R^1 = A, R^2 = NHAc, R^3 = H, R^4 = OAc
9 R^1 = β-D-Glcp, R^2 = NHAc, R^3 = H, R^4 = OH
15 R^1 = B, R^2 = R^4 = OAc, R^3 = H
16 R^1 = B, R^2 = NHAc, R^3 = H, R^4 = OAc
17 R^1 = β-D-Galp, R^2 = NHAc, R^3 = H, R^4 = OH

A = 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl
B = 2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl

TABLE II

^{13}C CHEMICAL SHIFTS (p.p.m.) FOR COMPOUNDS **10–16**

Carbon atoms	*Compound*						
	10[a,c]	**11**[a,c]	**12**[b]	**13**[b]	**14**[b]	**16**[b]	**15**[a,d]
C-1	101.2	102.2	99.5, 99.8	99.1	99.15	98.7	98.5
C-2	83.1	82.5	73.6	74.2	74.4	73.5	73.8
C-3	69.9	196.5	145.8, 147.2	56.0	56.0	55.8	67.3
C-4	83.1	82.0	73.6	78.7	78.1	63.7	62.6
C-5	63.4	66.6	65.4	59.1	59.1	66.9	65.7
C-6	69.9	69.9	69.6	69.1	69.3	62.3	61.9
C-7	102.4	104.0	102.0, 102.3	102.1	105.6		
C-1′	103.9	104.0	100.4	100.2	100.3	100.6	100.8
C-2′	69.9	69.9	69.9	68.6	68.7	68.5	68.1
C-3′	71.4	71.7	70.9	70.8	70.8	70.8	70.0
C-4′	68.9	68.7	68.6	67.0	66.9	68.1	66.9
C-5′	71.4	71.7	70.9	71.1	70.8	71.2	70.0
C-6′	62.8	62.6	61.3	61.3	61.3	61.3	61.1
O-CH_3	56.2	56.4	56.1	58.2	58.2	59.2	55.2
C-CH_3	21.8	21.6, 21.7	20.7	19.0, 20.5	19.3, 20.6	18.9, 20.5	20.4, 20.7
C_6H_5	127.8, 129.4 130.2, 139.2	127.7, 129.5 130.5, 138.5	126.1, 126.4 128.2, 129.2 129.4, 136.1 136.9	126.4, 128.1 129.0, 137.3			
C_6H_{11}					25.7, 26.4 27.5, 41.8		
COO	170.8, 171.2 173.3	170.6, 170.9 171.3	169.7, 170.1 170.3, 170.6	169.3, 169.9 170.0, 170.6	169.4, 170.2	169.4, 169.9 170.4, 170.6	169.3, 169.5 169.9, 170.4

[a]In $(CD_3)_2SO$. [b]In $CDCl_3$. [c]Ref. 11. [d]Ref. 1.

deoxy-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-allopyranoside (**5**). The ^{13}C-n.m.r. spectrum of **5** contained a signal for *C*-NHAc at δ 56.1, in place of the signals (δ 145.8 and 147.2) due to C-3 in **3**. Also, for **5**, the signal for C-4 was shifted downfield by 5.4 p.p.m. and that for C-5 was shifted upfield by 4–7 p.p.m. in comparison with the corresponding signals for **3**. The minor fraction (16%) was identified as methyl 3-acetamido-4,6-*O*-cyclohexylmethylene-3-deoxy-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-allopyranoside (**6**). The ^{13}C-n.m.r. spectrum of **6**, in addition to the changes observed for **5**, contained no signals for aromatic carbons but signals in the range δ 25–41 corresponding[5] to the cyclohexane ring. Also, the signal at δ 102.2 for Ph-*C*H in **5** was replaced by one at δ 105.65.

Likewise, reduction of **12** gave methyl 3-acetamido-4,6-*O*-benzylidene-3-deoxy-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-allopyranoside (**13**, 72%) and methyl 3-acetamido-4,6-*O*-cyclohexylmethylene-3-deoxy-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-allopyranoside (**14**, 15%).

Debenzylidenation of **5** with methanolic hydrogen chloride followed by acetylation gave methyl 3-acetamido-4,6-di-*O*-acetyl-3-deoxy-2-*O*-(2,3,4,6-tetra-

O-acetyl-β-D-glucopyranosyl)-α-D-allopyranoside (**8**). Deacetylation of **8** afforded methyl 3-acetamido-3-deoxy-2-*O*-β-D-glucopyranosyl-α-D-allopyranoside (**9**). Likewise, **13** was converted into methyl 3-acetamido-4,6-di-*O*-acetyl-3-deoxy-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-allopyranoside (**16**) and thence into methyl 3-acetamido-3-deoxy-2-*O*-β-D-galactopyranosyl-α-D-allopyranoside (**17**).

Hydrolysis of **8** with 4M HCl gave (g.l.c.) glucose and 3-amino-3-deoxy-D-allose[6]. Likewise, hydrolysis of **16** gave D-galactose and 3-amino-3-deoxy-D-allose[7].

EXPERIMENTAL

General methods. — T.l.c. was performed on Kieselgel 60 F_{254} with *A*, chloroform–acetone (4:1); and *B*, 1-propanol–ethyl acetate–water (3:2:1). Amino sugars were detected with ninhydrin, and others by charring with sulphuric acid. Column chromatography was performed on Kieselgel 60 (230–400 mesh). G.l.c. was performed with a Pye Unicam 104 gas chromatograph equipped with a flame-ionisation detector and a column packed with 15% of XE-60 on Gas Chrom Q (100–120 mesh) at 180°. Optical rotations were determined with a Perkin–Elmer Model 242 polarimeter. I.r. spectra were recorded with a UR-20 Zeiss apparatus. ^{1}H-N.m.r. spectra (80 MHz) were recorded at room temperature with a Tesla Model BS 407 spectrometer, and ^{13}C-n.m.r. spectra (22.53 MHz) with a Jeol FX 90Q spectrometer for solutions in $CDCl_3$ (internal Me_4Si).

Methyl 4,6-O-benzylidene-3-deoxy-3-hydroxyimino-2-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α-D-ribo-hexopyranoside (**3**). — To a solution of **2**[8] (3.06 g, 5 mmol) in dichloromethane (20 mL) was added, with stirring, a solution of hydroxylamine hydrochloride (0.58 g, 8.3 mmol) in pyridine (15 mL). After 24 h at room temperature, the mixture was poured into ice–water and extracted with chloroform. The extract was washed successively with dilute sulfuric acid, water, aqueous sodium hydrogencarbonate, and water, dried ($MgSO_4$), and concentrated. Column chromatography (solvent *A*) of the syrupy residue yielded crystalline **3** (2.70 g, 87%), which was pure by t.l.c. and which, after recrystallisation from ethanol, had m.p. 192–195°, $[\alpha]_D^{26}$ −10.5° (*c* 1, chloroform), R_F 0.5 (solvent *A*). ^{1}H-N.m.r. data: δ 11.60 and 11.85 (2 s, 1 H, *Z*- and *E*-NOH), 7.35–7.65 (m, 5 H, Ph), 5.76 (s, 1 H, PhC*H*), 4.90 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.50 (d, 1 H, $J_{1',2'}$ 8 Hz, H-1'), 3.45 (s, 3 H, OMe), and 2.05–1.95 (m, 12 H, 4 OAc).

Anal. Calc. for $C_{28}H_{35}NO_{15}$: C, 53.76; H, 5.64; N, 2.24. Found: C, 53.66; H, 5.52; N, 2.22.

Methyl 4,6-O-benzylidene-3-deoxy-2-O-β-D-glucopyranosyl-3-hydroxyimino-α-D-ribo-hexopyranoside (**4**). — A solution of **3** (0.313 g; 0.5 mmol) in methanol (30 mL) was mixed with methanolic sodium methoxide (from 30 mL of methanol and 0.5 g of sodium). The mixture was left at room temperature overnight, neutralised with Dowex 50 (H^+) resin, and concentrated to dryness. The residue crystallised from ethanol, to give **4** (0.214 g, 93%), m.p. 219–220°, $[\alpha]_D^{26}$ −10° (*c* 1,

methyl sulphoxide), R_F 0.7 (solvent *B*). N.m.r. data (Me_2SO): ^1H, δ 11.23 (s, 1 H, NOH), 7.30–7.40 (m, 5 H, Ph), 5.62 (s, 1 H, PhH), and 3.32 (s, 3 H, OMe); ^{13}C, δ 145.8 and 145.0 (C=NOH *Z* and *E* isomers), 137.4–126.3 (Ph), 100.6, 99.3 (C-1,1'), 77.0 (C-3'), 76.7, 76.4 (C-2,4), 73.7, 73.2 (C-2',4'), 69.0 (C-6), 65.2 (C-5), 60.9 (C-6'), and 54.6 (OMe).

Methyl 3-acetamido-4,6-O-benzylidene-3-deoxy-2-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α-D-allopyranoside (**5**). — A solution of **3** (0.625 g, 1 mmol) in tetrahydrofuran (30 mL) was shaken with pre-reduced Adams' catalyst (0.5 g) and hydrogen at 100 atm. for 24 h at room temperature, filtered, and concentrated. The crude, syrupy amine was treated conventionally with pyridine (10 mL) and acetic anhydride (10 mL) for 24 h at room temperature. The residue was subjected to column chromatography (chloroform–acetone, 9:1) to give, first, **6** (0.103 g, 16%) and then **5** (0.446 g, 70%). Recrystallisation of **5** from ethanol gave material having m.p. 172–174°, $[\alpha]_D^{26}$ +1.3° (*c* 5, chloroform), R_F 0.43 (solvent *A*). ^1H-N.m.r. data: δ 7.95 (d, 1 H, NH), 7.48–7.35 (m, 5 H, Ph), 5.50 (s, 1 H, PhC*H*), 4.95 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.45 (d, 1 H, $J_{1',2'}$ 8 Hz, H-1'), 3.35 (s, 3 H, OMe), 2.12–2.02 (m, 12 H, 4 OAc), and 1.87 (s, 3 H, NAc).

Anal. Calc. for $C_{30}H_{39}NO_{14}$: C, 56.51; H, 6.16; N, 2.20. Found: C, 56.40; H, 6.09; N, 2.25.

Recrystallisation of **6** from ethanol gave methyl 3-acetamido-4,6-*O*-cyclohexylmethylene-3-deoxy-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-allopyranoside, m.p. 173–175°, $[\alpha]_D^{26}$ +25° (*c* 1, chloroform), R_F 0.70 (solvent *A*). ^1H-N.m.r. data: δ 8.05 (d, 1 H, $J_{NH,3}$ 2 Hz, NH), 5.55 (s, 1 H, $C_6H_{11}CH$), 4.95 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.76 (d, 1 H, $J_{1',2'}$ 8 Hz, H-1'), 3.47 (s, 3 H, OMe), 2.07–1.97 (m, 21 H, 7 Ac), and 1.78–1.12 (m, 11 H, C_6H_{11}).

Anal. Calc. for $C_{30}H_{45}NO_{14}$: C, 55.98; H, 7.05; N, 2.17. Found: C, 55.68; H, 7.03; N, 2.05.

Methyl 3-acetamido-4,6-di-O-acetyl-3-deoxy-2-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α-D-allopyranoside (**8**). — Compound **5** (0.320 g, 0.5 mmol) was treated with methanolic 1% hydrogen chloride (20 mL) at room temperature overnight. The mixture was concentrated to dryness, and methanol was distilled several times from the residue which was then treated conventionally with pyridine (10 mL) and acetic anhydride (10 mL) at room temperature overnight. The product was purified by column chromatography (chloroform–acetone, 9:1), to yield amorphous **8** (0.307 g, 95%), $[\alpha]_D^{26}$ +29° (*c* 1, chloroform), R_F 0.48 (solvent *A*). ^1H-N.m.r. data: δ 7.86 (d, 1 H, NH), 4.95 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.60 (d, 1 H, $J_{1',2'}$ 8 Hz, H-1'), 3.35 (s, 3 H, OMe), and 2.06–1.97 (m, 21 H, 7 Ac).

Anal. Calc. for $C_{27}H_{39}NO_{17}$: C, 49.92; H, 6.05; N, 2.16. Found: C, 50.09; H, 6.19; N, 2.05.

Methyl 3-acetamido-3-deoxy-2-O-β-D-glucopyranosyl-α-D-allopyranoside (**9**). — A solution of **8** (0.130 g, 0.2 mmol) in methanol (5 mL) containing freshly prepared sodium methoxide (from 0.1 g of sodium) was kept overnight at room temperature, neutralised with Dowex 50 (H^+) resin, and concentrated, to yield

syrupy **9** (0.061 g, 87%) which, after purification by p.c. (solvent *B*), had $[\alpha]_D^{26}$ +12° (*c* 1, water), R_F 0.54 (solvent *B*).

Methyl 4,6-O-benzylidene-3-deoxy-3-hydroxyimino-2-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-ribo-hexopyranoside (**12**). — The oxime **12** was prepared from **11**[9] (3.06 g, 5 mmol) as outlined above for the oxime of **3**. Column chromatography (chloroform–acetone 9:1) of the product gave **12** (2.63 g, 85%), m.p. 184–186° (from ethanol), $[\alpha]_D^{26}$ −41° (*c* 1, chloroform), R_F 0.56 (solvent *A*). ^{1}H-N.m.r. data (Me_2SO): δ 11.42 (s, 1 H, NOH), 7.42–7.25 (m, 5 H, Ph), 5.55 (s, 1 H, PhC*H*), 5.00 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.85 (d, 1 H, $J_{1',2'}$ 8 Hz, H-1'), 3.50 (s, 3 H, OMe), and 2.15–2.00 (m, 12 H, 4 Ac).

Anal. Calc. for $C_{28}H_{35}NO_{15}$: C, 53.76; H, 5.64; N, 2.24. Found: C, 53.82; H, 5.51; N, 2.20.

Methyl 3-acetamido-4,6-O-benzylidene-3-deoxy-2-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-allopyranoside (**13**). — Compound **12** (0.625 g, 1 mmol) was hydrogenated as described above for the preparation of **5**. Column chromatography (chloroform–acetone, 9:1) of the product gave **14** (0.096 g, 15%) and **13** (0.460 g, 72%). Recrystallisation of **13** from ethanol gave material having m.p. 138–140°, $[\alpha]_D^{26}$ +16.5° (*c* 1, chloroform), R_F 0.52 (solvent *A*). ^{1}H-N.m.r. data: δ 8.12 (d, 1 H, NH), 7.42–7.30 (m, 5 H, Ph), 5.50 (s, 1 H, PhC*H*), 4.98 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.70 (d, 1 H, $J_{1',2'}$ 8 Hz, H-1'), 3.47 (s, 3 H, OMe), 2.16–1.97 (m, 12 H, 4 OAc), and 1.87 (s, 3 H, NAc).

Anal. Calc. for $C_{30}H_{39}NO_{14}$: C, 56.51; H, 6.16; N, 2.20. Found: C, 56.66; H, 6.05; N, 2.16.

Methyl 3-acetamido-4,6-*O*-cyclohexylmethylene-3-deoxy-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-allopyranoside (**14**) was amorphous, $[\alpha]_D^{26}$ +30° (*c* 1, chloroform), R_F 0.60. ^{1}H-N.m.r. data: δ 8.00 (d, 1 H, $J_{NH,3}$ 4 Hz, NH), 5.55 (s, 1 H, $C_6H_{11}CH$), 5.12 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.67 (d, 1 H, $J_{1',2'}$ 8 Hz, H-1'), 3.42 (s, 3 H, OMe), 2.12–1.92 (m, 15 H, 5 Ac), and 1.72–1.12 (m, 11 H, C_6H_{11}).

Anal. Calc. for $C_{30}H_{45}NO_{14}$: C, 55.98; H, 7.05; N, 2.17. Found: C, 55.92; H, 7.06; N, 2.20.

Methyl 3-acetamido-4,6-di-O-acetyl-3-deoxy-2-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-allopyranoside (**16**). — Treatment of **13** (0.32 g, 0.5 mmol) with acid, as described above for the preparation of **8**, afforded syrupy **16** (0.29 g, 90%), $[\alpha]_D^{26}$ +17° (*c* 1, chloroform), R_F 0.52 (solvent *A*). ^{1}H-N.m.r. data: δ 7.95 (d, 1 H, $J_{NH,3}$ 2 Hz, NH), 5.07 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 4.57 (d, 1 H, $J_{1',2'}$ 7 Hz, H-1'), 3.40 (s, 3 H, OMe), and 2.15–1.95 (m, 21 H, 7 Ac).

Anal. Calc. for $C_{27}H_{39}NO_{17}$: C, 49.92; H, 6.05; N, 2.16. Found: C, 49.87; H, 6.11; N, 2.13.

Methyl 3-acetamido-3-deoxy-2-O-β-D-galactopyranosyl-α-D-allopyranoside (**17**). — Compound **16** (0.130 g, 0.2 mmol) was treated with methanolic sodium methoxide as described for the preparation of **9**. After purification, **17** was obtained as a syrup (0.066 g, 95%), $[\alpha]_D^{26}$ +12° (*c* 1, water), R_F 0.50 (solvent *B*).

REFERENCES

1 A. TEMERIUSZ, B. PIEKARSKA, J. STĘPIŃSKI, AND J. RADOMSKI, *Pol. J. Chem.*, 55 (1981) 783–791.
2 W. FUNCKE AND C. VON SONNTAG, *Carbohydr. Res.*, 69 (1979) 247–251.
3 P. J. BEYNON, P. M. COLLINS, AND W. G. OVEREND, *J. Chem. Soc., C*, (1969) 272–281.
4 W. FUNCKE, C. VON SONNTAG, AND A. KLEMER, *Carbohydr. Res.*, 71 (1979) 315–318; P. FINCH AND Z. M. MERCHANT, *ibid.*, 76 (1979) 225–232.
5 E. PRETSCH, T. CLERC, J. SEIBL, AND W. SIMON, *Tabellen zur Strukturaufklärung organischer Verbindungen mit spectroskopischen Methoden*, Springer–Verlag, Berlin, 1976, p. c70.
6 K. ONODERA, S. HIRANO, AND N. KASHIMURA, *Carbohydr. Res.*, 6 (1968) 276–289.
7 F. W. LICHTENTHALER, *Methods Carbohydr. Chem.*, 6 (1972) 250–265.
8 Z. PAWLAK, *Rocz. Chem.*, 46 (1972) 737–739.
9 Z. PAWLAK, A. TEMERIUSZ, AND A. MIODUSZEWSKA, *Rocz. Chem.*, 47 (1973) 2373–2375.
10 P. MCARDLE, J. O. WOOD, E. E. LEE, AND M. J. CONNEELY, *Carbohydr. Res.*, 69 (1979) 39–46.
11 A. TEMERIUSZ, B. PIEKARSKA, J. RADOMSKI, AND J. STĘPIŃSKI, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 9–10 (1980) 587–591.